PNL-MA-599

ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM

Volume 2: Sample Preparation Methods

Battelle
Pacific Northwest Laboratories

PNL-MA-599

Analytical Chemistry Laboratory Department

ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM

Volume 2: Sample Preparation Methods

Upon termination or transfer this manual shall
be returned to
Document Control, K3-70

Approved for Use
and Application by

A. G. King
Department Manager

Battelle
Pacific Northwest Laboratories
Richland, Washington

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-MA-599-Vol.2-1
Page 1 of 1

A.

Document Number: See Attachment Revision Number: ____

Document Title: See Attachment

Document's Original Author: See Attachment

Effective Date of ICN: 12 / 23 / 92

Change Requested by: AG King

B. Action: Place the attached procedures in PNL-MA-599 manual, Volume 2. Place this ICN and attachment with the Table of Contents.

C. Effect of Change: Incorporates the procedures from the PNL-MA-597 manual into PNL-MA-599.

D. Reason for Change/Description of Change:

Incorporates the procedures from PNL-MA-597 manual into PNL-MA-599 manual by changing the procedure numbers. This eliminates the need for maintaining two sets of technical procedures. Procedural references in these procedures have been updated. See attachment for the procedures to be incorporated into PNL-MA-599 manual, Volume 2.

E. Approval Signatures:
(Please sign and date)

Type of Change: (Check one): X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert Date: 12/23/92

Approval Authority: AG King A. G. King Date: 12/23/92

Other Approvals: ____ Date: __/__/__

: ____ Date: __/__/__

ICN- PNL-MA-599- Vol.2-1

New Doc#	Rev.	Author	Document Title	Old Doc#
PNL-ALO-136	0	MR Weiler	Preparation of test samples, bioassay quality control program	7-40.67

PNL-MA-599 ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM
Volume 2: Sample Preparation Methods

April 5, 1993

TABLE OF CONTENTS

DOCUMENT NUMBER	REV NUM	NO. OF ICNS ISSUED	TITLE	EFFECTIVE DATE
PNL-ALO-101	1	2	ACID DIGESTION FOR METALS ANALYSIS	05/11/92
PNL-ALO-102	0	2	FUSION OF HANFORD TANK WASTE SOLIDS	01/08/93
PNL-ALO-103	1	1	WATER LEACH OF SLUDGES, SOILS, OTHER SOLID SAMPLES	05/11/92
PNL-ALO-104	0	0	EXTRACTION PROCEDURE TOXICITY	04/30/90
PNL-ALO-105	0	2	PROCEDURE FOR PREPARATION OF SAMPLES TO BE COUNTED BY GAMMA-RAY SPECTROSCOPY	05/07/92
PNL-ALO-106	0	4	ACID DIGESTION FOR PREPARATION OF SAMPLES FOR RADIOCHEMICAL ANALYSIS	09/26/90
PNL-ALO-107	0	2	LEACH PROCEDURE FOR PREPARING SLUDGES, SOILS, AND OTHER SOLID SAMPLES FOR FREE CYANIDE ANALYSIS	05/11/92
PNL-ALO-108	0	2	AQUEOUS LEACH OF SLUDGES, SOILS AND OTHER SOLID SAMPLES FOR ANION ANALYSIS	05/17/91
PNL-ALO-109	0	0	MICROWAVE DIGESTION OF GLASSES AND SLURRIES FOR ICP/MS ANALYSIS	07/15/91
PNL-ALO-110	0	0	TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) EXTRACTION FOR INORGANIC CONTAMINANTS	05/26/92
PNL-ALO-111	0	0	LEACH/DISSOLUTION OF NETRON ACTIVATED METAL SPECIMENS FOR RADIOCHEMICAL ANALYSIS	09/09/92
PNL-ALO-120	0	2	EXTRACTION OF SINGLE-SHELL TANK SAMPLES FOR THE ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS	12/11/92

DOCUMENT NUMBER	REV NUM	NO. OF ICNS ISSUED	TITLE	EFFECTIVE DATE
PNL-ALO-121	0	1	PREPARATION AND CLEANUP OF HYDROCARBON CONTAINING SAMPLES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS	06/24/92
PNL-ALO-122	0	2	CLEANUP OF HYDROCARBON CONTAINING SAMPLES FOR THE ANALYSIS OF SEMI-VOLATILE ORGANIC COMPOUNDS	06/24/92
325-A-29	0	0	RECEIVING OF WASTE TANK SAMPLES IN ONSITE TRANSFER CASK	03/08/89
PNL-ALO-130	0	0	RECEIPT AND INSPECTION OF SST SAMPLES	08/03/89
325-EXT-1	0	0	RECEIPT AND EXTRUSION OF CORE SAMPLES AT 325A SHIELDED FACILITY	08/08/89
325-A-30	0	0	CLEANING AND SHIPPING OF WASTE TANK SAMPLES	08/08/89
PNL-ALO-135	0	0	HOMOGENIZATION OF SOLUTIONS, SLURRIES AND SLUDGES	08/03/89
PNL-ALO-136	0	0	PREPARATION OF TEST SAMPLES, BIOASSAY QUALITY CONTROL PROGRAM	02/04/91

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-101.2 R1
Page 1 of 1

A.

Document Number: PNL-ALO-101 Revision Number: 1

Document Title: Acid Digestion for Metals Analysis

Document's Original Author: RT Steele

Effective Date of ICN: 5/11/92

Change Requested by: TE Jones

B. **Action:**

Deleting ACT 89.1 and replacing with established records management practices.

Replace all pages due to new format.

Incorporated ICN 101.1 R1.

C. **Effect of Change:**

Brings procedure into compliance.

D. **Reason for Change/Description of Change:**

ACT NOW Directive 89.1 no longer in existence.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert Date: 5/7/92
Approval Authority: AG King Date: 5/7/92
Other Approvals: BM Gillespie Date: 5/11/92
: ______ Date: / /

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-101.1
Page 1 of 1

A. Document Number: PNL-ALO-101 Revision Number: 1
Document Title: Acid Digestion for Metal Analysis
Document's Original Author: R. T. Steele

Effective Date of ICN: 4/8/91

Change Requested By: M. W. Urie

B. Action:

Change final dilution volume for Soil/Sediment sample preparation of CERCLA samples from 250 mL to 200 mL. Pen and Ink changes in.

C. Effect of Change:

This change brings PNL-ALO-101 into strict compliance with CLP sample preparation protocols.

D. Reason for Change/Description of Change

Reason: Although approved, this procedure is not in strict compliance with CLP protocol for sample preparation of soils and sediments. This ICN has been requested by CERCLA clients and is required to continue CERCLA support.

Description:

6.1.4 step 5) .. Note and 6.1.4 step 6).. Note

Change "250 mL with acidified water (approximately 2.5% (v/v) HCl and 5% (v/v) HNO_3 to" to "200 mL (or other volume approved by Cognizant Scientist and client) to"

E. Approval Signatures

(Please Sign and Date)

Type of Change: (Check (✓) one)

( ) Minor Change (X) Major Change

Process Quality ~~QS&R~~ Department Concurrence: GKConte Date: 3/29/91
Approval Authority: Date: 3/29/91
Other Approvals: Barb M Gillespie Date: 4/2/91
: Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-101, ACID DIGESTION FOR METALS ANALYSIS

APPLICABILITY

The procedure provides methods for acid digestion of water and soil/sediments samples for analysis of metals by ICP or AA. It may also be used to prepare samples for analysis of radionuclides. The methodology is consistent with CLP Inorganic acid digestion for metals.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within ±10% of the stated value.

b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ±5 in the next digit located beyond the last one stated.

Author Date RT Steele	Project Mgr. Date BM Gillespie	QAD Representative Date GK Gerke
Technical Reviewer Date BM Gillespie	Line Mgr. Date PF Salter	Other Date ALL ORIGINAL SIGNATURES ON FILE

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-101	1	09/26/90	1 of 7

2.0 Quality Control

All quality control data shall be maintained and available for easy reference or inspection.

Two quality control options (A and B) are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. The analyst will recognize the need to use option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

A. Employ a minimum of one method blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. A matrix spike sample may be periodically employed to ensure that the correct procedure is followed and that all equipment is operating properly at the analysts discretion or upon client request.

B. For all SOWs written by WHC for CERCLA protocol requests for analysis, employ a minimum of one method blank per sample batch (20 samples or less) to determine if contamination is occurring. Analyze at least one duplicate sample per sample batch (20 samples or less of the same matrix). A duplicate sample is a sample brought through the whole sample-preparation and analytical process. At least one matrix spike sample shall be employed for every sample batch (a sample batch is 20 samples or less of samples with the same basic matrix, i.e., soils, water, sludge, etc.). A matrix spike duplicate and/or laboratory control sample may be analyzed with any 20 samples if so directed by a Test Instruction (TI).

3.0 Apparatus and Materials

1) 250 mL beaker or other appropriate vessel.

2) Watch glasses

3) Thermometer that covers range of 0° to 200°C

4) Whatman No. 42 filter paper or equivalent

5) Hot plate, steam bath or hot water bath

6) 100 + 250 ml volumetric flasks

4.0 Reagents

1) ASTM Type II water (ASTM D1193)

2) Concentrated Nitric Acid (sp. gr. 1.41)

3) Concentrated Hydrochloric Acid (sp. gr. 1.19)

4) Hydrogen Peroxide (30%)

5) Acidified water 2.5% (v/v) HCl, 2% (v/v) HNO_3, 5% (v/v) HNO_3

5.0 Water Sample Preparation

5.1 Acid Digestion Procedure for Furnace Atomic Absorption Analysis

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 1 mL of (1:1) HNO_3:H_2O and 2 mL 30% H_2O_2 to the sample. If a spike sample is required or desired, (e.g., required by TI or ARF), add an appropriate amount of a spike solution containing the analytes of interest as defined in the TI or ARF to a duplicate or one of the samples being prepared and label the sample with the sample ID and "spike." This sample is not to be considered the duplicate sample for meeting QC requirements. The spike solution shall be made from the standard stock solutions defined in the analytical procedure for the analyte of interest. The amount of each analyte in the spike is determined by the cognizant scientist and should be near the value expected for the sample or at a minimum at a detectable amount (3-5 times the instrument detection limit). Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled (Type II) water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

If Sb is to be determined by furnace AA, use the digestate prepared for ICP/flame AA analysis.

5.2 Acid Digestion Procedure for ICP and Flame AA Analyses

Shake sample and transfer 100 mL of well-mixed sample to a 250-mL beaker, add 2 mL of (1:1) HNO_3:H_2O and 10 mL of (1:1) HCl:H_2O to the sample. If a spike sample is required or desired, (e.g., required by TI or ARF), add an appropriate amount of a spike solution containing the analytes of interest as defined in the TI or ARF to a duplicate or one of the samples being prepared and label the sample with the sample ID and "spike." This sample is not to be considered the duplicate sample for meeting QC requirements. The spike solution shall be made from the standard stock solutions defined in the analytical procedure for the analyte of interest. The amount of each analyte in the spike is determined by the cognizant scientist and should be near the value expected for the sample. Cover with watch glass or similar cover and heat on a steam bath or hot plate for 2 hours at 95°C or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material. (NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.) Adjust sample volume to 100 mL with deionized distilled (Type II) water. The sample is now ready for analysis.

Concentrations so determined shall be reported as "total".

6.0 Soil/Sediment Sample Preparation

6.1 Acid Digestion Procedure for ICP, Flame AA and Furnace AA Analyses

6.1.1 Scope and Application

This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (AAS) or by inductively coupled plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by AAS or ICP for the following metals:

- Aluminum
- Antimony
- Arsenic
- Barium
- Beryllium
- Bismuth
- Cadmium
- Calcium
- Chromium
- Cobalt
- Copper
- Iron
- Lead
- Magnesium
- Manganese
- Nickel
- Potassium
- Selenium
- Silver
- Sodium
- Thallium
- Vanadium
- Zinc

(Bismuth has been added to the CLP method list of metals)

6.1.2 Summary of Method

A representative 1 g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed or heated with either nitric acid or hydrochloric acid. Hydrochloric acid is used as the final reflux acid for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn. Nitric acid is employed as the final reflux acid for the furnace AA analysis of As, Be, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and

Zn. A separate sample shall be dried for a percent solids determination (See PNL-ALO-504).

(Bi has been added to the list of CLP metals analysis for furnace AA).

6.1.3 Sample Preservation and Handling

Soil/sediment (nonaqueous) samples shall be refrigerated at 4°C (±2°) from receipt until analysis when required by SOW, ARF or TI.

6.1.4 Procedure

1) Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01gms) a 1.0 to 1.5 gm portion of sample and transfer to a beaker. If a spike sample is required or desired, (e.g., required by TI or ARF), add an appropriate amount of a spike solution containing the analytes of interest as defined in the TI or ARF to a duplicate or one of the samples being prepared and label the sample with the sample ID and "spike." This sample is not to be considered the duplicate sample for meeting QC requirements. The spike solution shall be made from the standard stock solutions defined in the analytical procedure for the analyte of interest. The amount of each analyte in the spike is determined by the cognizant scientist and should be near the value expected for the sample or at a minimum at a detectable amount (3-5 times instrument detection limit).

2) Add 10 mL of 1:1 nitric acid (HNO_3:H_2o), mix the slurry, and cover with a watch glass. Heat the sample to 90°C in a hot water bath or 95°C on a hot plate for 10 minutes. Allow the sample to cool, add 5 ml of concentrated HNO_3, replace the watch glass, and heat for 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

3) After the second heating step has been completed and the sample has cooled, add 2 ml of Type II water and 3 ml of 30% hydrogen peroxide (H_2O_2). Return the beaker to the hot water bath or hot plate for warming to start the peroxide reaction. Care must be taken to ensure losses do no occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the beaker.

4) Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged. (NOTE: Do not add more than a total of 10 mL 30% H_2O_2).

5) If the sample is being prepared for the furnace AA analysis of Sb, the flame AA or ICP analysis of Al, Sb, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, K, Ag, Na, Tl, V, and Zn, add 5 ml of 1:1 HCl:H_2O and 10 ml of Type II water, return the covered beaker to the hot water bath or hot plate, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with Type II water. NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted sample has an approximate acid concentration of 2.5% (v/v) HCl and 5% (v/v) HNO_3. Dilute the digestate to ~~250 mL with acidified water (approximately 2.5% (v/v) HCL and 5% (v/v) HNO_3)~~ 200 mL (or other volume approved by cognizant scientist and client) to maintain constant acid strength. The sample is now ready for analysis.

6) If the sample is being prepared for the furnace analysis of As, Be, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Se, Ag, Tl, V, and Zn, if using a hot water bath heat for an additional two hours. If using a hot plate heat until the volume has been reduced to 2 ml, add 10 ml of Type II water, and warm the mixture. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 ml with Type II water.

   NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material. The diluted digestate solution contains approximately 2% (v/v) HNO_3. Dilute the digestate to 250 ml with acidified water (approximately 2% v/v HNO_3) to maintain constant acid strength. For analysis, withdraw aliquots of appropriate volume, and add any required reagent or matrix modifier. The sample is now ready for analysis.

   (Bi has been added to the CLP list of metals for furnace AA analysis).

6.1.5 Calculations

1) A separate determination of percent solids must be performed. (See PNL-ALO-504)

2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C - Concentration (mg/L)
V - Final volume in liters after sample preparation
W - Weight in kg of wet sample
S - % Solids/100

7.0 Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the ACT NOW Directive 89.1~~ established records management practices.

8.0 References

Modification by committee of Method 3050, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, July 1982

CLP SOW for Inorganic Analysis, SOW 788 7/88, Rev. 2, 2/89, Exhibit D, pg. D-5.

Battelle
Pacific Northwest Laboratories

Project Number ________________

Internal Distribution

PNL-MA-599 Manual Holders
File/LB

Date March 10, 1993

To Distribution

From Rose Nipper Rose

Subject Corrected Pages for ICN-PNL-ALO-102.2-R0

The subject ICN was not duplicated correctly. Please replace the pages stated below with the attached pages. Please destroy the pages that were duplicated incorrectly. If you have any questions, please give me a call at 376-9782.

ICN-PNL-ALO-102.2

Replace the ICN and pages 1 and 2 with the attached ICN and pages 1 and 2.

Thank you.

/rmn

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-102.2, RO
PAGE 1 OF 1

A. Document Number: PNL-ALO-102 Revision Number: 0
Document Title: Fusion of Hanford Tank Waste Solids
Document's Original Author: RT Steele

Effective Date of ICN: JAN [illegible] 1993

Change Requested by: RT Steele

B. Action:

Replace pages 1 and 2 with the attached pages 1 and 2.

C. Effect of Change:

1) To give flexibility to analysis.

2) To ensure sample spattering doesn't occur.

D. Reason for Change/Description of Change:

Reason

1) Procedure too restrictive for Tank matrices.

2) To prevent unwanted and uncontrolled acid-base reactions resulting in sample loss during fusion process.

Description

1) Section 1.0 - Changed capacity of volumetric flask from "250 ml" to "various capacities"

2) Section 2.0, Step 4 - Changed this sentence to "Adjust sample pH to 7.0 or greater..."

3) Section 2.0, Step 10 - Deleted "250 ml."

See redline text on page 2 of procedure.

E. Approval Signatures
(Please sign and Date)

Type of Change (Check (✓) one)
(✓)Minor Change ( )Major Change

PQ Department Concurrence: TL Ehlert TL Ehlert Date: 12/21/92
Approval Authority: AG King Date: 12/23/92
Other Approvals: RT Steele Rick [illegible] Steele Date: 12/21/92

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-102, FUSION OF HANFORD TANK WASTE SOLIDS

APPLICABILITY

This procedure will provide a uniform method for performing a fusion on various solid samples bringing them into solution in an acid media for subsequent analysis.

A fusion technique can be used for most solid samples to bring them into solution for further analysis. Each solid sample is unique, and may require that the Cognizant Scientist make minor changes to the parameters described in this procedure.

DEFINITIONS

None

RESPONSIBLE STAFF

The staff responsible for implementing this procedure are:

- Cognizant Scientist
- Technician

PROCEDURE

1.0 Equipment and Materials

- Deionized Type II Water
- Potassium Nitrate, crystals, reagent-grade
- Potassium Hydroxide, pellets, reagent-grade
- Sodium Peroxide, reagent-grade
- Hydrochloric Acid, 6 M - prepare by diluting 50 (±1) ml of reagent grade concentrated hydrochloric acid to 100 (±1) ml with deionized Type II water.
- Potassium Hydroxide saturated solution
- Sodium Hydroxide saturated solution
- Eppendorf Automatic Pipet, 100, 500, or 1000 µl
- Crucibles, nickel or zirconium
- Ultrasonic Bath
- Heat Lamp

Author Date RT Steele	Project Mgr. Date TE Jones	QAD Representative Date SL English
Technical Reviewer Date TE Jones	Line Mgr. Date WC Weimer	Other Date ALL ORIGINAL SIGNATURES ON FILE

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-102	0	08/03/89	1 of 3

- Hot Plate
- Muffle Furnace
- Analytical Balance, 4-place
- 10 cc Plastic Syringe
- Glass transfer pipet
- Volumetric Flask, various capacities ~~250 ml~~

2.0 Sample Fusion

Dry, weighed sludge samples are fused in either a nickel or zirconium crucible. The fused samples are then leached with deionized water, acidified and diluted to volume. The samples are then analyzed by the appropriate methods as required.

1. Sample viscosity permitting, thoroughly mix the sample to be fused.

2. Weigh into a tared crucible a selected sample size that produces approximately 1/4 gram dry weight. Weigh the sample to within 0.001 gram.

3. Add deionized water and disperse the sample evenly throughout the crucible. An ultrasonic bath may facilitate the rate of dispersal.

4. Adjust sample pH to 7.0 or greater (using indicator paper) using saturated KOH (Ni crucible) or NaOH (Zr crucible) with Eppendorf pipet.

5. Dry the sample under a heat lamp.

6. Reweigh the crucible to obtain sample dry weight.

7. Based on the dried weight of sample, add a ten-fold amount of flux to the crucible (KNO_3 0.5g + KOH in Ni; Na_2O_2 in Zr)

8. Complete the fusion in a muffle furnace by heating the sample to 500 ± 50°C and holding for 30 minutes at temperature.

9. Cool the melt to room temperature.

10. Leach the melt with deionized water and transfer the sample to a ~~250 ml~~ volumetric flask using a 10 cc plastic syringe and a glass transfer pipet.

11. Rinse the crucible with 50 ml of 6 <u>M</u> HCl and transfer to the flask.

12. Give the crucible a final water rinse and transfer to the volumetric flask.

Note: The transfer process should be completed such that there is enough dead space in the volumetric flask to allow heating.

13. If the fused solids sample is not completely in solution, heat the volumetric flask to the boiling point.

14. Cool the volumetric flask to room temperature and dilute to volume with deionized water. This solution or a suitable aliquot is used for sample analysis.

3.0 Records

Records will be maintained and controlled so as to conform to requirements of PAP-70-1701. Laboratory Records Books (LRB) and Analytical Report Cards provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the Act Now Directive 89.1~~ established records management practices.

4.0 Procedure Qualification

This procedure is considered qualified due to its dependence on well understood chemical principles.

INTERIM CHANGE NOTICE (ICN)

ICN - PNL-ALO-103.1 R1
Page 1 of 1

A.

Document Number: PNL-ALO-103 **Revision Number:** 1

Document Title: Water Leach of Sludges, Soils and other Solid Samples

Document's Original Author: RT Steele

Effective Date of ICN: 5/11/92

Change Requested by: TE Jones

B. **Action:**

Deleting ACT 89.1 and replacing with established records management practices.

Replace all pages due to new format.

C. **Effect of Change:**

Brings procedure into compliance.

D. **Reason for Change/Description of Change:**

ACT NOW Directive 89.1 no longer in existence.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 5/7/92
Approval Authority: AG King A. G. King **Date:** 5/7/92
Other Approvals: BM Gillespie **Date:** 5/11/92
: ______ **Date:** / /

TITLE: PNL-ALO-103, WATER LEACH OF SLUDGES, SOILS AND OTHER SOLID SAMPLES

APPLICABILITY

This procedure defines the method of sample preparation for the analysis of water soluble, inorganic constituents present in sludges, soils, and other solid samples. This procedure was developed by PNL to address the need for a preparation procedure for solid samples for analysis of the leachable anion content.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within ± 10% of the stated value.

b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

Author Date RT Steele	Project Mgr. Date BM Gillespie	QAD Representative Date GK Gerke
Technical Reviewer Date BM Gillespie	Line Mgr. Date PF Salter	Other Date ALL ORIGINAL SIGNATURES ON FILE

2.0 Quality Control

All quality control data shall be maintained and available for easy reference or inspection.

Two quality control options (A and B) are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. The analyst will recognize the need to use option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

A. Employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. A matrix spike sample may be periodically employed to ensure that correct procedure is followed and that all equipment is operating properly at the analysts discretion or upon client request.

B. For all SOWs written by WHC for CERCLA protocol requests for analysis, employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Analyze one duplicate sample for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample-preparation and analytical process. A matrix spike sample shall be employed for every 20 samples analyzed or per every set of samples, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with any 20 samples if so directed by a Test Instruction (TI).

3.0 Equipment and Materials

- Four-place Analytical Balance weighing to 0.001 g or better
- Erlenmeyer Flask, 125 ml
- Ultrasonic Cleaner
- Nalgene Disposable Filtering Apparatus, 0.45 µm pore size
- Plastic Bottle, 125 ml
- Deionized Type II Water
- Nalgene Stopper

4.0 Sample Leaching

A one to ten gram sample of sludge, soil or other solid material (wet weight) is contacted with 100 ml of deionized Type II water, filtered and the leachate analyzed for inorganic constituents as required.

1. Sample viscosity permitting, thoroughly mix the sample to be analyzed. If the sample cannot be thoroughly mixed due to viscosity, the presence of large particles (cobbles, pebbles, etc.), contact the cognizant scientist or Technical Task Leader for instruction on how to proceed.

2. Into a tared 125 ml Erlenmeyer flask, weigh a 1 to 10 (±.1) gram sample. Record the weight to the nearest 0.01 gram. If a spike sample is required or desired, (e.g., required by TI or ARF), add an appropriate amount of a spike solution containing the analytes of interest as defined in the TI or ARF to a duplicate of one of the samples being prepared and label the sample with the sample ID and "spike." This sample is not to be considered the duplicate sample for meeting QC requirements. The spike solution shall be made from the standard stock solutions defined in the analytical procedure for the analyte of interest. The amount of each analyte in the spike is determined by the cognizant scientist and should be near the value expected for the sample, or at a minimum, at a detectable amount (3-5 times the instrument detection limit).

3. Add 100 (±5) grams of Type II water to the flask and record the weight to the nearest 0.01 gram.

4. Place the stoppered flask into a ultrasonic bath and agitate one hour at ambient temperature.

5. Filter the sample with a 0.45 µm nalgene disposable filtering apparatus and using the building vacuum. Discard the solids and filter.

6. Transfer the filtrate to a labeled 125 ml plastic bottle. This solution or a suitable aliquot is used for sample analysis.

7. Store leachate in accordance with requirements defined in the relevant, specific analysis procedure.

5.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70 PAP-70-1701. Laboratory Records Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the Act Now Directive 89.1~~ established records management practices.

6.0 References

M. L. Jackson, Soil Chemical Analysis (1958), Prentice Hall, Inc. Sixth Printing (1970) by the author, Dept. of Soil Science, University of Wisconsin, Madison, Wis. 53706.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-104, EXTRACTION PROCEDURE TOXICITY

APPLICABILITY

The Extraction Procedure (EP) is designed to simulate the leaching a waste will undergo if disposed of in a sanitary landfill. This test is designed to simulate leaching that takes place in a sanitary landfill only. It is a laboratory test in which a representative sample of a waste is extracted with distilled water maintained at a pH of 5 using acetic acid. The extract obtained from the EP (the "EP Extract") is then analyzed to determine if any of the thresholds established for the eight elements (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) are exceeded. If the EP Extract contains any one of these substances in an amount equal to or exceeding the levels specified in Table 1, the waste possesses the characteristic of Extraction Procedure Toxicity and is a hazardous waste.

TABLE 1. Maximum Concentration of Contaminants for Characteristic of EP Toxicity

EPA Hazardous Waste Number	Contaminant	Maximum Concentration (mg/l)	Analysis Method/Procedure
D004	Arsenic	5.0	GFAA/PNL-ALO-214
D005	Barium	100.0	ICP/PNL-SP-7
D006	Cadmium	1.0	ICP/PNL-SP-7
D007	Chromium	5.0	ICP/PNL-SP-7
D008	Lead	5.0	ICP/GFAA/PNL-SP-7 /PNL-ALO-216
D009	Mercury	0.2	CVAA/PNL-ALO-213
D010	Selenium	1.0	GFAA/PNL-ALO-215
D011	Silver	5.0	ICP/PNL-SP-7

Author	**Date** 4/5/90	**Project Mgr.**	**Date** 4/5/90	**QAD Representative** SL English	**Date** 4-6-90
Technical Reviewer	**Date** 4/5/90	**Line Mgr.**	**Date** 4/6/90	**Other** N/A	**Date**
Procedure No. PNL-ALO-104	**Revision No.** 0	**Effective Date** APR 30 1990		**Page** 1	**of** 4

DEFINITIONS

None

RESPONSIBLE STAFF

The staff responsible for implementing this procedure are:

- Project Manager
- Task Leaders
- Technical Staff

PROCEDURE

1.0 Apparatus and Materials

1.1 Extractor: For purposes of this test, an acceptable extractor is one that will impart sufficient agitation to the mixture to (1) prevent stratification of the sample and extraction fluid and (2) ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. Mechanical stirring will be used in the hot cells.

1.2 pH Meter:

1.3 Filter holder: A filter holder capable of supporting a 0.45-μ filter membrane and able to withstand the pressure needed to accomplish separation. Suitable filter holders range from simple vacuum units to relatively complex system that can exert up to 5.3 kg/cm^3 (75 psi) of pressure.

1.4 Filter membrane: Filter membrane suitable for conducting the required filtration shall be fabricated from a material which: (1) is not physically changed by the waste material to be filtered, and (2) does not absorb or leach the chemical species for which a waste's EP Extract will be analyzed.

2.0 Digestion Procedure

2.1 Place 10 ± 0.2 grams of material into a beaker and add 160 ml of deionized water.

2.2 After the solid material and deionized water are placed in the beaker, the operator should begin agitation and measure the pH of the solution in the beaker. If the pH is greater than 5.0, the pH of the solution should be decreased to 5.0 ± 0.2 by adding 0.5 N acetic acid. If the pH is equal to or less than 5.0, no acetic acid should be added. The pH of the solution should be monitored, as described below, during the course of the extraction and, if the pH rises above 5.2, 0.5 N acetic acid should be added to bring the pH down to 5.0 ± 0.2. However, in no event shall the aggregate amount of acid added to the solution exceed 4 ml of acid per gram of solid. The mixture should be agitated for 24 hr and maintained at 20°-40°C (68°-104°F) during this time. It is recommended that the operator monitor and adjust the pH during the course of the extraction as follows:

2.2.1 A pH meter should be calibrated in accordance with the manufacturer's specifications.

2.2.2 The pH of the solution should be checked and, if necessary, 0.5 N acetic acid should be manually added to the extractor until the pH reaches 5.0 ± 0.2. The pH of the solution should be adjusted at 15-, 30-, and 60-min intervals, moving to the next longer interval if the pH does not have to be adjusted more than 0.5 pH units.

2.2.3 The adjustment procedure should be continued for at least 6 hr.

2.2.4 If, at the end of the 24-hr extraction period, the pH of the solution is not below 5.2 and the maximum amount of acid (4 ml per gram of solids) has not been added, the pH should be adjusted to 5.0 ± 0.2 and the extraction continued for an additional 4 hr, during which the pH should be adjusted at 1-hr intervals.

2.3 At the end of the extraction period, deionized water should be added to the extractor in an amount determined by the following equation:

$$V = (20)(W) - 16(W) - A$$

where:

V = ml deionized water to be added

W = weight in g of solid charged to extractor

A = ml of 0.5 N acetic acid added during extraction

2.4 The material in the extractor should be separated into its component liquid and solid phases in the following manner.

2.4.1 Allow slurries to stand to permit the solid phase to settle (wastes that are slow to settle may be centrifuged prior to filtration) and set up the filter apparatus.

2.4.2 Wet the filter with a small portion of the waste's or extraction mixture's liquid phase. Transfer the remaining material to the filter holder and apply vacuum or gentle pressure (10-15 psi) until all liquid passes through the filter. Stop filtration when air or pressurizing gas moves through the membrane. If this point is not reached under vacuum or gentle pressure, slowly increase the pressure in 10 psi increments to 75 psi. Halt filtration when liquid flow stops.

2.5 Extract Digestion

EP-Tox extracts are digested following PNL-ALO-101.

2.6 The liquid is the extract and should be analyzed for the presence of any of the contaminants specified in Table 1 using the Analytical Procedures identified in Table 1. All of these analytical methods are included in PNL-MA-599.

3.0 Quality Control

Quality control requirements will be defined in the appropriate Test Instructions.

4.0 References

Method 1310, SW-846, 2nd ed., Test Methods for Evaluating Solid Waste, EPA Office of Solid Waste and Emergency Response, April 1984.

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-105.2 R0
Page 1 of 1

A.
Document Number: PNL-ALO-105 **Revision Number:** 0

Document Title: Procedure for Preparation of Samples to be counted by Gamma-Ray Spectroscopy

Document's Original Author: EA Lepel

Effective Date of ICN: 5/7/92

Change Requested by: TE Jones

B. **Action:**
Deleting ACT 89.1 and replacing with established records management practices.

Replace all pages due to new format.

C. **Effect of Change:**
Brings procedure into compliance.

D. **Reason for Change/Description of Change:**
ACT NOW Directive 89.1 no longer in existence.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 5/7/92
Approval Authority: AG King **Date:** 5/7/92
Other Approvals: ______ **Date:** / /
: ______ **Date:** / /

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-105.1
Page 1 of 1

A. Document Number: PNL-ALO-105 Revision Number: 0
Document Title: Procedure for Preparation of Samples to be counted by Gamma-Ray Spectroscopy
Document's Original Author: E. A. Lepel

Effective Date of ICN: 4/26/91

Change Requested By: E. A. Lepel

B. Action:

Please destroy old procedure and replace with the procedure attached.

C. Effect of Change:

To allow for more efficient use of manpower when handling radioactive samples. Additionally, reduced personnel exposure and reduced liklihood of workplace contamination would result.

D. Reason for Change/Description of Change

To allow for more efficient use of manpower when handling radioactive samples. Additionally, reduced personnel exposure and reduced liklihood of workplace contamination would result.

Description of Change: See attached

E. Approval Signatures

(Please Sign and Date)

Type of Change: (Check (✓) one)

( ) Minor Change [✓ Major Change]

Process Quality
~~QS&R~~ Department Concurrence: G Stoetzke, QE Date: 4/10/91
Approval Authority: Date: 4/11/91
Other Approvals: Date: 4/12/91
: B M Gillespie Date: 4/15/91

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-105, PROCEDURE FOR PREPARATION OF SAMPLES TO BE COUNTED BY GAMMA-RAY SPECTROSCOPY

SCOPE

This procedure shall be used to prepare samples for gamma energy counting on germanium spectrometers (See PNL-ALO-464). The samples may be liquids, solids (soils, sediments, etc.), air filters, vegetation, or other miscellaneous samples. This procedure was developed by PNL Scientists for the preparation of samples to be counted by gamma-ray spectroscopy.

APPLICABILITY

This procedure covers the preparation of samples to be counted in the 329 Laboratory Gamma-Ray Spectroscopy facilities.

DEFINITIONS/ACRONYMS

ARF - Analytical Request Form
LRB - Laboratory Record Book
LTC - Large Tuna Can
STC - Small Tuna Can
TI - Test Instruction

RESPONSIBLE STAFF

Counting Room Manager
Cognizant Scientist/Analyst

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) A tolerance limit can be stated with a measurement value given in a method, or 2) if a tolerance limit is

Author Date EA Lepel	Project Mgr. Date BM Gillespie	QAD Representative Date GK Gerke
Technical Reviewer Date KH Abel	Line Mgr. Date JM Latkovich	Other Date ALL ORIGINAL SIGNATURES ON FILE

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-105	0	09/26/90	1 of 6

not stated with a measurement value, then the following system of tolerances shall be in effect:

a. When two or more significant figures are specified, the tolerance limit is ±5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL; 450 g means 450 ± 5 g; 369 mL means 369.0 ± 0.5 mL.

b. If a single significant figure is specified, the actual measurement shall be within ± 5% of the stated value. For example, 20 mL means a volume between 19 and 21 mL.

2.0 Equipment and Materials

Balances - Mettler PC4400 electronic balance. Dual range balance of 0.01-400.00 g and 1.0-4000.0 g
Large tuna can sealer
Small tuna can sealer
Drying oven
Hot plate
Mortar and pestle
Assorted polyethylene bottles
White plastic tape
Large tuna can (LTC) made of aluminum, 5.9-cm dia x 2.8-cm height, 220 g usable capacity
Small tuna can (STC) made of aluminum, 3.4-cm dia x 2.4-cm height, 80 g usable capacity
Shatterbox to pulverize rock chips into a fine powder. Made by SPEX Industries Inc., Mutuchen, NJ
Assorted volumetric glassware and beakers.
Dessicator and dessicant

3.0 Sample Preparation Procedures

The large variety of samples that have been processed in the Low-Level Counting Rooms have resulted in a number of "standard" sample geometries. The number of sample geometries have been minimized because each geometry requires calibration of that detector system. Typical sample geometries are:

TABLE 1: Typical Geometries Used in Gamma Counting

	Geometry	Containment
1)	Sealed large tuna can (LTC) ≤220 g (solid)	sealed LTC, sealed in a poly bag
2)	Sealed small tuna can (STC) ≤80 g (solid)	sealed STC, sealed in a poly bag
3)	125-ml poly bottle - 10,20,50,100 ml (liquid)	screw cap, tape, sealed in poly bag
4)	500-ml poly bottle - 500 ml (liquid)	screw cap, tape, sealed in poly bag
5)	9-oz jar - 50,100,150,200 ml (liquid or solid)	screw cap, tape, sealed in poly bag
6)	1-in. x 6-in. petri dish (solid)	tape, sealed in poly bag
7)	Point source on card	tape on both sides, (plastic bag)
8)	Scintillation vial - 1,5,10,20 ml (liquid)	screw cap, tape, sealed in poly bag
9)	2-dram poly vial (solid or liquid)	heat seal vial and poly bag
10)	2/5,2/27 and 2-dram poly vial (solid or liquid)	snap cap heat sealed, in poly bag
11)	Marinelli beaker - 1 L, 2 L (liquid or solid)	tape, poly bag
12)	Filter - 47 mm (solid)	heat-sealed in poly bag
13)	3-in. dia puck, 1/2-in. thick (1/2" x 3") (solid)	PVC ring, tape, mylar or poly bag

The choice of a specific geometry is based on the type of sample (whether solid or liquid), the amount of sample available, whether that geometry has been calibrated for that type of sample, and the amount of sample preparation required to get the sample into a specific geometry. The sample geometry is determined for each sample by the cognizant staff member/analyst. For some kinds of samples, little or no sample preparation is required before counting a sample.

3.1 Liquid Samples

Liquid samples may be counted directly by putting the appropriate amount of liquid into the correct container. In addition, liquid samples may result from other chemical preparation or concentration procedures. In that case, it is assumed that a procedure is in effect to cover those additional steps.

3.1.1 Choose the appropriate sample geometry (container) from Table 1 based on the volume and type of liquid available and accuracy required.

3.1.2 Using clean containers, transfer the appropriate volume by weighing into the chosen container. The sample volume shall be one of the volumes listed in Table 1 associated with the selected container geometry unless otherwise specified in a Test Instruction (TI), Analytical Request Form (ARF), or other documentation from the client. Seal the container with the lid, wrap with plastic tape, and label with sample identification (ID).

3.1.3 Seal the sample and container into a plastic bag to prevent cross contamination and contamination of the counting cave.

3.1.4 Record in the LRB the sample ID, sample geometry chosen, weight and volumes taken, and balance number.

3.1.5 Sample is ready for gamma counting (see PNL-MA-599, PNL-ALO-464). Transfer the sample to the appropriate storage cabinet in the Counting Rooms (Rooms 13C, 14C, 4D, 329 Building) to await counting.

3.2 Solid Samples

Solid samples, such as soils, sediments, rocks, gravel, resings, etc., may be counted without any sample preparation. Depending on the degree of accuracy of the analysis and the concern with respect to homogeneity of the sample, the samples may be reduced to a fine powder using the SPEX shatterbox. In both cases, a geometry is chosen from Table 1.

After the geometry has been chosen, the non-radioactive sample must be dried before taking an aliquot for counting. Equivalently, a small aliquot (2-5 g) may be used to determine the moisture content while an undried aliquot is counted. If this is done, the data obtained must be corrected to reflect "Dry Weight." Generally, it is easier to dry the total amount of material first and then take an aliquot for counting.

However, for radioactive samples (expecially hotter samples), it is best to take an aliquot and measure the sample as received. An additional small aliquot may be used to determine the moisture content. From the standpoint of personnel exposure and ALARA, this would be preferred method for radioactive samples.

3.2.1 Choose the appropriate counting geometry (container) based on the type and size of the sample, and the accuracy required. Record choice in LRB.

3.2.2 Determine the moisture content of the sample. If the dried sample is nonradioactive, the whole sample may be dried or equivalently a small aliquot (2-5 g) may be dried. If the sample is radioactive, a small aliquot (2-5 g) may be used for the moisture determination.

Put an aliquot of the sample into a tared container and determine the WET weight. Record weight and balance number in LRB. Place the container in the drying oven for about 16 hr at about 110°C. If the sample is dry, remove it and let it cool to room temperature in a desiccator. Determine the DRY weight and record in LRB. An unstable balance display is indicative of: a) a container that hasn't cooled to ambient temperature, or b) hydrostatic changes in the sample. If this is the case, place the sample back into the drying oven and dry for at least 1 hour (maximum of 24 hours). Let the sample cool to room temperature in a desiccator, and then reweigh. If the difference in sample weights is ≤0.01 g between the first and second weighings, constant weight has been achieved. The final dry weight obtained is the dry weight of the sample. If not, repeat the drying process until constant weight is achieved. Transfer the sample to a container for storage and label with sample ID if not doing the next step.

3.2.3 If requested by TI, ARF, or documentation from the client, and for non-radioactive samples only, pulverize the sample to a fine powder using the SPEX Shatterbox. Take an aliquot of sample and place into the sample chamber. Run the Shatterbox for 2-10 min to produce a fine powder. Transfer the powder to a container for storage and label.

3.2.4 Transfer a known amount of dried solid to the container in which the analysis will be made. The container shall be chosen from Table 1. Typically, this will be the large tuna can geometry which can hold up to 220 g of dry solid material. Record in the LRB the weight of the sample and the balance used, and label the sample with the sample ID.

3.2.5 Sample is ready for gamma counting (See PNL-MA-599, PNL-ALO-464). Transfer the sample to the appropriate storage cabinet in the Counting Rooms (Rooms 13C, 14C, 4D, 329 Building) to await counting.

3.3 Air Filters

3.3.1 Choose the appropriate geometry (container) for the air filter to be counted. The 329 Roof Filters have been counted in the 1 x 6 geometry, where the 47 mm filters have been counted individually.

3.3.2 Prepare the sample according to the geometry chosen, and record in LRB. Seal in a plastic bag. Record sample ID on the plastic bag or sample card that accompanies the sample.

3.3.3 Sample is ready for gamma counting (See PNL-MA-599, PNL-ALO-464). Transfer the sample to the appropriate storage cabinet in the Counting Rooms (Rooms 13C, 14C, 4D, 329 Building) to await counting.

3.4 Vegetation

Vegetation samples may have minimal or extensive sample preparation prior to gamma counting. If the preparation steps are extensive, they shall be covered under an appropriate procedure supplied by the requester.

The amount of sample dictates the geometry (container) to be used. If there is plenty of sample, it can be pressed into a "Marinelli" geometry (container); otherwise it may be counted in a LTC.

3.4.1 Based on the amount of sample, choose the sample geometry (container) in which the samples are to be counted.

3.4.2 To the appropriate geometry container, add the vegetation material. Determine the net weight of the material by weighing.

3.4.3 Record in the LRB the geometry chosen, sample weight, and the balance identification.

3.4.4 Sample is ready for gamma counting (See PNL-MA-599, PNL-ALO-464). Transfer the sample to the appropriate storage cabinet in the Counting Rooms (Rooms 13C, 14C, 4D, 329 Building) to await counting.

4.0 Records

Records will be maintained and controlled so as to conform to requirements of PAP-70-1701. Laboratory Record Books (LRBs) and Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the Act Now Directive 89.1~~ established records management practices.

INTERIM CHANGE NOTICE
ICN

ICN-PNL-ALO-106.4
PAGE 1 OF 1

A. Document Number: PNL-ALO-106.4 Revision Number: 0

Document Title: Acid Digestion for Preparation of Samples for Radiochemistry /Analysis

Document's Original Author NL Wynhoff

Effective Date of ICN: 02/08/93

Change Requested by: RS Strebin, Jr.

B. Action: Replace pages 1 through 4 with the attached pages 1 through 5.

C. Effect of Change: Add a HCl leach procedure, and allow different acids to be used for leaching.

D. Reason for Change/Description of Change:

Reason:

1. Need to use HCl to leach a set of samples.
2. Add an alternate leach process to the procedure.

Description:

1. Renamed section 6 to Soil HCl Leach.
2. Added sections 6.1 through 6.7.
3. Records section is now numbered 7.0.

See redline text in procedure.

E. Approval Signatures:
(Please Sign and Date)

Type of Change (Check (✓) one)
(✓) Minor Change ( ) Major Change

QP Concurrence: TL Ehlert TL Ehlert Date: 2/8/93
Approval Authority: AG King Date: 2/18/93
Other Approvals: NL Wynhoff Date: 2/12/93
: Date:

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-106.3 R0
Page 1 of 1

A.

Document Number: PNL-ALO-106 **Revision Number:** 0

Document Title: Acid Digestion for Preparation of Samples for Radiochemical Analysis

Document's Original Author: NL Wynoff

Effective Date of ICN: 5/12/92

Change Requested by: TE Jones

B. **Action:**

Deleting ACT 89.1 and replacing with established records management practices.

Replace all pages due to new format.

C. **Effect of Change:**

Brings procedure into compliance.

D. **Reason for Change/Description of Change:**

ACT NOW Directive 89.1 no longer in existence.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X **Minor** ___ **Major**

Process Quality Department: TL Ehlert TL Ehlert **Date:** 5/7/92

Approval Authority: AG King **Date:** 5/7/92

Other Approvals: TE Jones **Date:** 5/12/92

: **Date:** / /

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-106.2
Page 1 of 1

A. Document Number: PNL-ALO-106 Revision Number: 0
Document Title: Acid Digestion for Preparation of Samples for Radiochemical Analysis
Document's Original Author: N. L. Wynhoff

Effective Date of ICN: 4/26/91

Change Requested By: NL Wynhoff

B. Action:
Replace pages 3 and 4.

C. Effect of Change:

Allow analyst to address operational needs during the leaching procedure that the original procedure did not allow for.

D. Reason for Change/Description of Change If sample volume is reduced by evaporation, additonal solids may precipitate. It may then be necessary to repeat the filtering as in previous steps. Also, it may be useful to reduce leachate volume before dilution to a known volume.

Add the following before the last sentence in Section 4.5, "If a ppt forms, repeat Step 4.4."
To the end of Sec. 5.7, add, "It may be useful to evaporate the leach solution to a lower volume before dilution to a known volume. If a ppt forms, filter and discard ppt"
Add the following before the last sentence in Section 5.8, "If a ppt forms, filter and discard the ppt."

E. Approval Signatures

(Please Sign and Date)

Type of Change: {Check (✓) one}

( ) Minor Change (X) Major Change

Process Quality Department Concurrence: GKGerbe, QE Date: 3/15/91
Approval Authority: Date: 3/18/91
Other Approvals: B.M Gillespie Date: 3/18/91
: Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-106, ACID DIGESTION FOR PREPARATION OF SAMPLES FOR RADIOCHEMICAL ANALYSIS

APPLICABILITY

The procedure provides methods for acid digestion of radionuclides in water and soil/sediment samples for analysis by alpha, beta or gamma counting. For soil/sediment analysis an acid leach is employed. This method was developed by PNL radioanalytical scientists, and is based on over 10 years experience in analyzing a variety of samples for radionuclides by alpha, beta, or gamma counting techniques.

DEFINITIONS/ACRONYMS

ml - milliliter
um - micrometer
ppt - precipitate
g - grams

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

(a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however shall be within ± 10% of the stated value.

Author Date NL Wynoff	Project Mgr. Date BM Gillespie	QAD Representative Date GK Gerke
Technical Reviewer Date TE Jones	Line Mgr. Date P Salter	Other Date ALL ORIGINAL SIGNATURES ON FILE

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-106	0	09/26/90	1 of 5

(b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Reagents, Equipment and Materials

Nitric acid - 8 M. 50 mls Type II water and 50 mls reagent grade acid or multiples thereof.

Nitric acid - concentrated 16 M.

Hydrochloric acid - 6 M. 50 mls Type II water and 50 mls reagent grade acid or multiples there of.

Hydrochloric acid - concentrated, 12 M.

ASTM Type II water (ASTM D1193).

Hot plate.

Pyrex beakers, 50 ml, 250 ml (or other appropriate vessel).

Watch glasses, to fit above beakers.

Filter apparatus - appropriately sized for volume of sample filtered.

Filters - glass microfiber or membrane, 1.5 μm effective retention or better, sized to fit above filter apparatus (or equivalent).

3.0 Quality Control

Quality control requirements are defined for each specific radiochemical analysis in the specific radiochemical analysis procedure. The analyst shall refer to the appropriate analysis procedure for guidance on QC requirements in that analysis. Analysis procedures are specified for a sample or group of samples by a TI or ARF. If an analysis procedure is not specified in a TI or ARF, then the Cognizant Scientist shall determine the appropriate procedure to be used for the requested analysis for the sample(s).

4.0 Water Sample Preparation

4.1 Shake sample and transfer at least 100 ml of well-mixed sample to a 250 ml glass beaker. (If more than 100 ml sample is needed to reach detectable levels, evaporate, at below boiling temperatures, the sample to about 100 ml.) Record initial sample volume.

4.2 If directed by a cognizant scientist, add radionuclide tracer/spike as required by the requested analysis. The spike/tracer amount shall be specified by the Cognizant Scientist. It is should be close to the expected amount of nuclide present or at the minimum, a detectable amount (3x5 times the instrument detection limit). Place the spike/tracer for blanks or standards into 100 ml of Type II water.

Note: Record exact volume, isotope and calibrated activity of tracer solution in the LRB or Data Sheet as specified in the analysis procedure(s).

4.3 Add 10 ml of $8MHNO_3$ to the sample. Cover with a watch glass or similar cover. Heat on a hot plate for 2-3 hours at 100 ± 20°C or until sample volume is reduced to between 25 and 50 ml. Make certain sample does not boil. Cool sample to room temperature.

4.4 If visible solids are present, filter to remove insoluble material except do not filter samples if preparing samples for Sr analysis only. Samples may not be filtered for any analyses upon client request in an ARF, SOW or TI.

Note: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

4.5 Adjust sample volume to meet the needs of the radionuclide separation procedure requested. If a ppt forms, repeat Step 4.4. The sample is now ready for analysis.

5.0 Soil/Sediment Sample Preparation

5.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 10.0 g portion of sample and transfer to a beaker. Record weight in the LRB or on the data sheet.

5.2 If directed by a Cognizant Scientist, add radionuclide tracer/spike as required by the requested analysis. The spike/tracer amount shall be specified by the Cognizant Scientist. It is should be close to the expected amount of nuclide present or at the minimum, a detectable amount (3x5 times the instrument detection limit). Place the spike/tracer for blanks or standards into the 10 ml 8 M nitric acid of the next step.

Note: Record exact volume, isotope and calibrated activity of tracer solution in the LRB or on laboratory data sheets as specified in the analysis procedure.

5.3 Add enough 8 M HNO_3 to cover the sample (about 10 ml), mix the slurry, and cover with a watch glass. Heat the sample to to 100 ± 20°C) and reflux for 10 - 30 minutes without boiling. Add 10 ml of concentrated HNO_3, replace the watch glass, and reflux for 10 - 30 minutes. Do not allow the volume to be reduced to less than 5 ml while maintaining a covering of solution over the bottom of the beaker.

5.4 Allow the sample to cool to room temperature. Filter. Save filtrate in a labelled beaker.

5.5 Return the ppt and filter to the beaker. Repeat steps 5.3 and 5.4 one time, adding filtrate to the previously saved filtrate.

5.6 Return the ppt and filter to the beaker. Add enough water to cover the sample, mix the slurry and cover with a watch glass. Heat sample to 100 ± 20°C) and reflux 10 - 30 minutes without boiling. Repeat step 5.4, adding filtrate to the previously saved filtrate.

5.7 If the entire sample leach solution will not be used for a single analysis, dilute sample to a known volume and record the volume. It may be useful to evaporate the leach solution to a lower volume before dilution to a known volume. If a ppt forms, filter and discard ppt.

5.8 Take aliquots for analysis and adjust the volume of these aliquots to meet the needs of the radionuclide separation requested. Aliquot volume will be determined by the Cognizant Scientist. Use Type II water for dilution and evaporation for volume reduction. If a ppt forms, filter and discard the ppt. The sample is now ready for analysis.

6.0 Soil HCl Leach - This section is an alternative to section 5.0.

6.1 Mix the sample thoroughly. If rocks are present estimate the fraction but do not analyze. Weigh a 1.0 to 10.0 gm portion of sample and transfer to Erlenmeyer flask or a beaker. Record the sample weight.

6.2 If directed by a Cognizant Scientist, add radionuclide tracer/spike. Record the tracer added. Place the spike/tracer for blanks or standards into 10 ml 6 M HCl, which is the first reagent in step 6.3.

NOTE: Record exact volume, isotope and the spike/tracer identification.

6.3 Add enough 6 M HCl to cover the sample (10-50mL), add a stir bar and cover with a watch glass. Heat the sample with stirring, to near boiling for 4-12 hours.

6.4 Add 1 mL of conc HNO_3 to the sample and heat to near boiling with stirring for 2-12 hours.

6.5 Allow the sample to cool, then filter the sample using a fiberglass filter in a filter unit. Wash the soil on the filter with 6 M HCl until no yellow color is removed then wash the soil with up to 10 ml of water.

Note: Steps 6.3 and 6.5 may be repeated if requested by the Cognizant Scientist using H_2O, HCl or HNO_3. All the leaches are combined.

6.6 Adjust the sample volume to meet the needs of the separation procedure requested. If a ppt forms, consult Cognizant Scientist.

6.7 The sample is now ready for analysis.

7.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. All record of weights, volumes, and spike/tracer conc./vol. shall be on Alpha or Beta Counting Data Sheets, LRBs or Sample Record log data sheets (depending on analysis requested). Laboratory Record Books will be used in accordance with established records management practices.

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-107.2 R0
Page 1 of 1

A.

Document Number: PNL-ALO-107 **Revision Number:** 0

Document Title: Leach Procedure for Preparing Sludges, Soils and other Solid Samples for Free Cyanide Analysis

Document's Original Author: KH Pool

Effective Date of ICN: 5/11/92

Change Requested by: TE Jones

B. **Action:**

Deleting ACT 89.1 and replacing with established records management practices.

Replace all pages due to new format.

C. **Effect of Change:**

Brings procedure into compliance.

D. **Reason for Change/Description of Change:**

ACT NOW Directive 89.1 no longer in existence.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 5/7/92
Approval Authority: AG King A.G. King **Date:** 5/7/92
Other Approvals: BM Gillespie B.M. Gillespie **Date:** 5/11/92
: ______ **Date:** / /

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-107.1
Page 1 of 3

A. Document Number: PNL-ALO 107.1 Revision Number: 0
Document Title: LEACH PROC./FREE CYANIDE
Document's Original Author: K. POOL

Effective Date of ICN: 10/01/91

Change Requested By: P.K. MELETHIL

B. Action

REPLACE PAGES 3 AND 4.

C. Effect of Change

1. Reduction in sample size and leachate volume.
2. Allow use of IC eluant (PNL-ALO-271) for leaching in addition to 0.02 N NaOH.
3. Allow use of sonication for extraction in additon to magnetic stirring.

D. Reason for Change/Description of Change

1. To reduce sample waste and minimize radiation exposure to operator.
2. To reduce disturbance in column chemistry by matrix matching of leachate and eluant.
3. Sonication is as effective or better as an extraction device than mechanical stirring for small samples. (See procedure PNL-ALO-103).

E. Approval Signatures

(Please sign and date)

Type of Change: (Check (✓) one)

☐ Minor Change ☒ Major Change

Process Quality Department: GK Gerke GKGerke Date: 10/4/91
Approval Authority: AG King Date: 10/6/91
Other Approvals: B Gillespie Date: 10/4/91
: Date: / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-107, LEACH PROCEDURE FOR PREPARING SLUDGES, SOILS AND OTHER SOLID SAMPLES FOR FREE CYANIDE ANALYSIS

APPLICABILITY

This procedure defines the method of sample preparation for the analysis of free cyanide present in sludges, soils, and other solid samples. This procedure was developed by PNL to address the need for a preparation procedure for solid samples for analysis of the leachable free cyanide content.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) State with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

a) Unless otherwise specified, all values for measurements stated in the methods (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within ± 10% of the stated value.

Author Date KH Pool	Project Mgr. Date BM Gillespie	QAD Representative Date GK Gerke
Technical Reviewer Date BM Gillespie	Line Mgr. Date P Salter	Other Date ALL ORIGINAL SIGNATURES ON FILE

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-107	0	09/26/90	1 of 4

b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ± 5 in the next digit located beyond the last one stated.

2.0 Quality Control

All quality control data shall be maintained and available for easy reference or inspection.

Two quality control options (A and B) are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA requirements. Option B shall then be followed. The analyst will recognize the need to use option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a Statement of Work (SOW), and these will be conveyed to the analyst through a TI.

A. Employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Run duplicate analysis upon client request. A matrix spike sample may be periodically employed to ensure that correct procedure is followed and that all equipment is operating properly at the analysts discretion or upon client request.

B. For all SOWs written by WHC for CERCLA protocol requests for analysis, employ a minimum of one blank per sample batch (20 samples or less) to determine if contamination is occurring. Analyze one duplicate sample for every 20 samples or for each set, whichever is smaller. A duplicate sample is a sample brought through the whole sample-preparation and analytical process. A matrix spike sample shall be employed for every 20 samples analyzed or per every set of samples, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with any 20 samples if so directed by a Test Instruction (TI).

3.0 Equipment and Materials

- Analytical balance weighing to ±0.01 g or better
- Magnetic stirrer and teflon coated stir bars
- 0.45 μm pore size syringe fitters
- Poly bottles, 4 oz. (125 ml)
- Deionized ~~Type II~~ water: Water shall be used for sample, standard and reagent dilutions such that no cyanide above the method detection limit are found in it.

- 10 N NaOH - dissolve 400 g NaOH pellets in 1 liter Type II deionized water, store in poly bottle
- 0.02 N NaOH - 2 ml of 10 N NaOH dissolved in 1 liter Type II deionized water
- IC Eluant - See procedure PNL-ALO-271 (Free Cyanide Analysis)
- 100 ml graduated cylinder

4.0 Sample Leaching

A ~~one to ten gram~~ sample of sludge, soil or other solid material (wet weight) is contacted with ~~100 ml of~~ 0.02 N NaOH or IC eluant, and at the time of analysis a portion of the slurry is injected into the ion chromatograph sample loop after filtering through a 0.45 μm pore size syringe filter. The sample to leachate weight ratio should be between 10-100.

4.1 Sample viscosity permitting, thoroughly mix the sample to be analyzed. If the sample cannot be thoroughly mixed due to viscosity, the presence of large particles (cobbles, pebbles, etc.), contact the cognizant scientist or Technical Task Leader for instruction on how to proceed.

4.2 ~~Into a tared 4 oz poly bottle, weigh a 1 to 10 (±0.01) gram sample.~~Weigh sample into a bottle and record sample ~~the~~ weight to the nearest 0.01 gram. If a spike sample is required or desired, (e.g., required by TI or ARF), add an appropriate amount of a cyanide spike solution as defined in the TI or ARF to a duplicate of one of the samples being prepared and label the sample with the sample ID and "spike." This sample is not to be considered the duplicate sample for meeting QC requirements. The spike solution shall be made from a standard stock solution defined in the analytical procedure for free cyanide. The amount of cyanide in the spike is determined by the cognizant scientist and should be near the value expected for the sample, or at a minimum, at a detectable amount (3-5 times the instrument detection limit).

4.3 ~~Using a graduate cylinder, add 100 (±2) ml of 0.02 N NaOH to the poly bottle.~~ Add either 0.02 N NaOH or IC eluant to the sample and record the volume within ±2%.

4.4 Add a teflon coated stir bar to the poly bottle, secure cap to bottle, and magnetically stir or sonicate for a minimum of 1 hour.

4.5 Store the slurry in a refrigerator at 4 ± 2°C until analysis can be performed, but not longer than 5 working days.

4.6 Store the filtered leachate in a refrigerator at 4° ± 2°C.

5.0 Records

Records will be maintained and controlled so as to conform to requirements of PNL-MA-70 PAP-70-1701. Laboratory Records Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the Act Now Directive 89.1~~ established records management practices.

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-108.2 R0
Page 1 of 1

A.

Document Number: PNL-ALO-108 **Revision Number:** 0

Document Title: Aqueous Leach of Sludges, Soils, and other Solid Samples for Anion Analysis

Document's Original Author: PF Salter

Effective Date of ICN: 5/7/92

Change Requested by: TE Jones

B. **Action:**

Deleting ACT 89.1 and replacing with established records management practices.

Replace all pages due to new format.

C. **Effect of Change:**

Brings procedure into compliance.

D. **Reason for Change/Description of Change:**

ACT NOW Directive 89.1 no longer in existence.

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 5/7/92
Approval Authority: AG King **Date:** 5/7/92
Other Approvals: JM Robbins J. Robbins **Date:** 5/7/92
: ______ **Date:** / /

TITLE: PNL-ALO-108, AQUEOUS LEACH OF SLUDGES, SOILS, AND OTHER SOLID SAMPLES FOR ANION ANALYSIS

APPLICABILITY

This procedure defines the method of sample preparation for the analysis of water soluble, inorganic anionic constituents present in sludges, soils, and other solid samples. This procedure was developed by PNL to address the need for a preparation procedure for solid samples for analysis of the leachable anion content. The procedure may be used for the preparation of samples for the analysis of Cl, F, NO_3, PO_4, NO_2, and SO_4.

It should be noted that for samples containing significant amounts of available (soluble) Ca, spike recoveries for PO_4, SO_4 and F may be low due to precipitation of $CaPO_4$, $CaSO_4$ and CaF_2 during the extraction. In that case, it is recommended that a water leach be conducted on a separate aliquot of the sample following the same extraction protocol defined in this procedure and that the water extract be analyzed for PO_4, SO_4 and F.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during an analysis shall be specified in the following manner: 1) state with a measurement value given in a method or 2) as specified below if not stated with a measurement value.

a) Unless otherwise specified, all values for measurements stated in this method (volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within ±10% of the stated value.

Author Date PF Salter	Project Mgr. Date BM Gillespie	QAD Representative Date GK Gerke
Technical Reviewer Date [illegible] Robbins	Line Mgr. Date PF Salter	Other Date ALL ORIGINAL SIGNATURES ON FILE

b) When one or more significant figures are given to the right of the decimal point, the tolerance limit if ±5 in the next digit located beyond the last one stated.

2.0 Quality Control

All quality control data shall be maintain and available for ease reference or inspection.

Two quality control options (A and B) are defined below. Option A shall be used unless a Statement of Work (SOW) written by a client defines CERCLA related requirements. Option B shall then be followed. The analyst will recognize the need to use option B when a Chain-of-Custody (COC) defines a Test Instruction (TI). Additional QC samples may be requested by a client in an Analytical Request Form (ARF) or a SOW, and these will be conveyed to the analyst through a TI.

A. Employ a minimum of one blank per sample batch (≤ 20 samples) to determine in contamination is occurring. Run duplicate analysis upon client request. A matrix spike sample may be periodically employed to ensure that the correct procedure is followed and that all equipment is operating properly at the analyst's discretion or upon client request.

B. For all SOWs written by WHC or CERCLA protocol request for analysis, employ a minimum of one blank per sample batch (≤ samples of similar matrix type) to determine if contamination is occurring. Analyze one duplicate sample for every 20 samples or for each set of similar matrix type, whichever is smaller. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A matrix spike sample shall be employed for every 20 samples or per smaple set of similar matrix type, whichever is smaller. A matrix spike duplicate and/or laboratory control sample may be analyzed with any 20 samples if so directed by a TI.

3.0 Equipment, Materials and Reagents

3.1 Four-place Analytical Balance capable of accurately weighing to 0.001 g or better

3.2 Sample agitation system: Reciprocating shaker, vortex mixer, tumbler system (e.g., the system used in the EPA Toxicity Characteristics Leaching Procedure (TCLP) leach protocol), magnetic mixer with magnetic stir bars, or equivalent.

3.3 Container with lid or stopper suitable for use with one of the agitation systems in 3.2 --size is dependent on actual sample size and leachate solution volume selected. It is preferable that the container also be suitable for use with the centrifuge in 3.5.

3.4 Nalgene Disposable Filtering Apparatus, 0.45 μm pore size or equivalent.

3.5 Centrifuge and centrifuge tubes-/bottles-size is dependent on sample size and leachate solution volume selected. The centrifuge is operated at the highest, safe speed possible.

3.6 Nalgene plastic bottle, 40 mL or greater, or equivalent--

3.7 Deionized water of sufficient quality; similar to ASTM Type II reagent water (ASTM D1193), such that sample blanks produce concentrations below or at the instrument detection level --to be used for leachate solution preparation.

3.8 Carbonate-bicarbonate solution (0.24M carbonate, 0.3 M bicarbonate): dissolve 24.45 g of Na2CO3 (reagent grade) and 25.0 g NaHCO3 (reagent grade) in water and dilute to 1.0 L.

3.9 Dilute carbonate-bicarbonate (0.0024M carbonate, 0.003 bicarbonate): take 10.0 mL of carbonate-bicarbonate solution from Step 3.8 and dilute to 1.0L. Alternately, dissolve 1.0176g of Na2CO3 and 1.008g of NaHCO2 in water and dilute to 4.0L. Smaller quantities may be made by adjusting the amount of reagents used as long as the final concentration is the same.

4.0 Sample Leaching

A one to ten gram sample of sludge, soil or other solid material (wet weight) is mixed with approximately 100 mL of carbonate-bicarbonate solution, filtered and the leachate analyzed for inorganic constituents as required. To minimize laboratory waste production, a smaller sample size may be used as long as the leachate to sample ratio is at or within 10 to 100.

NOTE:
If analysis or experience indicates the samples contain sufficient free Ca to interfere with PO_4, SO_4, or F spike recoveries, ASTM Type II Water may be substituted for the carbonate-bicarbonate solution wherever this solution is called out in this procedure to prepare a suitable aqueous leachate for anion analysis.

4.1 Sample cohesiveness permitting, thoroughly mix the sample to be analyzed. If the sample cannot be thoroughly mixed due to cohesiveness or the presence of large particles (cobbles, pebbles, etc.), contact the cognizant scientist or Technical Task Leader for instructions on how to proceed.

4.2 Into a tared 125 mL container (or other suitable container depending upon sample size and agitation equipment to be used), weigh a 1 to 10 gram sample (wet weight). Record the weight to the nearest 0.01 gram. If a spike sample is required or desired, (e.g., required by a TI or ARF), add an appropriate amount of spike solution containing the analytes of interest as defined in the TI or ARF to a duplicate of one of the samples being prepared and label the sample with the sample ID and "spike." This sample is not to be considered the duplicate sample for meeting QC requirements. The spike solution shall be made from the standard stock solutions defined in the analytical procedure for the analyte of interest. The amount of each analyte in the spike is determined by the cognizant scientist and should be near the value expected for the sample, or at a minimum, at a detectable amount (3-5 times the instrument detection limit). Record the type, amount and concentration of the spike or spikes added to the sample in the LRB or the data sheet.

4.3 Add 100 (± 5) mL of the carbonate-bicarbonate solution from Step 3.8, unless directed to use solution from Step 3.9 in an ARF or TI, to the container from 4.2 and record the volume to the nearest 0.1 mL.

Alternately, 100 (± 5) grams of the carbonate-bicarbonate solution may be added to the container and the weight of solution added recorded to the nearest 0.01 gram.

4.4 Depending upon the agitation equipment being used, follow one of the steps below:

4.4.1 If using a magnetic stirrer, add a magnetic stir bar to the container from 4.3, stopper/close the container, place on the magnetic stirrer, and stir at high speed for approximately 1 hour at ambient temperature. Go to Step 4.5.

4.4.2 If using a reciprocating shaker, close/stopper the container, place in the shaker, and agitate for approximately 4 hours at ambient temperature. Go to Step 4.5.

4.4.3 If using a vortex mixer, close/stopper the container (usually a centrifuge tube), place on the mixer, and mix for 15 minutes. Go to Step 4.5.

4.4.4 If using a rotary system, close/stopper the container, place container in the rotary system, and mix for 1 hour at ambient temperature. Go to step 4.5.

4.5 If the sample is not already in a centrifuge tube or bottle, transfer the sample to an appropriately sized centrifuge tube or bottle. Do NOT use any solution to transfer the mixture -- quantitative transfer is not required. Save the original, uncleaned container for use in Step 4.6. Separate the solid and aqueous phase by centrifuging the sample at least 5 minutes. The supernatant should be clear and the solids well packed in the bottom of the centrifuge tube or bottle. If not, continue centrifuging until a clean separation is achieved (5-20 minutes longer). If a clean separation is still not achieved, contact the cognizant scientist for instructions on how to proceed. Pour or suction off the supernatant into a clean, dry beaker labeled with the sample ID. Go to 4.10 if not repeating leach.

4.6 Add 20-25 mL of carbonate/bicarbonate solution to the centrifuge bottle with the packed solids and stir to resuspend the solids. If measuring the solution by volume rather than by weight, record the volume of solution added to the nearest 0.1 mL (If measuring the solution added by weight, it is not necessary to weigh or record weight at this step.).

4.7 If the agitation method requires the use of a container other than the centrifuge tube or bottle, transfer the centrifuged solids from Step 4.5 back into the original container saved from 4.5. Reserve the centrifuge bottle/tube for use in Step 4.9.

4.8 Add 75-80 mL carbonate/bicarbonate solution to the sample container to make a total volume added of 100 (±5) mL. Record the volume added to the nearest 0.1 mL.

Alternately, if measuring the solution added by weight, add 75-80 grams of carbonate/bicarbonate solution to the sample and record the total weight of solution added to the nearest 0.1 mL of 100 (±5) grams.

NOTE: If necessary, when adding solution volume to the sample container, use some of this solution volume to rinse any solids remaining on any "stirring" apparatus (spatula, stirring rod, etc.) into the sample container.

4.9 Steps 4.4 and 4.5 may be repeated at the discretion of the cognizant scientist unless otherwise directed in a TI or ARF. Combine supernatants into one labeled container. Discard the solids.

4.10 Centrifuge combined supernatant from 4.9 or filter at least through a 0.45 µm Nalgene disposable filtering apparatus using the building vacuum. Discard any solids and the filter. Unfiltered supernatant may be discarded. (Only 1-2 mL of centrifuged or filtered leachate solution is required for anion analysis).

4.11 Transfer the filtrate to a labeled 40 mL plastic bottle. This solution or a suitable aliquot is used for sample anion analysis.

4.12 Store the filtered leachate at 4±2 °C until analyzed.

5.0 Records

Records shall be maintained and controlled to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Analytical Report Cards/Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with ~~the ACT NOW Directive 89.1~~ established records management practices.

6.0 References

M. L. Jackson, Soil Chemical Analysis (1958), Prentice Hall, Inc. Sixth Printing (1970) by the author, Department of Soil Science, University of Wisconsin, Madison, WI. 53706.

"Anions by Ion Chromatography" Procedure E.00-11 from The Environmental Measurements Laboratory Procedure Manual, HASL-300-Ed.25, (1982) US DOE, Volchot, HL and Planque, G., eds., NY, NY.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-109 - MICROWAVE DIGESTION OF GLASSES AND SLURRIES FOR ICP/MS ANALYSIS

APPLICABILITY

This procedure is applicable to the dissolution of glass samples and slurry samples for ICP/MS analysis using a microwave oven as a heat source. The microwave oven for which this procedure is intended is a CEM MDS 81D oven (or equivalent), which has a maximum power output of 600 watts. This procedure is intended to supplement (not supersede) PNL Technical Procedure PNL-ALO-280, and the CEM MDS 81D instruction manual.

DEFINITIONS/ACRONYMS

capping station - CEM (or equivalent) instrument used to tighten and loosen the vessel cap

HCl - hydrochloric acid

HF - hydrofluoric acid

program - a series of stages having specified power and duration

REE - Rare earth element(s)

stage - a portion of a program which has a constant, specified power (entered as a percentage of full power) for a specified duration of time (in seconds)

vessel - CEM teflon container (or equivalent) used for sample digestion

RESPONSIBLE STAFF

Trained ANALYST

- The trained ANALYST shall read and thoroughly understand the microwave oven instruction manual before operating.

Author Eric J. Wyse	**Date** 6/25/91	**Project Mgr.** W. Koppenaal	**Date** 7/15/91	**QAD Representative** GKGerke	**Date** 7/2/91
Technical Reviewer Mont Smith	**Date** 7/1/91	**Line Mgr.**	**Date** 7-8-91	**Other**	**Date**

Procedure No.	**Revision No.**	**Effective Date**	**Page**	**of**
PNL-ALO-109	0	JUL 15 1991	1	3

- The trained ANALYST shall apply this document and PNL-ALO-280 when performing sample preparation and analyses.

1.0 PROCEDURE

1.1 SLURRIES

1.1.1. Weigh approximately one gram of well-mixed slurry into a small, tared beaker (glass or plastic); make sure that measurements are obtained for both the empty beaker as well as the beaker with sample. Place in drying oven overnight at 90°C.

1.1.2. Remove sample and let cool to room temperature. Reweigh sample. Calculate the percentage of water the sample contains:

$$\%\ \text{water} = 100 * \left(1 - \frac{\text{dry sample in beaker - beaker}}{\text{wet sample in beaker - beaker}} \right)$$

1.1.3. Powder dried slurry with a mortar and pestle (if courseness necessitates). Weigh approximately 0.1 - 0.5 gram of dried slurry into a microwave vessel and record weight in "Sample Log-in and Preparation" LRB.

1.1.4. Add 4 mls 6N HCl followed by 5 mls HF; cap immediately using capping station. Prepare a procedure blank in similar manner.

1.1.5. Enter following program into microwave keypad:
Stage 1: 100% power for 1 minute
Stage 2: 50% power for 2 minutes
Stage 3: 20% power for 5 minutes
Begin program.

1.1.6. Allow to cool. Swirl digestate against sides and lid of closed vessel to rinse material which may have condensed on surface.

1.1.7. Repeat steps 1.1.5 and 1.1.6 up to four times or until dissolution is complete.

1.1.8. Transfer digestate into a clean, polybeaker using DI water. Transfer to a 50 or 100 ml teflon volumetric flask using DI water. Bring to volume with DI water.

1.1.9. Make necessary dilution(s) and add an appropriate internal standard(s); analyze by ICP/MS according to PNL-ALO-280.

1.2 GLASSES

1.2.1. Grind glass sample to a fine powder with a clean mortar and pestle. Weigh approximately 0.1 gram of dried slurry into a vessel and record weight in "Sample Log-in and Preparation" LRB.

1.2.2. Add 2 mls aqua regia and 5 mls HF; cap immediately using capping station. Prepare a procedure blank in a similar manner.

1.2.3. Enter following program into microwave keypad:
Stage 1: 100% power for 1 minute
Stage 2: 50% power for 2 minutes
Stage 3: 20% power for 5 minutes
Begin program.

1.2.4. Allow to cool. Swirl digestate against sides and lid of closed vessel to rinse material which may have condensed on surface.

1.2.5. Digestates may contain undissolved/residual material; samples containing rare earth elements will have fluoride precipitates present. Repeat step 1.2.3 as many as four times (or until dissolution is complete), allowing cooling between runs.

1.2.6. Even after four runs, the digestate may still contain fluorides. If REE concentrations are desired (and boron concentrations are not), add 1-2 grams of boric acid (high purity if available), or a saturated solution of boric acid dropwise until the precipitate disappears completely.

1.2.7. Transfer digestate into a clean, polybeaker using DI water. Transfer to a 50 or 100 ml teflon volumetric flask using DI water. Bring to volume with DI water.

1.2.8. Make necessary dilution(s) and add an appropriate internal standard(s); analyze by ICP/MS according to PNL-ALO-280.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-110, Toxicity Characteristic Leaching Procedure (TCLP) Extraction for Inorganic Contaminants.

APPLICABILITY

This procedure describes the method(s) used for the extraction of liquid, solid or multiphasic waste for regulatory classification regarding heavy metal contaminants. See the flowpath diagrams at the end of this procedure.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Technical Task Leader
Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Overview

This procedure is designed to determine the mobility of inorganic contaminants present in liquid, solid or multiphasic waste. Liquid waste, i.e., waste containing <0.5 percent dry solid material, is filtered and the filtrate is defined as the TCLP extract. For solid or multiphasic waste containing 0.5 percent solid material or more, the liquid fraction is separated and the solid phase is extracted with one of two HOAc-based extraction fluids. The extraction fluid used is determined by the alkalinity of the solid phase of the waste. The solid is reduced in particle size, if necessary, and extracted with an amount of extractant fluid 20 times the weight of the solid phase. The liquid extractant is to be separated from the solid phase by filtration. If compatible, the original liquid fraction is to be recombined with the extract, otherwise, both are to be analyzed separately and the results combined mathematically.

Author RT Steele	Date 2/27/92	Project Mgr. TE Jones	Date 2/27/92	QAD Representative GK Gerke	Date 2/27/92
Technical Reviewer MW Urie	Date 2/27/92	Line Mgr. AG King	Date 2/27/92	Other	Date
Procedure No. PNL-ALO-110	Revision No. 0		Effective Date FEB 27 1992	Page 1 of 10	

2.0 Apparatus

2.1 Agitation device capable of rotating extraction vessel end-over-end at a rate of 30 ± 2 rpm.

2.2 Extraction Vessel:
Depending on contaminants to be analyzed and the nature of the waste, it is recommended that type 316 stainless steel vessel, plastic or borosilicate glass bottles be used.

2.3 Filtration Device/Selection

2.3.1 Borosilicate glass fiber filter with a pore size of 0.6 to 0.8 microns. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. Vacuum filtration can only be used for wastes with low solids content (<10 percent) and for highly granular liquid containing wastes. All other types of wastes shall be filtered using positive pressure filtration.

2.3.2 Plastic disposable filter units, polystrene or polycarbonate bodies with cellulose nitrate membranes. Pore size the same as above. The rationale for using these plastic disposable filters is as follows:

2.3.2.1 There will be no need to reclean used filter assemblies thereby eliminating analytical verification checks and potential cross contamination of samples.

2.3.2.2 Quality Control measures will identify any sample contaminates resulting from the use of the filter assemblies.

2.4 pH Meter:
The meter shall be accurate to ±0.05 units at 25° C.

2.5 Laboratory Balance:
Any laboratory balance capable of weighing to within ±0.01 grams.

2.6 Drying Oven:
The oven shall be capable of maintaining a temperature of 100 ± 20 ° C.

3.0 Reagents

3.1 Deionized Water (DIW) free of any heavy metal constituents of interest.

3.2 Hydrochloric acid (1N) made from ACS reagent grade.

3.3 Nitric acid (concentrated)(1N) made from ACS reagent grade.

3.4 Sodium hydroxide (1N) made from ACS reagent grade.

3.5 Glacial acetic acid ACS reagent grade.

3.6 Extraction Fluids.

3.6.1 Extraction Fluid #1: 5.7ml HOAc ± 500 ml DIW ± 64.3 ml 1N NaOH all diluted to one liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.

3.6.2 Extraction Fluid #2: 5.7 ml HOAc diluted to one liter with DIW. When correctly prepared, the pH should be 2.88 ± 0.05.

4.0 Standards

This method assumes that the addition of standards will be to the extract(s) produced and not to the original sample(s) prior to leaching. Therefore, information regarding standard composition, volume, etc. will be found in the sample preparatory method being applied to the extract for the particular analyte of concern.

5.0 Quality Control

All quality control data shall be maintained and available for easy reference or inspection.

A minimum of one blank and one duplicate (using the same extraction fluid as used for the samples) shall be analyzed for every extraction batch.

6.0 Extraction Techniques

6.1 Preliminary Evaluations

6.1.1 Determination of Percent Solids

6.1.1.1 Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure (up to 50 psi).

6.1.1.2 If waste will yield no liquid when pressure is applied, i.e., it is 100% solids, proceed to step 6.1.2.

6.1.1.3 If the sample is liquid or multiphased, a liquid/solid separation is required.

6.1.1.3.1 Pre-weigh the filter and the filtrate container.

6.1.1.3.2 Mix the waste thoroughly to homogenize it as much as possible.

6.1.1.3.3 Weigh out a one to ten gram subsample of the waste and record the weight.

6.1.1.3.4 Quantitatively transfer the waste sample to the filter holder.

6.1.1.3.5 If greater than 1% of the original sample weight is left adhering to the container after transferring the waste to the filter, determine the weight of this residue and subtract it from the total sample weight in the calculation.

6.1.1.3.6 Gradually apply vacuum or gentle pressure (10 psi increments; 50 psi max) until air or pressurizing gas moves through the filter.

6.1.1.3.7 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

6.1.1.3.8 Determine the weight of the liquid phase and record the weight.

6.1.1.3.9 Subtract the weight of the liquid phase from the subsample weight (6.1.1.3.3) to obtain and record the solid phase weight.

6.1.1.3.10 Calculate the percent solids. See section 7.0.

6.1.1.3.11 If the weight percent solids is <0.5%, the filtrate is the extract. Proceed to 6.2.1.

6.1.1.3.12 Remove the solid phase and filter from the filter apparatus.

6.1.1.3.13 Dry the filter and solids at 100±20 ° C. until two successive weighings yield the same value within ± 1%. Record the final weight.

6.1.1.3.14 Calculate the percent dry solids. See section 7.0.

6.1.1.3.15 If the dry percent solids is <0.5%, then proceed to step 6.2.1

6.1.2 Particle Size Reduction for Solid Waste

6.1.2.1 Determine whether the particle size of the solid waste will pass through a 9.5mm screen (0.375 in.).

6.1.2.2 Reduce the particle size by crushing, cutting, or grinding until it will pass through the screen. Pay particular attention to the potential for adding unwanted contaminants to the sample from this process.

6.1.3 Determination of the Appropriate Extraction Fluid

6.1.3.1 Weigh out a one gram sieved subsample into a 125 ml erlenmeyer flask.

6.1.3.2 Add 20 ml of deionized water, cover with a watchglass, and stir vigorously for five minutes using a magnetic stirrer.

6.1.3.3 Measure and record the pH. If the ph <5.0, use extraction fluid #1. Proceed to step 6.2.2.

6.1.3.4 Add 0.5 ml 1N HCl, mix, cover, heat to 50 deg.C. and hold for 10 minutes.

6.1.3.5 Cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2.

6.2 Extraction Procedure

6.2.1 Waste that contains <0.5% solids

6.2.1.1 Prerinse a filtering apparatus with 1% HNO_3

6.2.1.2 Filter enough sample to provide the required amount of extract needed for the analytical scheme to be performed.

6.2.1.3 Acidify the filtrate with concentrated HNO_3 to a pH of <2 and store at 4 • C.

6.2.1.4 Prepare the extract for analysis following established sample preparatory procedures and the quality control requirements specified in the ARF or TI.

6.2.2 Solid or multiphased waste

6.2.2.1 If the waste is 100% solid, weigh out a 10 gram subsample of waste and proceed to step 6.2.2.2.7.

6.2.2.2 If the waste is multiphased, a liquid/solid separation is required.

6.2.2.2.1 Pre-weigh the container that will receive the filtrate.

6.2.2.2.2 Based on the percent solids data already determined, weigh out a subsample of the waste that provides 10 grams of solids for extraction following filtration.

6.2.2.2.3 Quantitatively transfer the sample to a 1% HNO_3 prerinsed filtration apparatus.

6.2.2.2.4 If greater than 1% of the original sample weight is left adhering to the container after transferring the waste to the filter, determine the weight of this residue and subtract it from the total sample weight for calculational purposes.

6.2.2.2.5 Gradually apply vacuum or gentle pressure (10 psi increments; 50 psi max) until air or pressurizing gas moves through the filter.

6.2.2.2.6 Weigh the filtrate and record the weight. The filtrate may now be prepared for analysis [Step 6.2.2.2.12.3) or stored at 4° C. until recombined with the solids extractant at a later time [Step 6.2.2.2.12.2].

6.2.2.2.7 Ensure that the solid portion of the waste will pass through a 9.5 mm screen.

6.2.2.2.8 Transfer the solid phase and the filter media (if present) to an extractor vessel.

6.2.2.2.9 Slowly add 200 ml of the appropriate extraction fluid to the extractor. Close the vessel tightly and secure in the agitation device.

6.2.2.2.10 Rotate at 30 ± 2 rpm for 15 minutes and check vessels for pressure buildup. Continue rotating for 18 ± 2 hours.

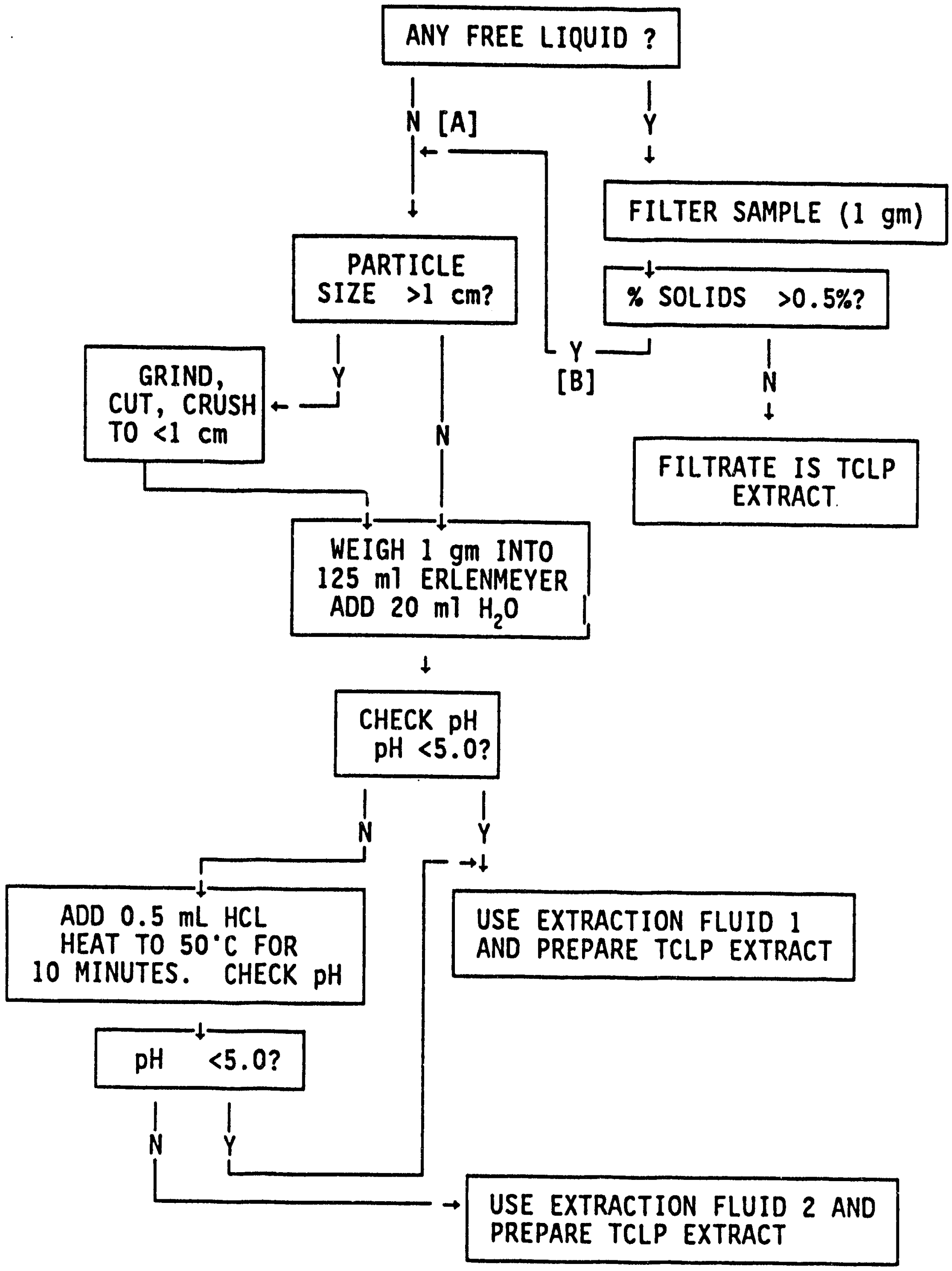
6.2.2.2.11 Following the extraction, separate the liquid and solid phases by filtration. Insure that the filtration appratus has been prerinsed with 1% HNO_3 prior to use.

6.2.2.2.12 Prepare the extract as follows:

6.2.2.2.12.1 If the original waste contained no liquid phase, the filtered extractant is defined as the TCLP extract.

6.2.2.2.12.2 If compatible, combine the filtered extractant with the filtered original liquid phase from step 6 above. The combined material is defined as the TCLP extract.

PRELIMINARY EVALUATION



[A] = 100% SOLIDS EXTRACTION
[B] = >0.5% SOLIDS EXTRACTION

6.2.2.2.12.3 If the two liquid phases are incompatible, do not combine them. Analyze them separately and combine the results mathematically.

6.2.2.2.13 Following collection of the TCLP extract, the pH of the extract shall be recorded.

6.2.2.2.14 Acidify the extract with concentrated nitric acid to a pH <2 only if precipitation does not occur when doing so.

6.2.2.2.15 Whenever possible, refrigerate (4 deg.C.) all stored extracts until analyzed.

6.2.2.2.16 Prepare the extract for analysis following established sample preparatory procedures and the quality control requirements specified in the ARF or TI.

7.0 Calculations

7.1 Determine the percent solids as follows:

$$\% \text{ Solids} = \frac{\text{Weight of solid phase}}{\text{Total Weight of the waste}} \times 100$$

7.2 Determine the percent dry solids as follows:

$$\% \text{ Dry Solids} = \frac{\text{(Weight of dry waste + filter)-tared weight of filter}}{\text{Total weight of the waste}} \times 100$$

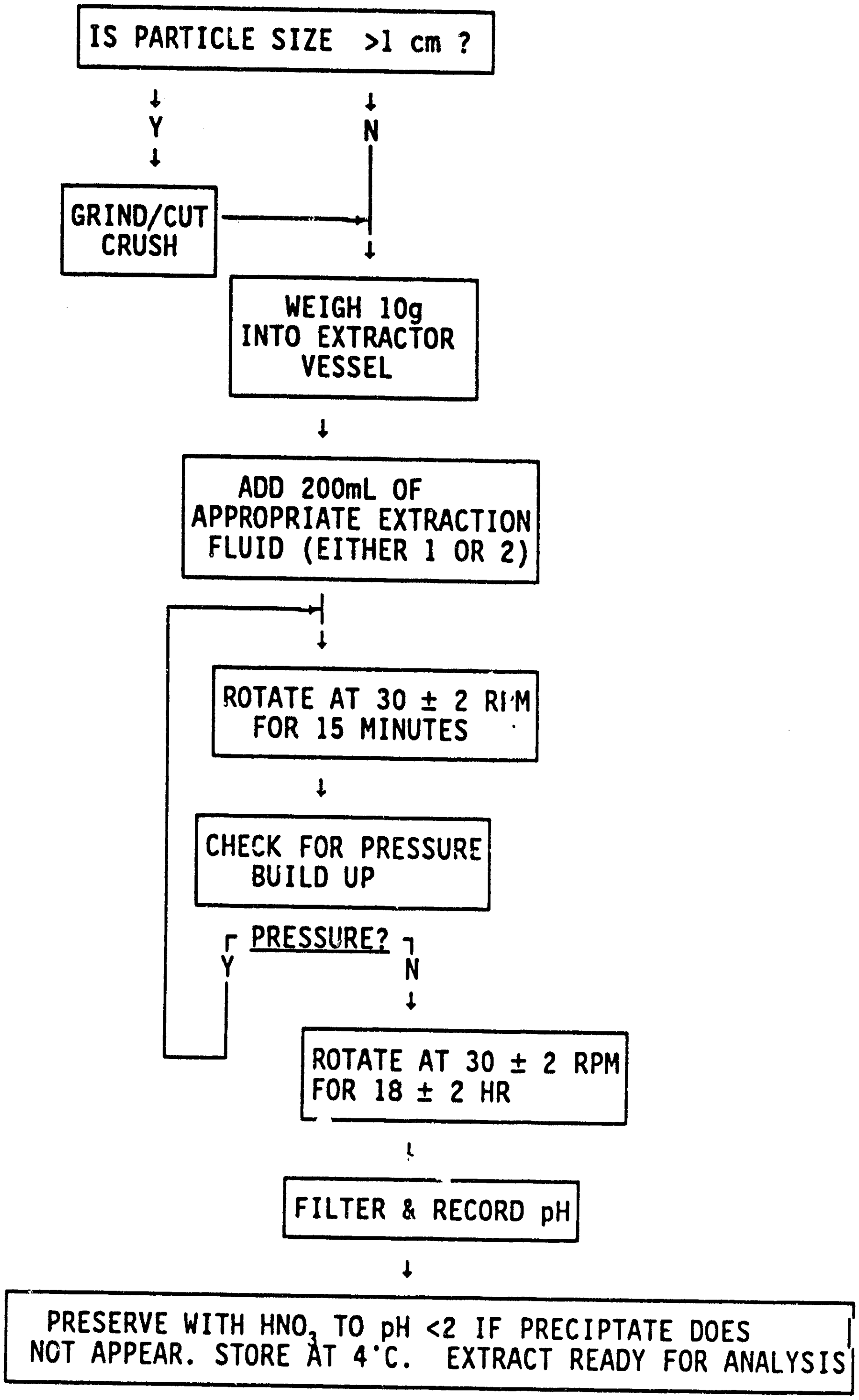
8.0 Records

Records shall be maintained and controlled so as to conform to requirements of PNL-MA-70, PAP-70-1701. Laboratory Record Books (LRB) and Data Sheets provide a mechanism for control of most records. Laboratory Record Books will be used in accordance with Management Guide 3.8.

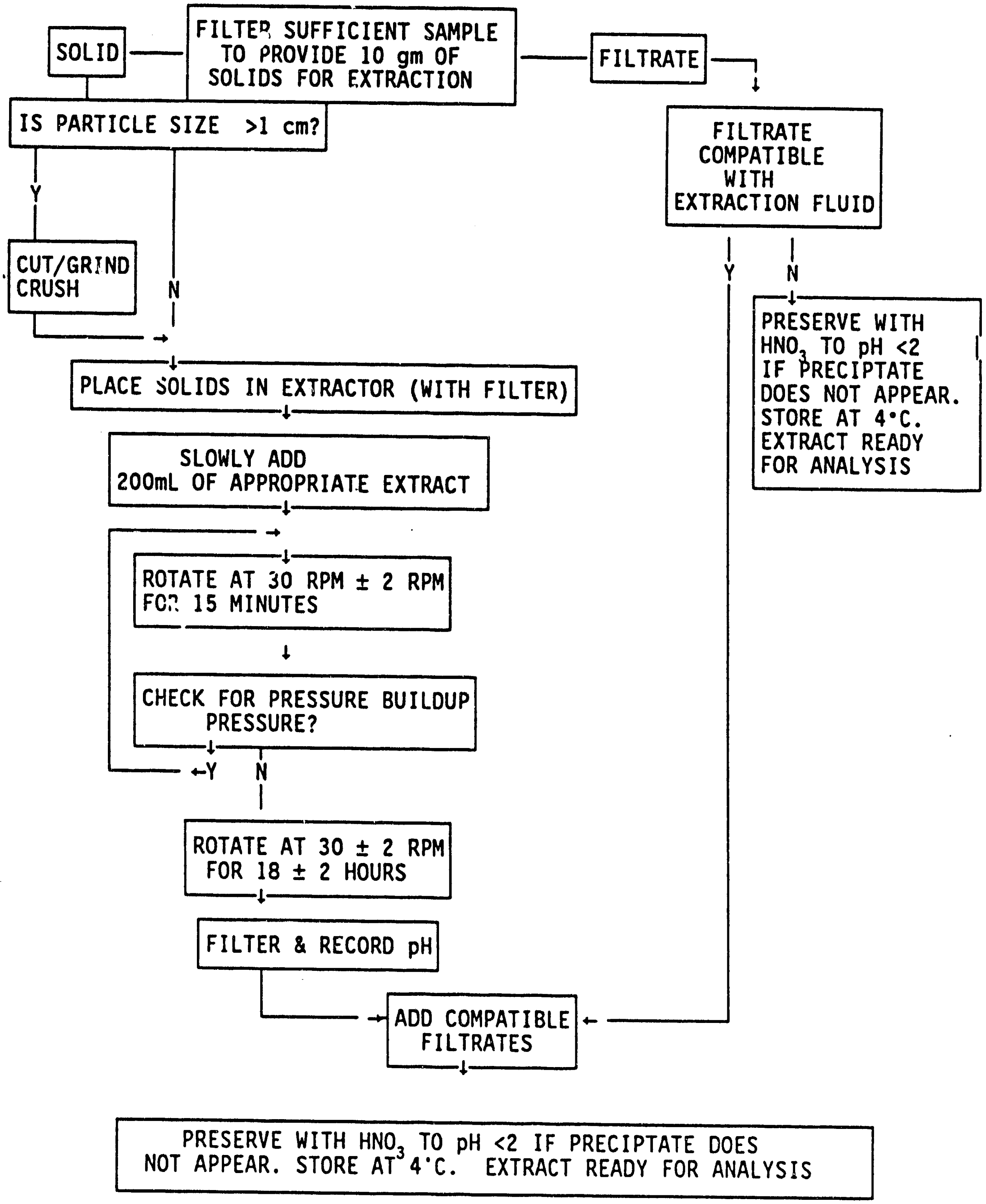
9.0 References

Federal Register, March 29, 1990, Vol. 55, No. 61.

100% SOLIDS


IS PARTICLE SIZE >1 cm ?
Y
N
GRIND/CUT CRUSH
WEIGH 10g INTO EXTRACTOR VESSEL
ADD 200mL OF APPROPRIATE EXTRACTION FLUID (EITHER 1 OR 2)
ROTATE AT 30 ± 2 RPM FOR 15 MINUTES
CHECK FOR PRESSURE BUILD UP
PRESSURE?
Y
N
ROTATE AT 30 ± 2 RPM FOR 18 ± 2 HR
FILTER & RECORD pH
PRESERVE WITH HNO3 TO pH <2 IF PRECIPTATE DOES NOT APPEAR. STORE AT 4°C. EXTRACT READY FOR ANALYSIS

≥0.5% SOLIDS but <100%



PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-111 LEACH/DISSOLUTION OF NEUTRON ACTIVATED METAL SPECIMENS FOR RADIOCHEMICAL ANALYSIS

APPLICABILITY

This procedure is used for surface decontamination of neutron activated metal samples and to acid leach the decontaminated surface or dissolve the sample for subsequent radiochemical and/or chemical analysis.

DEFINITIONS

Ultrex - J. T. Baker brand name of high purity acids. Term used in this procedure for convenience. Equivalent substitutes are just as effective.

Milli-Q - Millipore, Inc. trade mark for water purification system

conc - concentrated

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Tolerances

Tolerances for all measurements made during the dissolution, cleaning or leaching under this procedure shall be specified in some manner. A tolerance limit can be stated with a measurement value given in the method. If a tolerance limit is not stated with a measurement value, then the following system of tolerances shall be in effect:

a) Unless otherwise specified, all values for measurements stated in the methods (e.g., volume, weight, time, etc.) are approximate values. The actual measurements used, however, shall be within ±10% of the stated value.

b) When one or more significant figures are given to the right of the decimal point, the tolerance limit is ±5 in the next digit located to the right beyond the last one stated.

Author Date 8/26/92 VW Thomas	Project Mgr. S.K. Fadeff Date 3/25/92 SK Fadeff	QAD Representative TL Ehlert Date 8/25/92 TL Ehlert
Technical Reviewer Date 8-25-92 Strebin	Line Mgr. Date 9/2/92 AG King	Other Date

Procedure No. PNL-ALO-111	Revision No. 0	Effective Date SEP 0 9 1992	Page 1 of 5

2.0 Reagents

All chemicals used are Ultrex grade or equivalent grade unless otherwise specified. The water used is high purity (doubly-distilled-deionized or Milli-Q quality) water.

6 N HCl - 50 $^v/_o$ conc HCl in 50 $^v/_o$ water

8N HNO_3 - 50 $^v/_o$ conc HNO_3 in 50 $^v/_o$ water

conc HF

micro cleaning solution or equivalent

3.0 Supplies

15 ml glass screwcap vials

Balance, accurate to 1 mg

125 ml or 250 ml Pyrex glass and FEP Teflon beakers, precleaned

Pyrex ribbed and teflon watch glasses to fit beakers

Hot plate - stirrer

Teflon covered magnetic stir bars

Teflon covered tongs, forceps or tweezers

Plastic vials with caps to contain metal samples for weighing, precleaned

125 ml to 250 ml polyethylene bottles fitted with poly-seal caps, precleaned

100 ml volumetric flasks, glass and plastic or teflon

4.0 Chemical Procedure

Except where responsibility is specifically assigned to a cognizant scientist, the analyst may perform all work.

All pertinent data (e.g., aliquot volumes, weight, etc.), observations, and calculations shall be recorded in a project record in a manner traceable to the sample.

4.1 Surface decontamination of samples This process is intended to completely remove traces of fission products and transuranic radionuclide contamination deposited during cutting operations in the hot cell and to remove remnants of corrosion films formed on the metal surface during exposure to reactor coolant.

4.1.1 In a clean glass vial, immerse the sample in fresh, hot (e.g. 70° to 90°C) 6 N HCl for about 60 seconds.

4.1.2 Using clean Teflon coated tongs, lift the sample out of the acid and rinse with fresh 6 N HCl, or the acid can be poured out of the vial and the sample rinsed with fresh 6 N HCl, three times, pouring off the acid each time.

4.1.3 In a second clean vial, immerse the sample in fresh, hot (e.g. 70° to 90°C) 8 N HNO_3 for about 60 seconds.

4.1.4 Using clean Teflon coated tongs, lift the sample out of the acid and rinse with fresh 8 N HNO_3, or pour off acid and rinse sample three times with 8 N HNO_3, pouring off the acid each time.

4.1.5 Rinse the sample with water, place in beaker, and cover with Micro cleaning solution and a watch glass. Place the beaker with the sample into an ultrasonic cleaner for 5 to 10 minutes. Remove sample with clean Teflon forceps and rinse well with water.

4.1.6 Repeat Steps 4.1.1 through 4.1.5 using fresh acids for each repetition until fission product contamination is below levels of concern. (This decision will be made by the cognizant scientist.)

Note: The need for repetitive cleaning can be determined by the following: Place sample in a clean vial with 5 ml 8M HNO_3, cover, allow to stand for 15 to 20 minutes at 70 - 90°C for partial dissolution. Immerse sample in 5 ml hot (70 - 90°C) 6 N HCl for about 60 seconds. Remove the sample and rinse it well with water flushing the water into another beaker or slop jar. Allow the sample to dry on clean diaper paper. Set the sample into a clean tared plastic vial, cap the vial. Combine the 5 ml 8M HNO_3 and the 5 ml 6 N HCl and send to the radiochemistry lab for analysis by GEA for evidence of contamination (e.g., ^{137}Cs).

4.1.7 If the sample has not been dried and placed in a tared vial already, dry the sample on diaper paper. Transfer the sample into a clean, pre-tared plastic vial, cap the vial.

4.1.8 Weigh the vial with the sample to the nearest mg. Calculate the net sample weight.

4.2 Stainless Steel Samples: Dissolution or leaching of decontaminated sample to obtain an aliquot for analysis.

4.2.1 In a clean glass beaker, immerse the sample in 50 ml of 6 N HCL for 10 to 20 minutes. Use a watch glass to cover the beakers and minimize losses due to spattering.

4.2.2 If any sample is left, retrieve it with clean teflon coated forceps or equivalent, rinse the sample with water over the dissolution beaker, and dry on a diaper paper. Transfer the sample to the same or a new clean, pre-tared plastic vial, cap the vial, and re-weigh to the nearest mg. Calculate the net sample weight. (The difference between this weight and the weight from Step 4.1.8 is the dissolved sample weight.)

4.2.3 Transfer the leached/dissolved sample acid solution quantitatively to a 100 ml Class A or B glass volumetric flask using water as rinse. Dilute to volume with water. (This results in 100 ml of about 3 M HCL sample solution for subsequent aliquoting and analysis.)

4.2.4 Pour the sample solution (without further dilution) into a clean polyethylene bottle for storage. Aliquots of this solution are used for analysis.

4.3 Inconel Samples: Dissolution or leaching of decontaminated sample for analysis. The process used to leach/dissolve Inconel samples is identical to that above for stainless steel samples with the following exceptions.

4.3.1 In Step 4.2.1, use a Teflon beaker and add several drops (up to about 20) of conc HF throughout the dissolution/leaching process to facilitate dissolution of the Inconel.

4.3.2 In Step 4.2.3, use a 100 ml Class B plastic volumetric flask.

4.4 Zircaloy Samples: Dissolution or leaching of decontaminated sample for analysis. Dissolve sample in a hot (70 - 90°C) solution of 10 ml conc HNO_3 and 3 ml 50% HF acids. Add more HF dropwise, as necessary, to aid dissolution. Alternatively, and as directed by the cognizant scientist, a hot (70 - 90°C) solution of 25 ml 6 N HCl and 3-5 ml conc HF acids can be used to dissolve the zircaloy sample. Total volumes used above may be scaled up as directed by the cognizant scientist.

5.0 Calculations

5.1 Dissolved Sample Weight

mg dissolved sample = Net weight of cleaned sample minus Net weight of residue after final leaching/dissolution procedure

5.2 Aliquot Sample Weight

$$\text{mg sample in aliquot} = \frac{\text{(Aliquot volume in ml)(mg dissolved sample)}}{\text{100 ml}}$$

6.0 Specific Qualification

None required.

7.0 References

Sulcek, Zdenek, Povondra, Pavel, Methods of Decomposition in Inorganic Analysis, CRC Press.

Roberton, D.E., C.W. Thomas, N.L. Wynhoff, D.C. Hetzer, "Characterization of Long-Lived Activation Products in Spent Fuel Assembly Hardware and Reactor Pressure Vessel Steel," Nuclear Engineering and Design, Sept. 1989.

INTERIM CHANGE NOTICE
(ICN)

ICN- PNL-ALO-120.2 R0
Page 1 of 1

A. Document Number: PNL-ALO-120.1 Revision Number: 0
Document Title: Procedure for Extraction of Single Shell Tank Sample For the Analysis of SVOA Compounds

Effective Date of ICN: 12/11/92

Document's Original Author: R.W. Stromatt

Change Requested By: M.J. Steele

B. Action

Replace pages 1 through 9 with the attached pages 1 through 9.

C. Effect of Change

To modify the procedure so extractions of samples with special matrix problems are can be addressed individually.

D. Reason for Change/Description of Change

To improve extraction residues for analysis by GC/MS.

The modifications to the procedure will allow the cognizant scientist, with group leader approval, to modify the solvent and concentration of the surrogate and matrix spike solutions to accommodate special matrices which would impact the residues quality and cause GC/MS analysis problems. Recording these changes is also addressed. The pH recording accuracy is also addressed.

For description of changes, see redline and strike-out throughout the text.

E. Approval Signatures

(Please sign and date)

Type of Change: {Check (✓) one}

X Minor Change ☐ Major Change

QA Department Concurrence: Ethridge for Ehlert Date: 12/11/92
Approval Authority: AG King for Date: 12/11/92
Other Approvals: RW Stromatt Date: 12/11/92
: SG McKinley McKinley Date: 12/11/92
: EW Hoppe Hoppe Date: 12/11/92

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-120.1 R0
Page 1 of 1

A. Document Number: PNL-ALO-120 Revision Number: 0
Document Title: Procedure for Extraction of Single Shell Tank Sample For The Analysis of SVOA Compound
Document's Original Author: RW Stromatt

Effective Date of ICN: 10/21/92

Change Requested By: MJ Steele

B. Action

Replace pages 1 through 9 with the attached pages 1 through 9.

C. Effect of Change

To clarify procedure: to remove unclear, outdated and incorrect references, also to make changes that will meet the intent of the procedure regarding extraction solvent.

D. Reason for Change/Description of Change

To remove incorrect or outdated references.

To make the extraction solvent in the sample and the matrix spiked samples more similar.

Increase the concentration of the matrix spike solution so less volume is added to arrive at the same concentration. Clarify the procedure to assure the correct number and volume of surrogate and spike is added.

For description of changes, see redline and strike-out throughout text.

E. Approval Signatures

(Please sign and date)

Type of Change: {Check (✓) one}

(✓) Minor Change ( ) Major Change

PQ Department Concurrence: TL Ehlert Date: 10/21/92
Approval Authority: AG King Date: 10 21 92
Other Approvals: RW Stromatt Date: 10/21/92
: EW Hoppe Date: 10/21/92
Project Manager : SG McKinley Date: 10/21/92

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-120, PROCEDURE FOR EXTRACTION OF SINGLE SHELL TANK SAMPLES FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure describes the method used for the extraction of single shell tank samples and the subsequent preparation of the extract for the analysis of semivolatile organic compounds. This procedure may be used to support work performed in compliance with EPA Contract Laboratory Program (CLP) or other projects/programs as elected.

DEFINITIONS

None

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

1.0 This procedure is for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludge and other waste samples including single shell tank samples. The sonication process ensures intimate contact of the sample matrix with the extraction solvent. The method is divided into two sections based on the expected concentration of organic in the sample. The low concentration method (individual extractable organic components $\leq$20 mg/Kg) uses a larger sample size and a more rigorous extraction procedure. The medium concentration method (>20 mg/Kg individual extractable organic components) uses a smaller sample, less extraction solvent and is much simpler to perform. The procedure provides for adjustment of pH for samples which do not meet the pH 5-11 extraction criteria. Extracts are filtered and evaporated to a volume suitable for optional GPC cleanup procedures followed by screening and/or analyses by GC/FID or GC/MS.

2.0 Apparatus

a) Mortar and pestle.

b) 1-mm standard sieve.

Author Date RW Stromatt	Project Mgr. Date	QAD Representative Date SL English
Technical Reviewer Date EW Hoppe	Line Mgr. Date WC Weimer	Other Date ALL ORIGINAL SIGNATURES ON FILE

c) Sonicator - Ultrasonic cell disrupter: Heat Systems - Ultrasonic, Inc. Model W-385 (475 watt) sonicator or equivalent (power wattage must be a minimum of 375 with pulsing capability) using a no. 208 or no. 305 3/4" disrupter horn for low level analyses, and a no. 200 1/2" tapped disrupter horn and no. 419 1/8" standard taper microtip probe.

d) Oven, drying.

e) Desiccator.

f) Pasteur pipets, 1-ml.

g) Beakers 400-ml.

h) Pre-cleaned glass vials, greater than or equal to 20ml, with screw cap and Teflon liners.

i) Buchner funnel.

j) Filter paper, Whatman no. 41 or equivalent.

k) Glass conical funnel.

l) Filter flask, 500-ml.

m) Concentrator tube, 10-ml graduated (Kontes K-570050-1025 or equivalent).

n) Evaporator flask, 500-ml (Kontes K-570001-0500 or equivalent).

o) Snyder Column, three-ball macro (Kontes K-503000-0121 or equivalent).

p) Water bath evaporator, 8-position S-evap, SS boiling water bath Organomation Associates Catalog #12020 or equivalent.

q) N-evap, 12 position with SS water bath Organomation Associates Catalog #11155 or equivalent.

r) Boiling Chips, 10/40 mesh (silicon carbide or equivalent) solvent extracted or fired at 450°C for 24 hours, cooled in a desiccator and stored in vial with screw cap.

s) Balance, capable of accurately weighing 0.01 gram.

t) Spatula, stainless steel or Teflon.

u) Drying column, 20-mm ID. Pyrex^R chromatographic column with Pyrex^R glass wool at bottom. Note, the glass column may also be fitted with a Teflon stopcock and a fritted glass disc to retain the drying compound, however they are difficult to decontaminate after highly contaminated extracts have been passed through them. Use a small pad of glass wool to retain the drying compound. Prewash the glass wool with 50 ml of acetone followed with 50 ml of elution solvent prior to packing the column with the drying compound.

v) Centrifuge.

w) pH meter.

x) Snyder Column, 2 ball micro (Supelco 6-4694M or equivalent).

3.0 Reagents

a) Sodium sulfate, powdered or granular anhydrous and reagent grade, heated at 450°C for 8 hours, cooled in a desiccator and stored in a glass bottle. Baker anhydrous powder, catalog #73898 or equivalent.

b) Extraction solvents.

c) Sulfuric acid (H_2SO_4) and water (1:1, 1:10, 1:20 are commonly used).

d) 10 N NaOH.

4.0 Standards

a) Base Neutral Surrogate Compounds ~~Solution~~ and Acid Surrogate Compounds ~~Solution~~.

Surrogate standards are added to all samples, blanks, matrix spikes, matrix spike duplicates, and calibration solutions; the compounds specified are:

Base Neutrals ~~(1000 µg/1.0 ml)~~	Acids ~~(2000 µg/1.0 ml)~~
nitrobenzene - d_5	2,4,6-tribronophenol
terphenyl - d_{14}	2-fluorophenol
2-fluorobiphenyl	optional - 1 additional
optional - 1 additional	

b) Matrix Spike Compounds ~~solutions.~~

Base/Neutrals ~~(1000 µg/1.0 ml)~~	Acids ~~(2000 µg/1.0 ml)~~
1,2,4-trichlorobenzene	pentachlorophenol
acenaphthene	phenol
2,4-dinitrotoluene	2-chlorophenol

pyrene
N-nitroso-di-n-propylamine
1,4-dichlorobenzene
4-chloro-3-methylphenol
4-nitrophenol

The surrogate and matrix spike concentrations and solvent for sample preparation will be determined by the cognizant scientist with approval of the group leader. They may vary depending on sample matrix. Record all surrogate and matrix spike preparations in the Standards Laboratory Record Book. ~~Prepare separate surrogate and matrix spiking solutions at a concentration of 1000 µg/1.0 ml for base/neutral and 2000 µg/1.0 ml for acids in methanol.~~ Store the solutions at 4°C (±2°C) in amber glass Teflon-sealed containers. The solutions must be replaced after twelve months, or sooner, if comparison with quality control check samples indicate a problem.

5.0 Safety

a) Observe the general laboratory safety rules.

b) Follow the requirements of applicable RWPs.

c) Observe regulations for handling, storage and disposal of hazardous organic chemicals.

6.0 Quality Control

a) A reagent blank shall be subjected to exactly the same procedure for each set of samples.

b) A matrix spike and matrix spike duplicate [see section 4.0 (b)] shall be performed on one sample from each set of samples having the same sample matrix and/or to one sample from each group of 20 samples received as a group and/or originating from the same sample matrix. The matrix spike and matrix spike duplicate samples shall be subjected to the same procedure.

c) Base/neutral and acid surrogate spikes [see section 4.0 (a)] shall be added to all blanks, samples, and matrix spiked samples.

7.0 Analysis

7.1 Initial Sample Preparation

a) Verify that the sample has been received and logged into the Chemistry and Analysis Section.

b) Grind and/or mix the sample thoroughly.

c) Weigh out a subsample, (weight shall be specified by the cognizant scientist) for pH measurement - typically 1 to 2 grams.

d) Add 1-5 ml of water per each gram of sample and stir for 1 hour or until the pH stabilizes (.1 pH unit).

e) Determine pH of sample with glass electrode and pH meter while stirring. Record the pH to .1 pH units on 325-B Hot Cells Sample Preparation Sheet and/or Organic Extraction Bench Sheet.

Proceed with steps f and g only if the pH is outside the 5-9 ~~11~~ range:

f) Add H_2SO_4 or NaOH dropwise until the pH is within the 5-9 ~~11~~ range. Due to sample variability, it is recommended the sample be adjusted to pH 7-8.

g) Record sample weight, volume of water added to sample, pH (to .1 pH unit), volume and concentration of H_2SO_4 or NaOH added on the 325-B Hot Cells Sample Preparation Sheet and/or Organic Extraction Bench Sheet

h) Dispose of the sample used for the pH and acid/base adjustment measurement.

7.2 Extraction of Sample for Medium Level Semivolatile Organics

a) Weigh out a subsample for extraction. The weight shall be specified by the Cognizant Scientist and shall be recorded on the 325-B Hot Cells Sample Preparation Sheet and/or Organic Extraction Bench Sheet. (EPA suggested weight for the sample is 1 gram).

b) Add sample to a 40-ml pre-cleaned vial. If required, add a proportional amount of acid or base as calculated in steps 7.1 f-h. Mix thoroughly into soil.

c) Add anhydrous sodium sulfate at twice the weight of the combined sample and pH adjustment reagents. For 1 gram of sample, add 2 grams of powdered anhydrous sodium sulfate to the sample and mix well.

d) Add 100 ug of the Base/Neutral compounds and 200 ug of the Acid Compounds ~~1 ml of each surrogate spike solution~~ to the vial. Record all additions on the Organic Analysis Bench Sheet. [See section 4.0 (a)]

e) If the sample is chosen for matrix spike or matrix spike duplicate add 100 ug of the Base/Neutral matrix spike compounds and 200 ug of the Acid matrix spike compounds ~~100 ul of each matrix spike solution~~. Record all additions on the Organic Analysis Bench Sheet. [See section 4.0 (b)]

f) Add whatever volume of methylene chloride needed to bring the final solution volume to 10.0 ml (considering the added volume of surrogate and matrix spike).

g) Disrupt the sample with the 1/8 inch tapered microtip ultrasonic probe for 2 minutes at an output control setting 5 in the continuous mode. Note: before extraction mix the sample and make sure any lumps of the sodium sulfate are broken up and are free flowing using a clean glass rod or a clean spatula.

h) Loosely pack a disposable pipet with 2-3 cm glass wool and 2-3 cm of granular anhydrous sodium sulfate on top. Do not pre-rinse the column.

i) Filter the extract through the glass wool and collect 5.0 ml in a concentrator tube. Centrifugation may also be used in place of or in conjunction with step (j).

j) Place the concentrator tube in the N-evaporator with the water bath at (35°C) and evaporate the solvent to 0.5 ml using a gentle stream of nitrogen gas. The internal walls of the concentrator tube should be washed down with a small volume of methylene chloride during the operation. During the evaporation, the tube solvent level must be kept below the water level of the bath. The extract should never be allowed to become dry.

or

Attach a 2-ball micro-Snyder Column or equivalent to the concentrator tube which contains the extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre-wet the Snyder Column with methylene chloride. Place the K-D apparatus over a hot water bath (80 -90 C) and reduce the volume to approximately 0.5 ml. Remove from the water bath and allow to cool for approximately 10 minutes.

k) Transfer the 0.5 ml concentrate to a 2 ml screw top vial and bring to 1.0 ml from rinsate of the ampule and the Snyder Column using quantitative transfer. Label the vial with sample ID.

l) Submit the sample for GC/FID screening or GS/MS screening or GS/MS analysis.

m) Fill out the organic extraction bench sheet and submit it with the sample.

7.3 Extraction of Sample for Low Level Semivolatile Organics

a) Weigh out a sample specified by the cognizant scientist. (<u>Note</u>: EPA methodology recommends a 30 gram sample for the low level extraction. Record the sample weight on the Organic Bench Sheet .

b) Add the sample to a clean 400 ml beaker or equivalent.

c) If the sample pH determined in steps 7.1 a-e is outside the allowable range of pH 5-9 ~~11~~, add a proportional amount of H_2SO_4 or NaOH as determined in steps 7.1 f-h to obtain pH 7-8. Mix thoroughly.

d) Add 2 times the combined sample and pH adjustment reagents weight of sodium sulfate. For example, add 60 grams of anhydrous powdered sodium sulfate for a 29 gram sample with 1 gram of acid added.

e) Add 100 ml of 1:1 methylene chloride-acetone.

f) Add 100 ug of the Base/neutral compounds and 200 ug of the Acid compounds ~~1.0 ml of each surrogate spike solution~~ to ~~each~~ the sample. [see section 4.0 (a)]

g) If the sample is designated for matrix spiking or matrix spike duplicate, add 100ug of the Base/Neutral matrix spike compounds and 200 ug of the Acid matrix spike compounds ~~100 ul of each matrix spiking solution~~ [see standards section 4.0 (c)].

h) If the sample extract is to be cleaned up using Gel Permeation Chromatography (GPC) add a volume of spiking solutions specified by the cognizant scientist. Record the volume and source of the spiking solutions on the organic extraction bench sheet .

i) Place the bottom surface of the 3/4 inch sonicator disrupter horn about 1/2 inch below the surface of the solvent. Sonicate for 1 1/2 minutes with the W-385 using no. 208 3/4 inch standard disrupter horn with the output control knob set at 10 (or no. 305 3/4 inch tapped high gain Q disrupter horn at 5) and mode switch on "1 sec pulse" and % duty cycle at 50%.

j) Decant the filter extract through a #41 filter paper, or equivalent, approximately half filled with anhydrous sodium sulfate in a glass conical funnel. Centrifugation may also be used instead of or in conjunction with the above filtration. A sodium sulfate drying column must be used if the funnel drying method is not employed.

k) Repeat the above extraction 2 times.

l) Transfer the extracts to a Kuderna-Danish (K-D) concentrator consisting of a 10 ml concentrator tube, a 3 ball Snyder column and 500 ml evaporative flask. The concentrator should be cleaned per PNL-SA-41 and just prior to assembly should be rinsed with methylene chloride. One or two clean boiling chips should be added to the concentrator tube during the assembly to prevent bumping.

m) Place the K-D apparatus on a hot water bath (80 to 90°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot steam. Prewet the Snyder balls by adding a small amount of methylene chloride through the top of the condenser. At the proper rate of distillation the balls of the column will chatter continuously; but the chamber will not flood with vapor.

n) When the volume in the concentrator tube is below ~5 ml remove the K-D apparatus from the water bath and allow to cool ~ 10 minutes.

o) If screening is required, make the volume of the residue to 10 ml, 1 ml of the solution in the concentrator tube can be transferred to an autosampler and/or 2 ml vial and submitted for GC/FID screening or GC/MS screening. Normally low level extracts are concentrated as follows.

p) Place the concentrator tube in the N-evaporator with the water bath at (35°C) and evaporate the solvent to 0.5 ml using a gentle stream of nitrogen gas. The internal walls of the concentrator tube should be washed down with a small volume of methylene chloride during the operation. During the evaporation, the tube solvent level must be kept below the water level of the bath. The extract should never be allowed to become dry.

or

Attach a 2-ball micro-Snyder Column or equivalent to the concentrator tube which contains the extract and add a fresh silicon carbide boiling chip to the concentrator tube. Pre wet the Snyder Column with methylene chloride. Place the K-D apparatus over a hot water bath (80 -90 C) and reduce the volume to approximately 0.5 ml. Remove from the water bath and allow to cool for approximately 10 minutes.

q) Transfer the 0.5 ml concentrate to a 2 ml screw top vial and bring the volume to 1.0 ml using rinsates from the concentrator ampule and the Snyder Column, use quantitative transfer. Label the vial with sample ID.

Submit the sample for GC/FID screening or GS/MS screening or GS/MS analysis.

r) Fill out the organic extraction bench sheet and submit it with the sample.

REFERENCES

USA EPA Contract Laboratory Program, Statement of Work for Organic Analysis, 2/88.

USA EPA Test Methods for Evaluating Solid Waste, SW-846, 3rd Edition.

INTERIM CHANGE NOTICE *(ICN)*

ICN - PNL-ALO-121.1 RO
Page 1 of 1

A.
Document Number: PNL-ALO-121.1 RO **Revision Number:** 0
Document Title: PREPARATION AND CLEANUP OF HYDROCARBON CONTAINING SAMPLES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS
Document's Original Author: EW Hoppe

Effective Date of ICN: 06/24/92

Change Requested by:
PW Zimmerman, DH Varley
Clearance Administration

B. **Action:**

Replace pages 3 through 6, and 9 with new pages.

C. **Effect of Change:**

Approval for clearance.

D. **Reason for Change/Description of Change:**

Proper punctuation of trade names. References need to be publicly available.

See redline in sections 4.2, 4.8, 7.1.6, 7.2.1, 7.2.2, 7.2.3.
In the Reference section delete "Battelle".

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):
x Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert **Date:** 6/24/92
Approval Authority: AG King AG King **Date:** 6/24/92
Other Approvals: TE Jones **Date:** 6/24/92
: **Date:** / /

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-121, PREPARATION AND CLEANUP OF HYDROCARBON CONTAINING SAMPLES FOR THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure is useful for the analysis of volatile compounds in samples containing interfering quantities of normal hydrocarbons. This procedure was developed to remove normal paraffin hydrocarbons (NPH), typically C_{12} through C_{14}, often used as a non-miscible hydrostatic fluid for obtaining radioactive tank wastes on the Hanford site. When employing conventional purge and trap sample introduction methods, large quantities of heavy hydrocarbons, such as NPH, can be introduced into the analytical system. The resulting performance of the analytical system is drastically reduced and usually requires extensive hardware cleanup and maintenance. To avoid compromising an analytical system in this manner, this procedure should be utilized. Diluting the sample to reduce the hydrocarbon can be considered, however, often the dilution factor required may be several orders of magnitude. Use of this procedure in conjunction with most GC/MS methods increases the detection limits by approximately 50 times. Any sample matrix containing excessive quantities of normal hydrocarbons, such as waters, sorbents, or soils, are applicable to this procedure.

DEFINITIONS

NPH (Normal Paraffin Hydrocarbons)
CRQL (Contract Required Quantitation Limit)

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method employs a methanolic extraction of a sample followed by cleanup of the residue using C_{18} solid phase sorbent cartridges. A portion of the resultant residue from this preparation is analyzed using other procedures such as PNL-ALO-335, "GC/MS Analysis of Volatile Organic Compounds". Unless specifically mentioned within this procedure, there

Author Date E.W. Hoppe 1-28-92	Project Mgr. Date T.E. Jones 1/28/92	QAD Representative Date GK Gerke 1/28/92 G.K. Gerke
Technical Reviewer Date G.A. Ross 1-28-92	Line Mgr. Date for A.G. King 1-29-92	Other Date

Procedure No. PNL-ALO-121	Revision No. 0	Effective Date JAN 29 1992	Page 1 of 9

are no further deviations of the analytical methods used to analyze residues from this preparation.

1.2 This method may be used for the analysis of radioactive storage tank wastes which contain hydrocarbons in excessive quantity. This procedure does not allow for distinction between hydrocarbons introduced during the sampling process as contamination and those which are native to the tank wastes. An attempt to quantify any compound not included in the Volatiles Target Compound List (TCL) following use of this procedure without further validation is inappropriate.

1.3 This procedure may be used to remove oil from various matrices, such as soil. Before using this procedure, validation employing matrix spikes and establishing control limits for each distinct matrix should be considered.

2.0 SUMMARY OF METHOD

An aliquot (nominally 1 gram) of the sample is extracted with 5 mL of 90/10 methanol/water containing surrogate compounds. A 2 mL aliquot of the extract is syringe-pumped through a C_{18} Sep-Pak^R Cartridge and followed with 0.5 mL rinses with 90/10 methanol/water until a final volume of 5 mL is obtained. An analysis procedure specified by the cognizant scientist is then performed on the clean residue.

3.0 INTERFERENCES

3.1 "Purge and Trap" grades of methanol are typically of sufficient quality for use in this Procedure. Continued exposure of the methanol to the ambient air is not desirable. An approach to minimize this problem is to purchase several small quantities of methanol or aliquot larger amounts to several small containers to reduce exposure time.

3.2 Several target compounds are subject to substantial degradation under alkaline conditions. For example, under alkaline conditions, 1,1,2,2-Tetrachloroethane degrades and results for this analyte will be low. The degradation forms Trichloroethene and causes elevated results for this compound. In low moisture conditions, such as dry alkaline soils or where the presence of oil precludes water, the degradation may not be complete. Until validation of a suitable pH adjustment procedure is available, residues of low moisture alkaline soils should be analyzed immediately following the extraction procedure.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.01 g.

4.2 Vials: Pre-cleaned volatile (VOA) type 1.5 mL, 5 mL, 20 mL screw top with Teflon lined silicone backed closures.

4.3 Pipets: Pasteur type or equivalent.

4.4 Centrifuge: Bench top capable of achieving 2000 rpm.

4.5 Syringes: Gas-tight, 10 µL, 100 µL, 5.0 mL and other assorted sizes as required.

4.6 Syringe Valve: Two-way with Luer ends (three each).

4.7 Sep-Pak^R Cartridges: C_{18} Environmental (Waters) or equivalent.

4.8 Syringe Needle: Blunt tip, Luer or Luer-Lok, 19 gauge, 10 cm long, stainless steel.

5.0 REAGENTS

5.1 Methanol: Purge and Trap grade or equivalent.

5.2 Water: Obtained from a Nanopure water purification unit equipped with an Organic-free cartridge or equivalent.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples to be used for this procedure shall follow guidelines provided by the appropriate procedure and matrix, such as Procedure PNL-ALO-335.

6.2 It has been demonstrated that sample extraction residues may be stored 12 days at -10°C to -20°C, minimal or no headspace, and protected from light.

7.0 PROCEDURE

7.1 Extraction of Sample: These procedures may be performed remotely "hot cells" if the samples are highly radioactive.

7.1.1 Approximately 1 g of sample is accurately weighed into a 20 mL VOA vial. Record the weight to the nearest 0.01 g.

7.1.2 To all samples, add 5.0 mL of 90/10 methanol/water (v:v) solution which has been spiked with surrogate compounds at the concentration as specified in the defined analysis method. For example, if Procedure PNL-ALO-335 is specified: 12.5 µL of surrogate mix at a concentration of 2500 µg/mL is added.

7.1.3 If this is a matrix spike sample, add the concentration as specified in the defined analvsts method of spike compounds. For example, if Procedure PNL-ALO-335 is specified: 12.5 µL of the spike mix at a concentration of 2500 µg/mL is added.

7.1.4 Cap the vial containing the sample and spiked solution and shake for 1 minute. Allow the contents to settle for 10 minutes or until the liquid phase appears transparent.

7.1.5 If the liquid phase is noticeably cloudy or is not well separated, it will be necessary to centrifuge the residue. If the centrifuge is unable to accommodate the 20 mL vial, transfer as much of the liquid as possible to a clean appropriately sized vial. Centrifuge with the vial capped for three minutes at 2000 rpm.

7.1.6 Transfer the extracted liquid residue to a 5 mL vial. Cap the vial tightly with the Teflon side of the septa cap liner facing the sample. Remove from the hot cell if necessary. Record the date and time of extraction.

7.1.7 If not performing the cleanup immediately (see precautions in the "Interferences" section) store the residues for up to 12 days at -10°C to -20°C in a freezer appropriate for storage of flammable solvents. Store the residues away from other solvents as required of standards.

7.2 Residue Cleanup:

7.2.1 Immediately prior to use, an Environmental C_{18} Sep-Pak^R Cartridge is pre-conditioned by passing 5 mL of methanol followed by 5 mL of 90/10 methanol/water through the cartridge from a clean 5 mL Luer-Lok, gas-tight syringe. Discard the eluant.

7.2.2 Slowly take up 2 mL of the sample extract solution in a 5 mL gas-tight syringe equipped with a Teflon Luer-Lok and an 19 gauge, 10 cm needle. Pulling the sample too quickly into the syringe imparts excessive partial pressure to the residue and may result in lost volatile components.

7.2.3 Remove the needle from the syringe. Connect the sample syringe to a pre-conditioned Sep-Pak^R cartridge. Connect the other side of the cartridge to a three-port, Luer-Lok, 2-way valve. Connect a clean, 5 mL gas-tight receiving syringe to another port on the valve.

7.2.4 Adjust the valve so that there is flow between the two ports connecting the sample and receiving syringes. Slowly syringe the sample extract solution through the Sep-Pak^R cartridge and into the receiving gas-tight syringe.

7.2.5 Fill the sample syringe repeatedly with 0.5 mL rinses of 90/10 methanol/water. Pump the liquid through the cartridge and into the receiving syringe until a 5.0 mL final volume is obtained in the receiving syringe.

7.2.6 Close the valve. Invert the syringe several times to insure adequate mixing of the eluent.

7.2.7 If not performing the analysis the same day, the receiving syringe may be removed and an aliquot or all of the cleaned residue may be transferred to a 1.5 mL or 5 mL vial. No headspace shall remain in the 1.5 mL vial and little or no headspace should remain in the 5 mL vial. Record the date of cleanup.

7.2.8 Store the residues at -10°C to -20°C in a freezer appropriate for storage of flammable solvents. Store the residues away from other solvents as required of standards. The time from extraction and cleanup to analysis shall not exceed 12 days.

7.3 Analysis:

7.3.1 Transfer 100 μL of the cleaned residue to a purge vessel containing internal standards and 4.9 mL of reagent water. Attach the vessel to a purge and trap sample concentrator and purge as specified in the analytical method such as Procedure PNL-ALO-335. The attached control limits were calculated from data obtained using a heated purge. The heated purge, however, is regarded as optional for this procedure provided consistency is observed per the analytical method such as in Procedure PNL-ALO-335.

8.0 QUALITY CONTROL

8.1 Before processing samples, the analyst shall demonstrate through the analysis of a method blank that all glassware and reagents are interference free when used in the quantity as specified in this method. With each batch of samples, and whenever there is a change in reagents or the location of performing this procedure, a method blank shall be processed as a safeguard against chronic laboratory contamination. The blank samples shall be carried out through all stages of the sample preparation including matching the handling and storage times and location.

8.2 Standard quality assurance practices consistent with the analysis method shall be employed while using this method. Fortified samples shall be carried through all stages of sample preparation adhering to those parameters previously specified with the blank preparation.

8.3 Limits of uncertainty for all measurements shall be in accordance with PNL QA Plan MCS-033 Rev. 0. Briefly, the limit is ±5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL.

8.4 Control Limits:

8.4.1 Surrogate standard determinations shall be performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before extraction in order to monitor the preparation and analysis of samples.

8.4.2 Matrix spikes shall be performed at a frequency specified by Procedure PNL-ALO-335. Briefly, matrix spike and matrix spike duplicate analyses are required for each matrix and every 20 samples, the same as specified by the EPA-CLP SOW dated 2/88.

8.4.3 Control limits for this method were calculated in accordance with EPA and PNL QA Plan MCS-033 Rev 0 procedures. Table 1 provides surrogate recovery control limits and Table 2 provides spiking compound recovery limits obtained from analyses using Procedure PNL-ALO-335. Due to the limited quantity of data provided from validation study samples and sample matrices, all control limits for this method shall be considered advisory only. Currently, no action will be required if these control limits can not be met; however, these instances shall be noted in the case narrative.

TABLE 1. SURROGATE RECOVERY CONTROL LIMITS

Surrogate Compound	Level*	Recovery Limit(%)	RPD Limit
1,2-Dichloroethane-d_4	50 ug	69-120	50
Toluene-d_8	50 ug	63-133	50
4-Bromofluorobenzene	50 ug	69-127	50

All limits are for advisory purposes only
* At time of injection

TABLE 2. MATRIX SPIKE RECOVERY LIMITS

Matrix Spike Compound	Level*	Recovery Limit(%)	RPD Limit
1,1-Dichloroethene	50 ug	18-136	50
Trichloroethene	50 ug	01-229	50
Chlorobenzene	50 ug	71-129	50
Toluene	50 ug	56-160	50
Benzene	50 ug	74-110	50

All limits are for advisory purposes only
* At time of injection

9.0 METHOD PERFORMANCE AND SPECIFIC QUALIFICATION

9.1 Table 3 provides method accuracy and precision based on analysis of 18 surrogate spiked samples and 11 TCL spiked samples on three different matrices.

9.2 The validation of this procedure was performed using spikes of the complete Volatiles Target Compound List (TLC) from the USEPA-CLP, SOW dates 2.88, on a limited number of authentic single shell tank wastes and blank samples. See Reference 1.

TABLE 3. METHOD ACCURACY AND PRECISION

		Percent Recovery	
	Compound Name	Mean	Standard Deviation (n-1)
1)	*Bromochloromethane	100.0	0.0
2)	Chloromethane	62.5	18.5
3)	Bromomethane	69.5	16.6
4)	Vinyl Chloride	57.6	15.4
5)	Chloroethane	69.1	12.8
6)	Methylene Chloride	91.1	10.2
7)	Acetone	81.6	45.6
8)	Carbon Disulfide	40.4	25.6
9)	1,1-Dichloroethene	77.0	19.8

TABLE 3. METHOD ACCURACY AND PRECISION (continued)

		Percent Recovery	
	Compound Name	Mean	Standard Deviation (n-1)
10)	1,1-Dichloroethane	93.3	7.8
11)	trans-1,2-Dichloroethene	88.7	8.3
12)	cis-1,2-Dichloroethene	97.5	6.6
13)	Chloroform	100.0	6.7
14)	#1,2-Dichloroethane-d4	94.5	8.5
15)	1,2-Dichloroethane	93.4	8.4
16)	2-Butanone	74.0	39.8
17)	1,1,1-Trichloroethane	93.4	6.5
18)	Carbon Tetrachloride	89.6	8.3
19)	Vinyl Acetate	37.0	48.3
20)	Bromodichloromethane	96.1	8.0
21)	*1,4-Difluorobenzene	100.0	0.0
22)	1,2-Dichloropropane	95.3	5.8
23)	cis-1,3-Dichloropropene	100.0	6.0
24)	Trichloroethene	113.5	38.5
25)	Dibromochloromethane	87.1	10.6
26)	1,1,2-Trichloroethane	79.7	23.0
27)	Benzene	91.8	6.0
28)	trans-1,3-Dichloropropene	81.2	8.4
29)	Bromoform	79.6	13.6
30)	*Chlorobenzene-d5	100.0	0.0
31)	4-Methyl-2-Pentanone	70.0	33.6
32)	2-Hexanone	65.0	37.1
33)	Tetrachloroethene	90.9	15.3
34)	1,1,2,2-Tetrachloroethane	62.1	43.5
35)	Toluene	108.1	17.4
36)	#Toluene-d8	97.6	11.7
37)	Chlorobenzene	99.7	9.6
38)	Ethylbenzene	96.7	11.1
39)	Styrene	96.9	11.7
40)	p-Xylene	93.4	14.0
41)	o-Xylene	99.9	12.6
42)	#Bromofluorobenzene	98.0	9.7

* Compound is an Internal Standard
\# Compound is a Surrogate Spike

REFERENCES

1. Hoppe, E. W.; Ross, G. A.; Lucke, R. B.; Development and Validation of a Preparation and Cleanup Method for Hydrocarbon Containing Samples for the Analysis of Volatile Organic Compounds, Pending ~~Battelle~~ PNL Technical Report, 2/92.

2. PNL-ALO-335, GC/MS Analysis of Volatile Organic Compounds, Rev. 0, ~~Battelle~~ PNL Technical Procedure, 8-3-89.

3. QA Plan for Activities Conducted by the Analytical Chemistry Laboratory (ACL), QA Plan MCS-033, Rev. 0, 9-4-91

4. USEPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, SOW No. 2-88.

5. USEPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, Document Number OLM01.0, March 1990.

6. USEPA Office of Solid Waste, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, 11-86.

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-122.2 RO
Page 1 of 1

A.
Document Number: PNL-ALO-122.2 RO **Revision Number:** 0

Document Title: CLEANUP OF HYDROCARBON SAMPLES FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

Document's Original Author: EW Hoppe

Effective Date of ICN: 06/24/92

Change Requested by:
PW Zimmerman, DH Varley
Clearance Administration

B. **Action:**

Replace pages 1 through 6, and 11 with new pages.

C. **Effect of Change:**

Approval for clearance.

D. **Reason for Change/Description of Change:**

Proper punctuation of trade names. References need to be publicly available.

In sections 4.2, 4.14, 4.15, 7.1.8 and 7.3.10, change "teflon" to "Teflon".
In section 4.12, change "pyrex" to "Pyrex".
In the References section, delete "Battelle".

E. **Approval Signatures:**
(Please sign and date)

Type of Change: (Check one):

X Minor ___ Major

Process Quality Department: TL Ehlert TL Ehlert Date: 6/24/92
Approval Authority: AG King AG King Date: 6/24/92
Other Approvals: TE Jones TE Jones Date: 6/24/92
: Date: / /

INTERIM CHANGE NOTICE
ICN

ICN- PNL-ALO-122.1 RO
PAGE 1 OF 1

A. Document Number: PNL-ALO-122.1 RO Revision Number: 0
Document Title: CLEANUP OF HYDROCARBON SAMPLES FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS
Document's Original Author: EW HOPPE

Effective Date of ICN: 05/20/92

Change Requested by: EW HOPPE

B. Action:

Replace pages 1-4 with new pages 1-4.

C. Effect of Change:

To meet SST project requirements for extraction of drainable liquid samples of a small volume.

D. Reason for Change/Description of Change:

A procedure for the extraction of a small aliquot of drainable liquid does not exist.

The change will expand the application of the procedure allowing extraction of small aliquots of liquid using Acid-Base-neutral partitioning without increasing radioactive mixed waste and allow for minimal personal exposure.

See redline in sections 1.1, 2.0, and 7.1.1.

E. Approval Signatures
(Please sign and Date)

Type of Change (Check (✓) one)
( )Minor Change (X)Major Change

QS&R Department Concurrence: TL Ehlert TL Ehlert Date: 5/22/92
Approval Authority: AG King Date: 5/22/92
Other Approvals: TE Jones Date: 5/22/92
: Date: 5-22-92

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-122, CLEANUP OF HYDROCARBON CONTAINING SAMPLES FOR THE ANALYSIS OF SEMIVOLATILE ORGANIC COMPOUNDS

APPLICABILITY

This procedure is useful for the analysis of semivolatile compounds in samples containing interfering quantities of normal hydrocarbons. This procedure was developed to remove normal paraffin hydrocarbons (NPH), typically C_{12} through C_{14}, often used as a non-miscible hydrostatic fluid for obtaining radioactive tank waste samples on the Hanford site. Previously, diluting the sample to reduce the quantity injected into the analytical system has been the only available method of dealing with high concentration levels of hydrocarbons. Often the dilution required may be several orders of magnitude which also dilutes the analytes of interest and affects detection limits substantially. Use of this procedure in conjunction with most GC/MS methods does not require dilution and allows the stated detection limits to remain unchanged. Any sample matrix containing excessive quantities of normal hydrocarbons, such as waters, sorbents, or soils, are applicable to this procedure.

DEFINITIONS

NPH (Normal Paraffin Hydrocarbons)
CRQL (Contract Required Quantitation Limits)

RESPONSIBLE STAFF

Cognizant Scientist
Analyst

PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 This method is employed following extraction of a waste or soil using other procedures such as Procedure PNL-ALO-120 or PNL-ALO-344 or with a small liquid sample. In this procedure, residues from Procedure PNL-ALO-120 or PNL-ALO-344 or liquid samples are partitioned into their base-neutral and acidic components. The base-neutral fraction is cleaned using a silica gel column. Analysis of the cleaned fraction is per other methods such as Procedure PNL-ALO-345. Unless specifically mentioned within this procedure, there are no further deviations of the methods used to perform extractions or to analyze residues from this preparation.

Author Date E.W. Hoppe	Project Mgr. Date T.E. Jones	QAD Representative Date G.K. Gerke
Technical Reviewer Date R.W. Stromatt	Line Mgr. Date A.G. King	Other Date All original signatures on file

Procedure No.	Revision No.	Effective Date	Page
PNL-ALO-122	0	January 29, 1992	1 of 11

1.2 This method may be used for the analysis of radioactive storage tank wastes which contain hydrocarbons in excessive quantity. This procedure does not allow for distinction between hydrocarbons introduced during the sampling process as contamination and those which are native to the tank wastes. An attempt to quantify any compound not included in the Semivolatiles Target Compound List (TCL) following use of this procedure without further validation is inappropriate.

1.3 This procedure may be used to remove oil from various matrices, such as soil. Before using this procedure, validation employing matrix spikes and establishing control limits for each distinct matrix should be considered.

2.0 SUMMARY OF METHOD

An aliquot of the sample residue produced from a preceding extraction procedure or an aliquot of liquid sample is added to a volume of reagent water. The pH is adjusted to >11 and the base-neutral fraction is extracted into methylene chloride. The pH of the aqueous phase is again adjusted to <2 and the acid fraction is extracted into methylene chloride. Following concentration and exchange into cyclohexane, the base-neutral fraction is eluted through a silica gel (an amorphous silica with weakly acidic properties) column. The hydrocarbon fraction is discarded, followed by collection of the analyte fraction of interest. After concentration, the residue is now ready for GC/MS analysis along with the acid fraction.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminated solvents, reagents, or glassware. Particular care should be taken when plastic labware of any kind is in the laboratory. Substantial quantities of various phthalate esters, used as plasticisers, can contaminate the sample even from a small amount of solvent exposed to plastic surfaces.

3.2 If pre-packed silica cartridges are substituted for glass columns, it is imperative that the manufacturers lot is checked for contamination. Phthalate contamination is a primary obstacle using pre-packed commercial columns.

4.0 APPARATUS AND MATERIALS

4.1 Balance: Analytical, capable of accurately weighing 0.01 g.

4.2 Vials: Pre-cleaned 1.5 mL amber screw top with Teflon lined closures.

4.3 Pipets: Pasteur type or equivalent.

4.4 Kuderna-Danish (KD) Apparatus:

4.4.1 Concentrator tube: 10 or 25 mL with ground glass fitting and stopper.

4.4.2 Evaporation flask: KD type, 500 mL.

4.4.3 Snyder columns: Three ball macro and two ball micro or equivalent.

4.7 Oven: Capable of maintaining 150°C.

4.8 Water bath: Capable of temperature control and boiling water.

4.9 Boiling chips: Cleaned silicon carbide or equivalent.

4.10 Erlenmeyer flasks: 250 mL and as needed.

4.11 Beakers: 500 mL and as needed.

4.12 Chromatographic column: 250 mm long x 10 mm I.D. with Pyrex glass wool plug and Teflon stopcock or equivalent, including commercially available pre-packed cartridges.

4.13 Muffle furnace: Capable of maintaining 400°C for several hours.

4.14 Separatory funnel: 125 mL with Teflon stopcock.

4.15 Culture tube: Disposable 16 x 150 mm with screw top Teflon lined closures.

4.16 Centrifuge: Bench top with openings capable of holding 16 x 150 mm culture tubes and achieving 2000 rpm.

5.0 REAGENTS

5.1 Sodium Sulfate: Granular, anhydrous purified by heating at 400°C for at least 4 hours.

5.2 Water: In which an interferant is not observed at or above the CRQL for each parameter of interest.

5.3 Sodium hydroxide solution: 10 N, dissolve 40 g sodium hydroxide into reagent water and dilute to 100 mL.

5.4 Sulfuric acid solution: A.C.S grade or equivalent sulfuric acid and reagent grade water 1/1 (v/v).

5.5 Solvents: Cyclohexane, pentane, methylene chloride (pesticide quality or equivalent).

5.6 Silica gel: 100/200 mesh activated at 140°C for at least 16 hours in a beaker covered with foil. The silica gel should not exceed a 5 cm depth.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples to be used for this procedure shall follow guidelines provided by the appropriate procedure and matrix, for example Procedure PNL-ALO-344.

7.0 PROCEDURE

7.1 Acid/Base-neutral partitioning: Proceed to Section 7.2 when cleaning water extracted residues.

7.1.1 Quantitatively transfer the sample extract obtained from the appropriate extraction procedure such as Procedure PNL-ALO-344 or PNL-ALO-120 or prepare the liquid aliquot with the use of surrogates, spikes and blanks as in Procedure PNL-ALO-120 7.2(d) and 7.2(e) into a clean 16 x 150 mm culture tube or as specified in the applicable test instruction. Add 10 mL of reagent water.

7.1.2 Check the pH of the sample with wide range pH paper and adjust to pH >11 with sodium hydroxide solution.

7.1.3 Add 5 mL of methylene chloride to the culture tube. Extract the sample by shaking the culture tube for two minutes with periodic venting to release excess pressure.

7.1.4 Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, then centrifuging should be employed to mechanically aid the phase separation. If centrifuging is unsuccessful, the contents of the culture tube may be transferred to a 125 mL separatory funnel followed by an addition of 50 mL reagent water. All subsequent extractions are then performed using 20 mL of methylene chloride.

7.1.5 Collect the lower methylene chloride layer containing the base-neutral fraction using a pasteur pipet and transfer to a concentrator tube.

Repeat steps 7.1.3 through 7.1.5 two additional times. Save the base-neutral fraction for solvent exchange, Section 7.2.

7.1.6 Adjust the aqueous phase to pH <2 using the sulfuric acid solution. Perform three methylene chloride extractions as described in steps 7.1.3 through 7.1.5 collecting the acid fraction of the partition.

7.1.7 Add a boiling chip and concentrate the collected acid fractions using a micro KD apparatus. For analysis using Procedure PNL-ALO-345, when the apparent volume of the residue reaches 0.5 mL, about 5-20 minutes, remove the KD apparatus and allow it to drain and cool for at least 10 minutes.

7.1.8 Remove the micro Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of methylene chloride. Further, centrifuging may be required to remove small particulates in the residue if the radioactivity level exceeds desired levels. Adjust the volume to 1.0 mL. Transfer the residue to a 1.5 mL amber screw top vial. Cap with a Teflon lined closure. Proceed with the appropriate analysis on the acid residue.

7.2 Solvent exchange:

7.2.1 Transfer the sample extract obtained from the base-neutral partitioning procedure to a KD concentrator tube. Add a boiling chip.

7.2.2 Add 4 mL of cyclohexane and attach a micro Snyder column to the concentrator tube.

7.2.3 Place the assembled micro KD apparatus in boiling water so that the concentrator tube is partially immersed in the water.

7.2.4 When the apparent volume of the cyclohexane residue reaches 0.5 mL, about 5-20 minutes, remove the KD apparatus and allow it to drain and cool for at least 10 minutes.

7.2.5 Remove the micro Snyder column and rinse its lower joint into the concentrator tube with a minimum amount of cyclohexane. Adjust the volume to about 2 mL.

7.3 Column cleanup:

7.3.1 Prepare a slurry of 10 g of activated silica gel in methylene chloride and place this into a 10 mm I.D. chromatographic column. Tap the column several times to settle the silica gel. Allow 3-4 cm of unpacked space to remain in the column.

7.3.2 Elute the methylene chloride to 1-2 cm above the silica gel. Add 1-2 cm of anhydrous sodium sulfate to the top of the silica gel.

7.3.3 If using commercial pre-packed columns, begin their use here. Pre-elute the column with 40 mL of pentane. The rate for all elutions should be about 2 mL/minute. Discard the pentane eluate.

7.3.4 Just prior to exposure of the sodium sulfate layer to the air, transfer the 2 mL of cyclohexane base-neutral sample residue onto the column. Use an additional 2 mL of cyclohexane to rinse and complete the transfer. Continue to discard the column eluent.

7.3.5 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of pentane and continue elution of the column. Discard the pentane eluate.

7.3.6 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of 2/3 (v/v) methylene chloride/pentane. Collect this eluent into a 250 mL erlenmeyer flask or directly into a 500 mL KD flask equipped with a concentrator tube.

7.3.7 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL of methylene chloride to the column. Continue to collect the column eluent.

7.3.8 Just prior to exposure of the sodium sulfate layer to the air, add 25 mL 1/1 (v/v) of methylene chloride/acetone to the column. Collect the eluent until the column runs dry.

7.3.9 Concentrate the column eluent using the macro KD apparatus, followed by the micro KD apparatus if necessary, to whatever volume is required by the analysis procedure, for Procedure PNL-ALO-345 discontinue concentration when the apparent volume is 0.5 mL.

7.3.10 Remove the Snyder column and rinse the lower joint and KD flask into the concentrator tube. Adjust the final volume to 1.0 mL with methylene chloride. Transfer the residue to a 1.5 mL amber screw top vial. Cap with a Teflon lined closure. Proceed with the appropriate analysis on the residue.

8.0 QUALITY CONTROL

8.1 Before processing samples, the analyst shall demonstrate through the analysis of a method blank that all glassware and reagents are interference free when used in the quantity as specified in this method. With each batch of samples, and whenever there is a change in reagents or the location of performing this procedure, a method blank shall be processed as a safeguard against chronic laboratory contamination. The blank samples shall be carried out through the all stages of the sample preparation including matching handling and storage times and location.

8.2 Standard quality assurance practices consistent with the analysis method shall be employed while using this method. Fortified samples shall be carried through all stages of sample preparation adhering to those parameters previously specified with the blank preparation.

8.3 Limits of uncertainty for all measurements shall be in accordance with PNL QA Plan MCS-033 Rev. 0. Briefly, the limit is ± 5 in the next digit beyond the last one stated. For example, 5.0 mL means 5.0 ± 0.05 mL.

8.4 <u>Control Limits</u>:

8.4.1 Surrogate standard determinations shall be performed on all samples and blanks. All samples and blanks are fortified with surrogate spiking compounds before extraction and this cleanup procedure in order to monitor the preparation and analysis of samples.

8.4.2 Matrix spikes shall be performed at a frequency specified by the appropriate method such as PNL-ALO-344 or -120. Briefly, matrix spike and matrix spike duplicate analyses are required for each matrix and every twenty samples, the same as specified by the EPA-CLP SOW dated 2/88.

8.4.3 Control limits for this method were calculated in accordance with EPA and PNL QA Plan MCS-033 Rev 0 procedures. Table 1 provides surrogate recovery control limits and Table 2 provides spiking compound recovery limits obtained from analyses using PNL-ALO-345. Due to the limited quantity of data provided from validation study samples and sample matrices, all control limits for this method shall be considered advisory only. Currently, no action will be required if these control limits can not be met, however, these instances shall be noted in the case narrative. Additionally, these control limits were obtained from data which did not include the acetone column elution step.

TABLE 1. SURROGATE RECOVERY CONTROL LIMITS

Surrogate Compound	Level*	Recovery Limit(%)	RPD Limit
Nitrobenzene-d$_5$	100 ug	01-109	50
2-Fluorobiphenyl	100 ug	01-118	50
p-Terphenyl-d$_{14}$	100 ug	07-135	50
Phenol-d$_5$	100 ug	24-91	50
2-Fluorophenol	100 ug	14-92	50
2,4,6-Tribromophenol	100 ug	16-130	50

All limits are for advisory purposes only
* At time of injection in the validation study. Actual levels used in the procedure are typically 100-200 for acids and 100-50 ug for base-neutrals.

TABLE 2. MATRIX SPIKE RECOVERY LIMITS

Matrix Spike Compound	Level*	Recovery Limit(%)	RPD Limit
1,2,4-Trichlorobenzene	100 ug	01-117	50
Acenaphthene	100 ug	01-140	50
2,4-Dinitrotoluene	100 ug	01-149	50
Pyrene	100 ug	01-152	50
N-Nitroso-Di-n-Propylamine	100 ug	00-04	50
1,4-Dichlorobenzene	100 ug	01-82	50
Pentachlorophenol	100 ug	36-131	50
Phenol	100 ug	31-80	50
2-Chlorophenol	100 ug	28-86	50
4-Chloro-3-Methylphenol	100 ug	35-89	50
4-Nitrophenol	100 ug	33-114	50

All limits are for advisory purposes only
* At time of injection in the validation study. Actual levels used in the procedure are typically 100-200 for acids and 100-50 ug for base-neutrals.

TABLE 3. METHOD ACCURACY AND PRECISION

		--------Percent Recovery-------	
	Compound Name	Mean	Standard Deviation (n-1)
1)	*1,4-Dichlorobenzene-d4	100.0	0.0
2)	#2-Fluorophenol	52.9	13.0
3)	#Phenol-d5	57.7	11.1
4)	Phenol	55.8	8.2

TABLE 3. METHOD ACCURACY AND PRECISION (continued)

		--------Percent Recovery-------	
	Compound Name	Mean	Standard Deviation (n-1)
5)	bis(2-Chloroethyl)ether	15.7	23.3
6)	2-Chlorophenol	57.1	9.6
7)	1,3-Dichlorobenzene	30.4	17.2
8)	1,4-Dichlorobenzene	32.6	17.9
9)	Benzyl alcohol	4.1	3.2
10)	1,2-Dichlorobenzene	34.1	15.4
11)	2-Methylphenol	47.8	9.2
12)	bis(2-Chloroisopropyl)ether	23.1	34.3
13)	4-Methylphenol	50.7	8.4
14)	N-Nitroso-di-n-propylamine	1.0	1.1
15)	Hexachloroethane	19.5	15.7
16)	*Naphthalene-d8	100.0	0.0
17)	#Nitrobenzene-d5	17.5	30.4
18)	Nitrobenzene	23.8	34.9
19)	Isophorone	1.4	1.6
20)	2-Nitrophenol	66.5	11.2
21)	2,4-Dimethylphenol	22.1	13.0
22)	Benzoic acid	47.9	18.8
23)	bis(2-Chloroethoxy)methane	25.6	37.5
24)	2,4-Dichlorophenol	67.4	9.8
25)	1,2,4-Trichlorobenzene	43.5	24.3
26)	Naphthalene	51.3	19.3
27)	4-Chloroaniline	4.5	6.6
28)	Hexachlorobutadiene	27.0	20.7
29)	4-Chloro-3-methylphenol	61.9	9.1
30)	2-Methylnaphthalene	55.1	20.4
31)	*Acenaphthene-d10	100.0	0.0
32)	Hexachlorocyclopentadiene	17.8	15.2
33)	2,4,6-Trichlorophenol	70.5	11.4
34)	2,4,5-Trichlorophenol	67.0	10.7
35)	2-Chloronaphthalene	58.4	21.9
36)	#2-Fluorobiphenyl	58.3	19.8
37)	2-Nitroaniline	26.9	39.6
38)	Dimethylphthalate	2.3	2.5
39)	Acenaphthylene	55.6	23.2
40)	2,6-Dinitrotoluene	28.1	41.6
41)	3-Nitroaniline	6.6	11.3
42)	Acenaphthene	65.7	24.7
43)	2,4-Dinitrophenol	68.5	20.9
44)	4-Nitrophenol	73.8	13.6
45)	Dibenzofuran	64.6	24.4
46)	2,4-Dinitrotoluene	27.7	40.5
47)	Diethylphthalate	2.7	2.7
48)	4-Chlorophenyl-phenylether	30.6	22.2

TABLE 3. METHOD ACCURACY AND PRECISION (continued)

		Percent Recovery	
	Compound Name	Mean	Standard Deviation (n-1)
49)	Fluorene	67.8	25.5
50)	4-Nitroaniline	16.1	24.9
51)	*Phenanthrene-d10	100.0	0.0
52)	4,6-Dinitro-2-methylphenol	75.9	16.0
53)	N-Nitrosodiphenylamine	24.4	36.1
54)	#2,4,6-Tribromophenol	73.1	18.9
55)	4-Bromophenyl-phenylether	68.0	25.6
56)	Hexachlorobenzene	47.3	32.0
57)	Pentachlorophenol	83.4	15.9
58)	Phenanthrene	71.1	26.1
59)	Anthracene	62.0	27.5
60)	Di-n-butylphthalate	2.8	2.6
61)	Fluoranthene	70.8	25.7
62)	*Chrysene-d12	100.0	0.0
63)	Pyrene	72.7	26.4
64)	#Terphenyl-d14	70.7	21.4
65)	Butylbenzylphthalate	2.6	2.6
66)	3,3'-Dichlorobenzidine	1.1	3.2
67)	Benzo(a)anthracene	72.6	26.7
68)	Chrysene	77.7	27.7
69)	Bis(2-Ethylhexyl)phthalate	16.7	28.6
70)	*Perylene-d12	100.0	0.0
71)	Di-n-octylphthalate	10.0	13.6
72)	Benzo(b)fluoranthene	68.9	25.1
73)	Benzo(k)fluoranthene	69.5	26.3
74)	Benzo(a)pyrene	60.7	29.0
75)	Indeno(1,2,3-cd)pyrene	70.8	26.4
76)	Dibenz(a,h)anthracene	63.9	23.8
77)	Benzo(g,h,i)perylene	68.8	25.8

* Compound is an Internal Standard
\# Compound is a Surrogate Spike

9.0 METHOD PERFORMANCE AND SPECIFIC QUALIFICATION

9.1 Table 3 provides method accuracy and precision based on analysis of:

22 acid surrogate spiked samples
12 base-neutral surrogate spiked samples
17 acid TCL spiked samples
9 base-neutral TCL spiked samples

These data were obtained from three different matrices. As seen from Tables 1,2, and 3, the base-neutral ranges are quite wide.

The low number of determinations contributes substantially to variability. It is anticipated that the range will narrow when more data is available.

9.2 The validation of this procedure was performed using spikes of the complete Semivolatiles TCL from the USEPA-CLP, SOW dated 2/88, on a limited number of authentic single shell tank wastes and blank samples. See reference 1.

REFERENCES

1. Hoppe, E. W.; Stromatt, R. W.; Campbell, J. A., Development and Validation of a Cleanup Method for Hydrocarbon Containing Samples for the Analysis of Semivolatile Organic Compounds, Pending ~~Battelle~~ PNL Technical Report, 2/92.

2. PNL-ALO-120, Semivolatile Organic Extractions of Single Shell Tank Samples, Rev. 0, ~~Battelle~~ PNL Technical Procedure, 8-3-89.

3. PNL-ALO-344, Procedure for Sample Preparation of Samples for GC/MS Analysis for Semivolatile Organic Compounds, Rev. 0, ~~Battelle~~ PNL Technical Procedure, 4-26-91.

4. PNL-ALO-345, GC/MS Analysis of Extractable Semivolatile Organic Compounds, Rev. 0, ~~Battelle~~ PNL Technical Procedure, 8-3-89.

5. QA Plan for Activities Conducted by the Analytical Chemistry Laboratory (ACL), QA Plan MCS-033, Rev. 0, 9-4-91

6. USEPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, SOW No. 2-88.

7. USEPA Contract Laboratory Program, Statement of Work for Organic Analysis, Multi-Media, Multi-Concentration, Document Number OLM01.0, March 1990.

8. USEPA Office of Solid Waste, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, 11-86.

Battelle Pacific Northwest Laboratories	**SAFE OPERATING PROCEDURE** **MATERIALS & CHEMICAL APPLICATIONS**	PROCEDURE NO. 325-A-29
		PAGE 1 OF 3

TITLE RECEIVING OF WASTE TANK SAMPLES IN ONSITE TRANSFER CASK	REVIEW BY DATE:	ISSUE DATE August 8, 1989
BUILDING - ROOM 325 BUILDING ROOM 600 300 AREA		SUPERSEDES ISSUE DATED NEW

PREPARED BY G. M. RICHARDSON GMR	DATE 7-25-89	REVIEWED BY J. L. GREEN	DATE 7/25/89

REVIEWED AND APPROVED BY

ORGANIZATION	NAME	TITLE	DATE
Section Manager		Sect. Manager	7-27-89
Safety			8-8-89
PNL Building Manager			7-25-89
Program Manager		Sr Research Scientist	7/25/89
Radiation ~~Monitoring~~ Protection		Sr. Supervisor	7-25-89
REVIEW DUE DATES →			

I. GENERAL DESCRIPTION

Core samples in a sampler inside a capsule will be received in a Onsite Transfer Cask (H-2-38079) from 200 area waste tanks for analysis.

A. Work Description

1. Removal of cask from sample truck and placed in cask dolly.
2. Preparing and unloading cask.
3. All work shall be performed by two people with continuous RPT coverage.
4. Other SOP that applies.
    a. SOP-325-9-3 -- Operation of the 30/5 ton overhead crane.
5. RWP that applies.
    a. Room 603 RWP.

B. Supplemental Equipment Required

1. Unloading of cask.
    a. A radioactive waste box.
    b. Sheet of plastic.
    c. Industrial wipes.
    d. Cleaning solution.
    e. Masking tape.
2. Applicable prints.

a. On Site Transfer Cask--Dwg. #H-2-38079.

II. SAFETY

A. Radiological Hazards

1. Skin contamination.
2. Inhalation of radioactive material.
3. Radiation exposure.

B. Safety Hazards

1. Standing between truck and wall when flagging truck into unloading zone.
2. Smashing fingers due to moving cask.
3. Dropping cask face plate.

C. Alarm Device for Detection of Non-standard Operations

1. Area radiation alarms.

D. Special Precautions

1. Truck entry door shall be closed during unloading operation.
2. Cell port inner door shall be closed except when moving sample from cask into cell.
3. Exercise extreme caution when moving cask to and from the face of cell.
    a. Excessive swing will cause the cask to hit cell wall.
    b. The spread of contamination.

III. PROCEDURE

A. Removal of Cask From Sample Truck

1. RPT will check unloading area floor.
2. Truck is backed in through trucklock to Room 603 with assistance of operating personal.
3. The cask is removed from the truck and the truck is moved to trucklock and the rollup door closed.
4. The cask and dolly are moved to behind "B" cell.

B. Preparing and unloading Cask

Note: RPT shall provide continuous coverage.

1. Outer cell door is opened, and the door shielding plug is installed.
2. The cask is removed from cask dolly with Big Joe Lift and placed in vertical positions.
3. Tape a sheet of plastic below cell port to cask.
4. Remove face plate from cask.
5. Cask is moved to cell part and locked in place.
6. The push rod plug is removed and push rod is connected to cask.
7. Cask is moved to cell wall and aligned with cell port plug.
8. Inner cell door is opened, and push rod inserted into cask, moving liner and sampler into cell.
9. The liner is removed and push rod is pulled back into cask.
10. Inner door is closed.
11. Cask is moved back from cell.
12. Cask, door shielding plug and cell port are cleaned as necessary.
13. Remove push rod and replace push rod plug and cask face plate.
14. Plastic sheet is then removed and outer door is closed.
15. RPT checks the area.

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SAFE OPERATING PROCEDURE
MATERIALS & CHEMICAL APPLICATIONS

PROCEDURE NO. 325-EXT-1
PAGE 1 OF 2

TITLE RECEIPT AND EXTRUSION OF CORE SAMPLES AT THE 325A SHIELDED FACILITY
REVIEW BY DATE: JULY 26, 1989
ISSUE DATE August 8, 1989
BUILDING - ROOM 325A BUILDING ROOM 601 300 AREA
SUPERSEDES ISSUE DATED
PREPARED BY RD Scheele R. D. SCHEELE
DATE JULY 24, 1989
REVIEWED BY JL Green J.L. GREEN
DATE JULY 24, 1989

REVIEWED AND APPROVED BY

ORGANIZATION	NAME	TITLE	DATE
Section Manager		Section Manager	7/27/89
Safety			7-28-89
PNL Building Manager			7/24/89
Program Manager			7/24/89
Radiation ~~Monitoring~~ Protection		Sr. Supervisor	7/25/89
REVIEW DUE DATES →			

I. GENERAL DESCRIPTION

This procedure will be used to extrude samples received from waste tank core sampling operations.

II. PROCEDURE

1. Assemble associated paperwork.
2. Confirm that liner and sampler are labeled. If not prepare labels or labelling tags.
3. Place the plug end of the liner up on the front tray of B-Cell.
4. Screw an "I" bolt into the plug nut and loosen the nut with a 1½" wrench. Remove the plug using the "I" bolt.
5. Move the liner's front over a container.
6. Lift the bottom end of the liner and drain any oil from the liner into the dish. <u>Be careful the sampler doesn't slide out of the liner.</u>
7. When oil is all drained, remove the dish. Inspect the oil collected in the dish to determine whether any sample is present.
8. Lay rags out on front tray and move top end of liner to lip of tray. Lift bottom end of liner and slide sampler out of liner onto the rags.
9. Move liner to another cell for disposal.
10. Wipe sampler with rags. Remove the V-ring seal from the valve end of sampler with a 3/32" allen wrench.
11. Move extruder platform to forward position. Set torque and speed switches to 0 and the directional switch to brake.

12. Transfer the sampler into position on extruder. Position the sampler wires on top.

13. Place wooden block under back end of sampler (optional). Insert push rod into sampler and remove wooden block (if present). Seat and lock the push rod in back of extruder.

14. Clamp front end of sampler into position. Place sampler valve wrench into closed valve slot. (Horizontal is closed and Vertical is open). Clamp the back of the sampler to the extruder platform.

15. Place the weighed, labeled plastic container under extruder tray drain to collect any free fluid.

16. Open the valve by turning the valve counter-clockwise, (cutting the sampler wires may make opening the valve easier). Confirm that the valve is open using the mirror.

17. Turn on power to the extruder. Switch the directional switch to reverse and set the torque at less than or equal to 30. DO NOT EXCEED A TORQUE SETTING OF 30!

18. Begin extruding the sample by increasing the speed to no more than 50.

19. As the push rod and piston approach the valve, play close attention that the extruder does not bind or catch.

20. Continue extruding until the piston falls into the tray. If the piston binds at the valve or the extruder stops, evaluate the situation and take appropriate action. DO NOT FORCE EXCEED A TORQUE SETTING OF 30!

21. Drain the free liquid into the labeled liquid catch container.

22. Remove the tray and position for photographs. It is important the time that the sample spends on the open tray is minimized to prevent drying.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-130, PROCEDURE FOR THE RECEIPT AND INSPECTION OF SINGLE SHELL TANK (SST) SAMPLES

APPLICABILITY

This procedure is applicable to SST Samples delivered to the 325 building for characterization.

RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Cognizant Scientist
- Cognizant Technician

PROCEDURE

This procedure will be used to insure that all SST samples received at the 325 building are properly identified and that sufficient sample has been delivered for characterization.

1.0 Cask Receipt and Initial Cask Inspection

1.1 Obtain copy of <u>Chain of Custody</u> (COC) from driver.

Confirm that the cask ID is consistent with the COC. If the paperwork is not consistent with the cask received or is lacking the necessary identifiers, stop work and notify the cognizant Scientist or delegate. The cognizant Scientist or delegate will call the responsible shipping agent and resolve the discrepancy. Work will not proceed until the discrepancy has been resolved.

1.2 Inspection of Liner and Sampler

After transferring the liner and sampler into the shielded facility, confirm that the Liner ID is consistent with the COC.

If there is a discrepancy, the cognizant Scientist or delegate will contact the shipper and resolve the discrepancy. Work will not proceed until the discrepancy has been resolved.

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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
KD Scheele	7/28/89	Walter C. Weimer	7/31/89		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-130	0	AUG 03 1989	1	2

1.2.1 Confirm that the sampler ID is consistent with the COC.

1.2.2 If there is a discrepancy, the cognizant Scientist or delegate will contact the shipper and resolve the discrepancy. **Work will not proceed until the discrepancy has been resolved.**

3.0 Verification of Receipt of Sufficient Sample

3.1 Measure the height of the extruded solids sample and the volume of the drainable liquid. Calculate the volume of the solids by multiplying the height in cm by 5.1 cm^2. Sum the solids volume and the liquid volume. If the total volume received is <180 mL, notify the shipper or responsible Hanford prime contractor technical contact that we received less than the minimum sample volume and request guidance on how to proceed. The received sample may be put into a container, until guidance is provided. **Do no further work with the received sample until guidance is provided.**

3.2 If the drainable liquid is $\leq$10 mL, it will be added back to the solids when homogenized. If the drainable liquid is >10 mL, it will be analyzed separately.

3.3 Provide a physical description of the sample.

4.0 Quality Assurance

Work performed using this technical procedure will meet QA requirements as described in PNL-MA-70. All data generated using this procedure will be recorded on test instructions or on data sheets or directly in a Laboratory Record Book (LRB). All test instructions or data sheets will be filed in the program record files or entered into the appropriate LRB.

Changes to any of the record documents will be documented by crossing out the original information with a single line, and recording, initialling, and dating the change(s).

Battelle Pacific Northwest Laboratories	SAFE OPERATING PROCEDURE MATERIALS & CHEMICAL APPLICATIONS	PROCEDURE NO. 325-A-30 PAGE 1 OF 3

TITLE CLEANING AND SHIPPING OF WASTE TANK SAMPLERS	REVIEW BY DATE:	ISSUE DATE August 8, 1989
BUILDING - ROOM 325 BUILDING ROOM 600 300 AREA		SUPERSEDES ISSUE DATED NEW
PREPARED BY G. M. RICHARDSON Gmr	DATE 7-25-89	REVIEWED BY J. L. GREEN DATE 7/25/89

REVIEWED AND APPROVED BY

ORGANIZATION	NAME	TITLE	DATE
Section Manager		Sectn Manager	7/27/89
Safety			7-28-89
PNL Building Manager			7-25-89
Program Manager		Sr Research Scientist	7/25/89
Radiation ~~Monitoring~~ Protection		Sr. Supervisor	7-25-89
REVIEW DUE DATES →			

I. GENERAL DESCRIPTION

The purpose of this SOP is to clean, decontaminate, and return the waste tank samplers to the 200 Area.

A. Work Description

1. Cleaning of waste tank samplers.
2. Removing waste tank samplers from cell.
3. Shipping samplers to 200 Areas.
4. Removing samplers from cell shall be performed by two people with continuous RPT coverage.
5. Other SOP that applies.
    a. SOP-325-9-18 -- Cell transfer operation.
6. RWP that applies.
    a. Room 603 RWP.

B. Supplemental Equipment Required

1. Cleaning samplers.
    a. Sampler liner (2 each).
    b. Brushes for inside and outside of sampler.
    c. Micro clean solution.
    d. Clean rags.
    e. Wire to hang samplers.

2. Removing samplers from cell.
    a. Damp rags.
    b. DOT 7A type A approved PVC shipping containers.
    c. Tape.
    d. Plastic sleeving (4 in. and 6 in.).
3. Shipping of samplers to 200 Areas.
    a. Plastic sleeving.
    b. Tape.
    c. 200 Area sample truck.

II. SAFETY

A. Radiological Hazards

1. Skin contamination.
2. Inhalation of radioactive material.
3. Radiation exposure.

B. Safety Hazards

1. Tearing gloves on sharp edges.
2. Dropping sampler and shipping container.

C. Alarm Devices for Detection of Non-standard Operations

1. Area radiation alarms.
2. Tank level alarms.

D. Special Precautions

1. Exercise extreme caution when placing sampler into shipping container.
2. The spreading of contamination into the canyon.

III. PROCEDURE

A. Cleaning of Sampler

1. Place a sampler with a wire hanger attached in one of the two sampler liner, and add ~50mL of Micro Clean solution and fill liner with H_2O.

TITLE CLEANING AND SHIPPING OF WASTE TANK SAMPLERS	REVISION	SOP NO. 325-A-30
	DATE August 8, 1989	PAGE 2 OF 3

2. With wire hanger lift sampler up and brush the inside and outside of sampler.

3. Raise and lower sampler in solution to wash off solids.

4. Remove sampler from liner and secure wire hanger at other end of sampler.

5. Return sampler to solution and clean with brushes as in #2 and 3.

6. Raise sampler and rinse with H_2O.

7. Place sampler in second liner, add Micro Clean and H_2O.

8. Raise and lower sampler in solution, then lift out of solution and rise with H_2O and hang with wire hanger to dry.

B. Removal of sampler from cell

1. Tape end of 4 in. plastic sleeving and insert into PVC shipping container. Pull sleeving end over outside of container and tape.

2. Open outer door of "A" cell transfer mechanism and place a damp rag on tray. Roll tray into cell. Close outer door.

3. Place the dry sampler, valve first on tray and remove wire hanger.

4. Outer door is opened. If sampler is >3R outer door is closed and sampler is cleaned again. If <3R sampler is carefully transferred to PVC shipping container.

5. The end of plastic sleeving is taped shut, and end cap secured on the container.

6. Rag is removed from tray and RPT checks the area.

7. The PVC shipping container is placed in 6 in. plastic sleeving and taped.

C. Shipping samplers to 200 Areas

1. 200 Area sample truck is backed into trucklock to room 603.

2. The PVC shipping container is placed on truck and strapped in container rack.

TITLE CLEANING AND SHIPPING OF WASTE TANK SAMPLERS	REVISION	SOP NO.	325-A-30
	DATE August 8, 1989	PAGE 3	OF 3

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-135, LABORATORY PROCEDURE FOR HOMOGENIZATION OF SOLUTIONS, SLURRIES AND SLUDGES

APPLICABILITY

This procedure will be used to homogenize all sludges, slurries and solutions including composites prepared from previously homogenized samples.

DEFINITIONS

None

RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Analyst
- Cognizant Scientist

PROCEDURE

1.0 General Requirements

Due to the expected variability of the tank samples, the COGNIZANT SCIENTIST is responsible for selecting the method to be used for the homogenization of the sample. Several options are available, including the Omni Mixer, other mixer types, and manual methods. Procedures for several methods are provided.

The COGNIZANT SCIENTIST is responsible for preparing the test instructions to implement each step of this procedure and for supplying the analyst with the test instructions. Because of the nature and diversity of samples that will be analyzed using this procedure, the COGNIZANT SCIENTIST is responsible for assuring that the test instructions satisfy the requirements of this procedure and provide a unique sample or container identifier to insure sample traceability and control. The COGNIZANT SCIENTIST is also responsible to decide which homogenization method is appropriate for the sample.

The homogenization method used will be recorded in the appropriate Laboratory Record Book (LRB) or on the test instructions. A copy of the

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K L Scheele	7/28/89	R. E. [illegible]	7/31/89		

Procedure No.	Revision No.	Effective Date	Page	of
PNL-ALO-135	0	AUG 03 1989	1	4

test instructions will be entered into the LRB. The LRB will be supplied and maintained by the COGNIZANT SCIENTIST. The ANALYST may also record information in the LRB.

2.0 Procedure for Homogenization of Solutions

2.1 Equipment and Materials

- Teflon coated magnetic stir bar
- Variable speed magnetic stir plate

2.2 Homogenization of solutions

The primary method of homogenization of liquids will be stirring with a magnetic stir bar. The COGNIZANT SCIENTIST decides if this method provides adequate homogenization. An appropriately sized teflon coated magnetic stir bar is placed in the solution to be homogenized and the solution is placed on the magnetic stir plate. The speed of the stir plate is adjusted so that the entire solution is stirred. The duration of stirring is determined by the COGNIZANT SCIENTIST.

3.0 Homogenization with the Omni Mixer

3.1 Equipment and Materials

- Omni Mixer Assembly
- Omni Chamber Assembly

3.2 Omni Mixer Procedure

The primary method of homogenization of slurries and sludges will be mixing with the Omni mixer. The COGNIZANT SCIENTIST determines the proper Omni chamber assembly to be used for the sample based upon the size of the sample and the consistency of the sample. The COGNIZANT SCIENTIST also determines how long the sample will be homogenized and informs the analyst via test instructions as to these parameters.

The sample is transferred to the chamber filling the chamber to less than 60% of its capacity. The filled chamber is attached to the cover/rotor shaft/knife blade assembly making sure that the sample contacts the knife blade and shaft assembly. The cover is securely tightened, and the chamber assembly is attached to the motor by engaging the octagonal insert of the rotor shaft with the floating shaft of the motor. The cover is snugly screwed into the coupling adapter, and the entire Omni mixer is lowered on the support unit until the bottom of the chamber rests on the tray. The "speed" control is rotated 1 unit beyond where the knife blade begins to rotate as signified by the vibration of the chamber assembly. The sample is homogenized for the specified time as determined by the COGNIZANT SCIENTIST. At revolutions above 5000/min the chamber should be immersed in an ice bath or similar cooling vessel. Remove the entire chamber assembly from the motor before removing the cover from the chamber.

4.0 Other Procedures for Homogenization

4.1 Equipment and Materials

- Variable Speed Stirring Motor
- Glass or Teflon coated Stirring Rod
- Stainless Steel Rod
- Plastic Rod
- "Potato Masher"

4.2 Other Homogenization Procedures

The COGNIZANT SCIENTIST determines the homogenization method and time. The methods may include stirring with a stirring rod and variable speed motor, manually shaking the sample in its container, or forcing the sample through a stainless steel plate with small holes drilled in the plate.

For low viscosity slurries it may be appropriate to homogenize the slurry by stirring the solution with a stir rod and variable speed stirrer motor. The stirrer is placed in the slurry just above the bottom of the vessel and the speed of the stirrer is adjusted so that entire solution is stirred. The duration of stirring is determined by the COGNIZANT SCIENTIST. Another option is to stir the slurry using a magnetic stirrer and stir bar.

Low viscosity supernate samples may be homogenized by manually shaking the sample in its container as directed by the COGNIZANT SCIENTIST or using a magnetic stirrer and stir bar.

For high viscosity sludges, the options available to the COGNIZANT SCIENTIST include mixing with a stainless steel or plastic rod, or mixing with "potato masher". Another option is to homogenize the sample by forcing the sample through small holes drilled in a stainless steel plate or around a solid stainless steel plate that does not fill the chamber. The COGNIZANT SCIENTIST is responsible for selecting the best available method for the sample.

TITLE: PNL-ALO-136, (Replaces 7-40.67), PREPARATION OF TEST SAMPLES, BIOASSAY QUALITY CONTROL PROGRAM

1.0 APPLICABILITY

This procedure describes preparation of test samples for submission to bioassay program contract laboratories in implementation of program quality control requirements.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analytical Technician

4.0 QUALITY ASSURANCE

Special quality assurance requirements apply to certain Bioassay Quality Control Program operations:

1. RADIONUCLIDE STANDARD SOLUTIONS used in preparation of Program samples must qualify as one of the following types:

   a. DIRECTLY TRACEABLE (PRIMARY). Standards of this classification of radionuclide standard solution shall be derived by accurate gravimetric or volumetric dilution directly from a certified standard solution of that nuclide prepared and certified by NIST or a commercial or international body that participates in the USCEA/NIST Measurements Assurance Program.

      Certification documents for primary standard material shall be submitted to the Facilities and Procurement Quality Engineer for acceptance of the certification as soon as possible on receipt. Materials shall not be used until acceptance transmittal forms are received from the Facilities and Procurement Quality Engineer. Standard

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Technical Reviewer	Date	Line Mgr.	Date	Other	Date
LS Kellogg	1/27/91	LR Greenwood	1/30/91	All original signatures on file	

solutions derived from certified standard solutions shall be prepared using accepted laboratory techniques; preparation data shall be fully documented in a Laboratory Record Book.

b. INDIRECTLY TRACEABLE (SECONDARY). Standards of this classification are radionuclide solutions prepared from source materials of demonstrated isotopic purity that are not necessarily themselves directly traceable standards. Indirect traceability is established by comparison with a directly traceable certified solution or source of the same nuclide using an appropriate analytical measurement device and accepted measurement procedures. The Program cognizant scientist is responsible for evaluation of the measurement technique and statistical analysis of the resulting data. Preparation and calibration of this class of standard materials shall be fully documented in a Laboratory Record Book.

2. MICROPIPETTES used in preparation of program samples are reserved for exclusive use in the program and shall meet one of the following qualifications:

   a. CALIBRATED GLASS MICROPIPETTES are glass pipettes of 10 ul to 5000 ul capacity that are specially calibrated using mercury (10 ul through 900 ul capacity range) or ultra-high purity water (1000 μl through 5000 μl capacity range) and accepted techniques for the calibration of volumetric glassware.(1) At least 3 independent measurements shall be performed; standard deviation of the data shall not exceed 0.1% of the calculated average volume for pipettes smaller than 250 ul, 0.04% for larger pipetter. Calibration of this micropipette class shall be fully documented in a Laboratory Record Book. The pipettes shall be inspected for chipping of the beveled tip before each use, otherwise the initial calibration value remains valid until a pipette is physically damaged.

---

(1) Testing of Glass Volumetric Apparatus, U. S. Bureau of Standards Circular No. 602, Washington, D.C.

Practice for Calibration of Volumetric Ware, ASTM Specification E-542-85.

Specification for Volumetric Flasks, ASTM Specifications E-288-83.

b. UNCALIBRATED GLASS MICROPIPETTES are glass pipettes of 10 ul to 5000 ul capacity that meet Micropipette Sampling Inspection Program (July 1957) requirements but are not individually calibrated. Acceptance is based upon measurement of a statistical sample of a lot of pipettes of a given size. The statistical uncertainty in the calibration value used in the calculation of sample activity is determined as equal to the allowable tolerance in the specifications for that size pipette.

c. ADJUSTABLE AUTOMATIC PIPETTES are digitally presetable pipettes with disposable tips. Only pipettes of 10 ul through 100 ul range, and 100 ul through 1000 ul range that are setable to four significant figures in step units of the least significant figure shall be used in the program. These pipettes shall be qualified as operating within manufacturers specifications before use in preparation of a Program sample set by weighing pipetted aliquots of mercury or water, as appropriate to the aliquot size, one measurement at a value within 10% of the minimum setable aliquot and one measurement within 10% of the maximum setable aliquot in size. Statistical uncertainty of a pipetted aliquot used in calculation of sample activity is determined as a linear function of the manufacturers stated accuracy at the minimum and maximum useful settings (refer to Appendix 3). A pipette qualifies for use if the two pipetted test aliquots lie within the uncertainty of the respective aliquots pipette settings. Qualification data shall be recorded on the work copy of the sample preparation instructions.

3. WEIGHINGS shall be performed on a semi-micro analytical balance (adjustable micropipette qualification) and a 3 KG top-loading balance (urine aliquot weighing). Both instruments shall be qualified before use by verifying the weight of the designated reference weight, 100 milligrams and 2 KG, respectively. Results of qualification tests shall be recorded on the test forms maintained at each balance.

5.0 PROCEDURE

5.1 Discussion

The Bioassay Quality Control Program governs the preparation of bioassay test samples for submission to contract laboratories. The purpose of these samples is to implement program quality control requirements through generation of analytical performance data.

The Health Physics Section of Pacific Northwest Laboratory is responsible for administration of bioassay program analytical service contracts. Requests for test sample preparation are transmitted to the Analytical Chemistry Laboratory Department (ACL) in a specification letter; the letter is accompanied by appropriate containers for the completed test samples and an amount of "blank" urine sufficient for their preparation unless other arrangements have been previously agreed upon. Completed test samples are returned to the Health Physics Section together with complete documentation of the preparations.

The laboratory cognizant scientist or designated analytical technician shall generate written instructions for preparation of test samples in accordance with letter specifications. Although instructions can be prepared manually using data extracted from Standards Laboratory records and data files, this is most easily accomplished by means of the bioassay data processing program titled BAQC, a MicroVax computer system based program written in BASIC language and developed specially for this purpose. The output of the BAQC computer program is a detailed set of instructions for direct use in laboratory preparation that also serves as the required transmittal documentation that must accompany the completed test samples. At least two (2) copies of the documentation are printed: one to accompany the test samples on transmittal and another for retention in laboratory records. Detailed instructions in execution of the BAQC program is provided in Appendix 1 of this procedure.

5.2 Apparatus

Semi-Micro balance, 1 kg capacity (used for automatic pipette qualification tests)
Pan Balance, 3 kg capacity
Beakers, 4 liter capacity
Graduated cylinders, 500 milliliters and 250 milliliters capacity
Eppendorf automatic pipetters, adjustable, 10-100 ul and 100-1000 ul ranges
Micropipettes, glass, assortment of available sizes, 10 ul through 5000 ul
Plastic droppers
Teflon covered magnetic stirring bar, 1 inch or larger

5.3 Procedure

NOTE: TO PREVENT POSSIBLE RADIONUCLIDE CONTAMINATION, BIOASSAY TEST SAMPLES ARE PREPARED IN LABORATORY SPACE RESERVED FOR NONRADIOACTIVE OPERATIONS; APPARATUS IS RESERVED FOR BIOASSAY TEST SAMPLE PREPARATIONS ONLY. GLOVES ARE WORN DURING PREPARATIONS PRIMARILY AS BIOLOGICAL INFECTION PROTECTION; BIOASSAY TEST

SAMPLES ORDINARILY CONTAIN ONLY SUBTRACE AMOUNTS OF RADIONUCLIDE ACTIVITY

Step 1: Instructions will specify preparation of either an individual sample or a pool containing a stated number of samples at a specified individual weight plus a small excess. If instructions indicate the preparation is an individual sample in a single container, place a teflon-covered stirrer in that container, place on a 3 KG capacity balance, tare to zero weight, and proceed to prepare the sample directly in that container. If the preparation is an individual sample to be distributed into more than one container or is a pool of two or more individual sample components, place a teflon-covered stirring bar in a 4 liter capacity beaker and tare to zero weight on a 3 KG capacity balance.

Step 2: Weigh the total amount of "blank" urine specified in the instructions for the preparation into the container on the balance by pouring "blank" urine into the container to within 5 grams of the desired amount. Remove any foam or allow it to disperse, then carefully dry any liquid from the upper container walls using an absorbent tissue, and finally adjust to exact weight by "blank" urine addition or removal with a plastic dropper.

The capacity of the 3 KG balance may be exceeded if certain sample pools are prepared literally according to letter specifications:

If three samples are to be prepared as a pooled preparation, and the individual pool components are specified as 1000 grams each, balance capacity would be exceeded when a small excess is included. In such cases weigh exactly 3000 grams "blank" urine into the beaker, increase the tare to decrease the displayed weight by the amount of excess specified, and finally add more "blank" urine until 3000 grams displayed weight is obtained.

If a large enough number of individual pool components are specified such that the total weight exceeds the tare capacity of the 3 KG balance, prepare the pool at 500 grams "blank" urine each (or some other useful fraction of the requested amount) plus all the specified excess, then weigh the remainder of the requested weight as "blank" urine into each of the individual components after they are separated from the pool.

Step 3: Place the container with the weighed "blank" urine on a magnetic stirrer in a hood and adjust stirring speed to provide a maximum stirring vortex without generating foam. Accurately pipette the amount of each BAQC radionuclide standard solution specified in the instructions for the preparation into the container, rinsing the pipette three or four times with the contents of the container. Use an Eppendorf adjustable automatic pipetter of the appropriate range or a glass micropipette, as specified in the instructions; use of a pipette other than the type directed will invalidate the uncertainty values stated for nuclide activities on the transmittal report. Automatic pipettes shall be qualified before use. (Refer to Section 4.0, 2.c)

If the preparation is an individual sample, return the container to the 3 KG capacity balance, and proceed to Step 5.

Step 4: Place one or more of the provided containers, as specified for each individual sample or individual pool component in the specification letter, on the 3 KG balance and tare to zero weight. Weigh the test sample urine into the container(s) by pouring to within 5 grams of the required amount and finally adjusting to exact weight by addition or removal with a plastic dropper. If more than one container is specified the division between them is arbitrary. Any urine removed from the container(s) is returned to the beaker containing the test sample pool. Return the beaker to the stirrer.

Step 5: If the specification letter requests the addition of water to each individual sample or individual pool component, fill a graduated cylinder with slightly less distilled water than specified in the instructions, add it to the sample container(s), and then continue addition of distilled water with a plastic dropper to achieve the exact weight of water addition required. If more than one container is specified the division of the water between them is arbitrary, but do not dilute one container excessively compared to the other.

Step 6: If the preparation is an individual sample, remove the stirring bar and proceed to Step 7. If the preparation is a pool, repeat Steps 4 and 5 for each of the component samples of the pool. When all the component samples have been separated from the pool, the small remaining excess test sample is ordinarily discarded as waste urine. The beaker and the stirring bar must be thoroughly washed and dried between each additional preparation and before storage.

Step 7: Securely cap each container and apply the appropriate label. Preprinted labels are supplied by the Health Physics Section.

Step 8: Assemble all test samples together in a box, enclosing one copy of the preparation documentation. The second copy of the documentation shall be initialed by the technician, stapled to the specification letter, and filed with Bioassay Quality Control Program records.

Completed test sample sets shall be surveyed by a Radiation Protection Technician for release and shall be removed from the control zone to await transfer to the Health Physics Section.

Excess urine is discarded to the sanitary sewer.

5.4 Calculations

When the MicroVax based BAQC program is used to generate the laboratory instructions for a set of test samples, necessary data for Bioassay Quality Control Program nuclide standard solutions are retrieved from program data files, the required calculations performed, and the results printed to the output report. Since all data, excepting desired nuclide activity, is internal to the computer program, printed activities are always equivalent to the printed aliquot size. The output report shall be proofread to assure that the printed activities meet the specifications of the request letter. Useful nuclide standard solution data, pipette uncertainties, and selected intermediate calculation results such as decay interval are included so that all data necessary for verification by manual calculation is documented.

If the BAQC program is not used, radionuclide standard solution data shall be obtained from Standards Laboratory records; the instructions compiled by manual calculation, and the documentation manually generated using standard radiochemical calculation techniques. For convenience, data relating to uncertainties in pipetting are included in Appendices 2 and 3 of this procedure.

APPENDIX 1

THE BAQC BIOASSAY DATA PROCESSING PROGRAM - MICROVAX SYSTEM BASED

The MicroVax system based BAQC program is modular in structure; it incorporates one operations unit (BAQC.EXE), one sample data processing unit (BAPRO.EXE), one standard nuclide data management unit (BASTD.EXE), two standard nuclide data printout utility units associated with the standard nuclide data management unit (PRSTD.EXE and PRINDX.EXE), and standard nuclide data file (BASTD.DAT), and a standard nuclide index file (BAINDX.DAT). The functions and structural relationships of the various module units are illustrated in the program flow chart (Figure 1).

A NOTE ABOUT ERRORS IN INPUT

The BAQC program is written in MicroVax basic. Since this is a compiled language, an executable program can only be accessed at the beginning. In the event of error, it is not possible to exit from the program and then re-enter at an earlier point that will allow previously input data to be changed.

> If you detect an error in input response to a program prompt BEFORE THE RETURN KEY IS PRESSED, use the delete key to remove characters backward through the error, re-enter the remainder of the input correctly, and then press RETURN.
>
> If you detect an error in input AFTER THE RETURN KEY IS PRESSED, enter CONTROL C followed by a RETURN to abort program execution. When the DCL $ prompt is returned to the terminal screen, restart the program in the usual manner. All data must be re-entered from the beginning.
>
> If some action causes the program to fail, as indicated by the replacement of the flashing solid square prompt by the system $ prompt or by the printing of an error message to the terminal screen, proceed as follows:
>
> 1. Try to recover by pressing RETURN. In many cases the flashing square prompt will return and the data may be re-entered.
> 2. If this fails, proceed as above for AFTER THE RETURN KEY IS PRESSED.

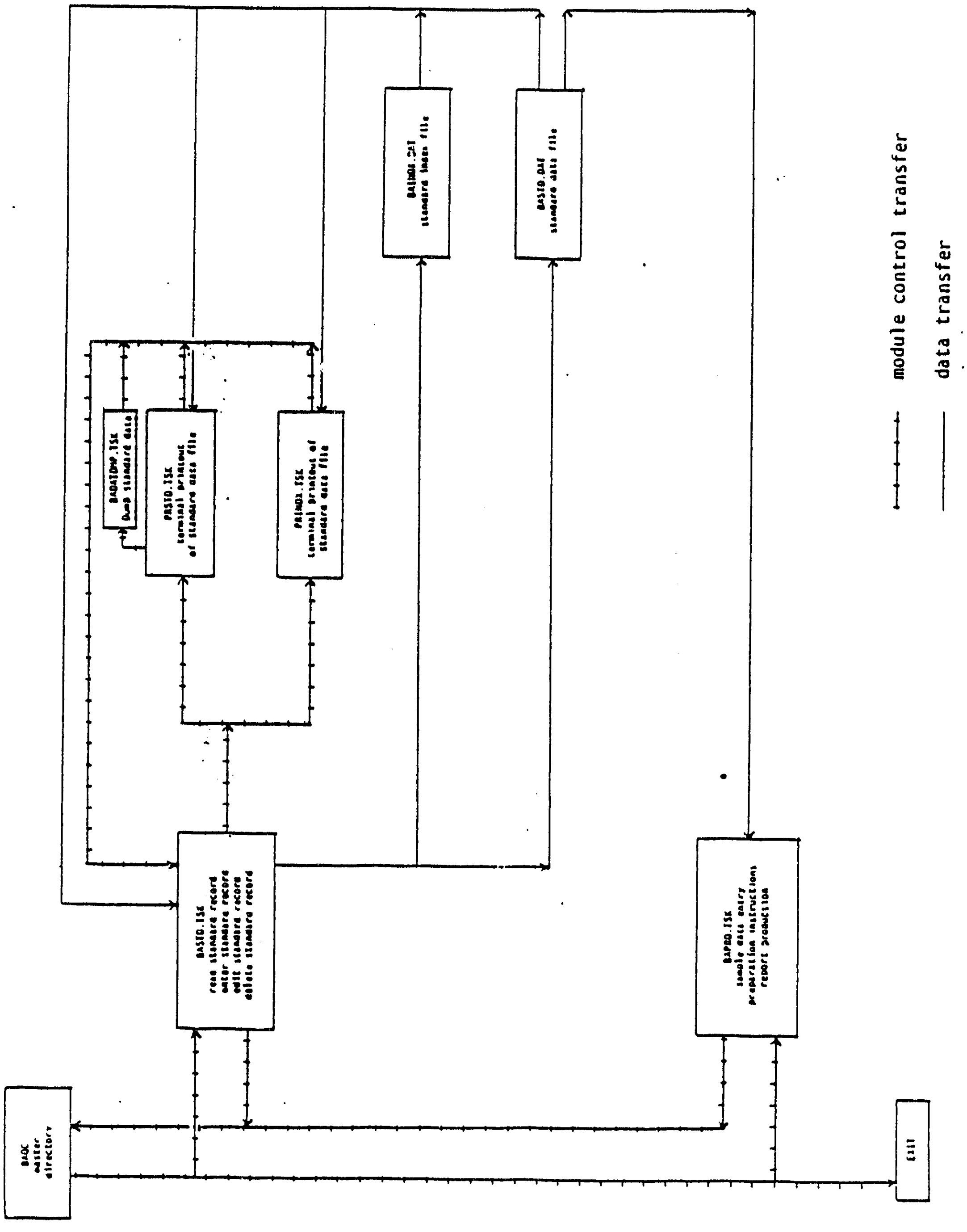
BAINDX.DAT
standard index file
BASTD.DAT
standard data file
BADATDMP.TSK
Dump standard data
PASTD.TSK
terminal printout
of standard data file
PRINDX.TSK
terminal printout of
standard data file
BASTD.TSK
read standard record
enter standard record
edit standard record
delete standard record
BAPRO.TSK
sample data entry
preparation instructions
report production
BAQC
master
directory
Exit
module control transfer
data transfer

Figure 1

This type of failure is most commonly caused by entry of data before the input from the proceeding prompt has been processed and the next prompt printed to the terminal screen, or by pressing a control key inadvertently. The BAQC program is designed to detect DATA TYPE errors and will reprompt if this sort of entry is made instead of aborting the program.

RUNNING THE BAQC PROGRAM

The BAQC program can be run from any terminal of the MicroVax system. Printed output is directed to the device designated as TXA3, currently the LaserJet Series II printer located in Room 300.

The LaserJet II is usually set to 60 lines per page form length. A maximum of 71 lines may be printed on a 8.5 x 11 inch page by changing the form length setting on the printer. A 60 line form length is generally adequate for most BAQC operations through you may want to increase the number of lines printed per page if only one or two lines appear on the last page of printout.

Before beginning any BAQC program operations that involve printing, check to verify that the printer power switch is ON, that the printer status is displayed as READY, that the printer paper tray contains paper, and that the printer is NOT set for MANUAL PAPER FEED. If these conditions are not met, printing is not possible, printing data will accumulate in the print buffer until it is full, and execution of the BAQC program will halt until the problem is corrected and the buffer contents are printed out.

All BAQC program module units are currently stored on MicroVax system disk DUBO under user identification code (UIC) 200,3. To execute the problem successfully, these two quantities must be set as defaults. Consult the MicroVax System Manager to obtain a SIGN ON CODE and a PASSWORD that will automatically set these requirements.

When a successful sign on has been accomplished and the system $ prompt is printed to the terminal screen, run the BAQC program by entering RUN BAQC followed by a <CR>.

BAQC PROGRAM OPERATIONS MENU

The operations menu is the directory unit of BAQC program; from it all operational modules can be accessed. All of the modules provide return to the OPERATIONS MENU when their execution is completed. Four numbered options are available:

1. PRODUCE BIOASSAY STANDARDS DATA REPORT processes data for the bioassay test samples that are to be produced, prompts selection of radionuclide standards from among those available in the bioassay standard nuclide data file, and prints a report that includes instructions for preparation of the individual test

samples together with their calculated component radionuclide activities. This report also serves as a transmittal document for the test samples.

2. READ AND EDIT BIOASSAY STANDARDS DATA FILE performs read, entry, edit, and delete operations upon the radionuclide standard data in the standards data file BASTD.DAT. Printout of the entire contents of this standards data file and of the standards index file BAINDX.DAT are also provided.

3. GENERATE RANDOM H20 ADDITION VOLUMES generates random numbers between 100 and 500 that are multiples of five. This option is used to generate truly random volumes of water that are sometimes added to test samples.

4. TERMINATE PROGRAM terminates program execution and returns the terminal to DEC Control Language (DCL) level.

Enter the NUMBER of the selected option, followed by a <CR> to execute the specific task.

If the program is terminated by selecting Option 4, TERMINATE PROGRAM, when the system DCL $ prompt appears on the terminal screen sign off the computer by entering LO (LOGOFF) followed by a <CR>.

1. PRODUCE BIOASSAY STANDARDS DATA REPORT

Selection of the PRODUCE BIOASSAY STANDARDS REPORT option from the OPERATIONS MENU begins execution of the bioassay standards preparation module BAPRO.TSK. Three information groups are involved in processing data for a bioassay standard sample preparation:

1. Program parameters that remain in effect during the entire current execution of the module. Report date, the reference date to which all radionuclide activities are decay corrected, and the signature to appear on the printed report are parameters of this type. Once entered, these quantities can be changed only by exiting from and then re-entering the BAPRO.EXE module.

2. Parameters specific to the current bioassay standard sample. Whether an individual sample or a pool that is to be subsequently divided into a group of samples is to be prepared, serial numbers and other sample labels, and sample size, are parameters of this type.

3. Nuclide data identifying the individual radionuclides to be introduced into a bioassay standard, the desired activity of each, and the selected radionuclide standard and aliquot to meet these specifications, are data of this type.

All bioassay standard samples to appear on the current report are entered; the input data is then processed and an analytical report is printed. Additional copies of the report may be optionally produced.

Bioassay standard samples are prepared to meet specifications issued by the PNL Health Physics Department. These specifications are issued in the form of a request letter, that is delivered to the laboratory together with the "blank" urine and bioassay sampling containers to be used in standard samples preparation.

ENTER REPORT DATE

This report date is printed as part of the report heading. Enter the date, followed by a <CR>. All printable characters, including the comma, are allowed. The suggested format is March 18, 1988.

ENTER REFERENCE (DECAY CORRECTED) DATE

Input of the MONTH, DAY and YEAR to which radionuclide activity is to be decay corrected are prompted in sequence. This reference date is the date specified for bioassay standard sample pickup in the request letter, unless otherwise specified. In response to each prompt enter the appropriate NUMERIC data, followed by a <CR>. Month must be entered numerically (JAN=1 ... DEC=12). Year may be entered in either full (1987) or short (87) form. Entry of alphabetic characters will result in input error.

ENTER THE NAME OF REPORT SIGNATOR

This is the name that is printed at the end of the report. Enter the appropriate name using an AB Smith format, followed by a <CR>. Entry of a <CR> only will cause the default signator, MR WEILER to be printed. The organization, CHEMISTRY & ANALYSIS, and Company, PACIFIC NORTHWEST LABORATORY, are automatically printed following the signator.

IS A GROUP OF SAMPLES TO BE PREPARED AS A POOL?

Bioassay standard samples may be prepared by two methods: (1) as single standards prepared individually; or (2) as sets of standards prepared as a single large aliquot or "pool" that is subsequently separated into the individual standard samples of the set. A maximum of 20 single standards and pool is allowed. When prompting begins for the 20th sample or group YOU ARE ENTERING THE

20TH AND LAST ALLOWED SAMPLE OR GROUP will be printed to terminal screen.

Enter Y, followed by a <CR>, if the request letter indicates the current samples are elements of a pool.

Enter N, followed by a <CR>, if pooled samples are not specified by the request letter.

Any entry other than Y or N will cause INVALID ENTRY to be printed to the terminal screen and the prompt to be repeated.

ENTER THE GROUP DESIGNATION

This is a label, usually consisting of a single alphabetic character, specified in the request letter, to apply to all samples derived from a given pool preparation. Enter the specified label, followed by a <CR>.

ENTER THE NUMBER OF SAMPLES (MAXIMUM 10 ALLOWED) IN THE GROUP

This is the number of individual samples that are to be derived from a given pool preparation. Total the number of samples in the request letter for which the current GROUP DESIGNATION is specified and enter this total, followed by a <CR>. Entries other than the integers 1 through 10 will cause INVALID RESPONSE to be printed to the terminal screen and the prompt to be repeated.

ENTER THE WEIGHT (GRAMS) OF [EACH] SAMPLE

Bioassay standards are prepared by weight rather than volume because the volumes are awkwardly large to handle with laboratory scale equipment, making weighing more accurate and convenient. Although the request letter may state the sample amount in liters, preparation is always performed on a weight basis assuming the density of the final standard sample is 1.00 grams per milliliter.

Enter a sample weight in GRAMS equal to the number of milliliters samples requested, followed by a <CR>.

ENTER THE EXCESS WEIGHT (GRAMS) OF POOL TO BE PREPARED

This prompt appears only if a Y response was entered to the IS A GROUP OF SAMPLES TO BE PREPARED AS A POOL? prompt. A slight excess of pool standard, usually 25 grams, is prepared to accommodate losses due to wetting of the mixing container and to simplify subsequent division of the pool into individual samples. That portion of the excess remaining after separation of the component standards is discarded.

Enter this excess, expressed in grams, followed by a <CR>.

The program now prompts input of the sample serial number and other labels. This data is printed together as a single line of header for the sample on the printed report. If the preparation is a pool sample, lines of each sample derived from the pool will be printed together as a group. The prompts will be repeated in sequence for each sample to be derived from a pool, each sequence of prompts labeled with a pool sequence number.

ENTER THE SAMPLE SERIAL NUMBER

Enter the serial number of the current sample in the exact format given in the request letter, followed by a <CR>. The length of a serial number is limited to 10 characters; entry of more than 10 characters will cause LIMIT LENGTH TO 10 CHARACTERS to be printed to the terminal screen and the prompt repeated.

ENTER THE SAMPLE PERSONNEL NAME

The name of an individual who has a record in Hanford Project dosimetry files may be specified in the request letter for each BLIND AUDIT sample. Enter the NAME followed by a <CR>. If the sample is not a blind audit sample and no alternate label is given in the request letter, enter only a <CR>. The entry is limited to 15 characters; entry of more than 15 characters will cause LIMIT LENGTH TO 15 CHARACTERS to be printed to the terminal screen and the prompt to be repeated.

ENTER ANY ADDITIONAL COMMENT

This entry allows up to 19 characters of additional note text to be added to a sample data header line. Water or other diluent added to a sample after preparation to disguise its amount is typically entered here. You may generate truly random amounts of water between 100 ml and 500 ml in magnitude in increments of 5 ml by running the GENERATE RANDOM H2O ADDITION VOLUMES (menu option 3) before beginning this report production. Enter the comment, followed by a <CR>. Entry of more than 19 characters will cause LIMIT LENGTH TO 19 CHARACTERS to be printed to the terminal screen and the prompt to be repeated.

WILL AN AUTOMATIC ADJUSTABLE PIPETTE BE USED TO PERFORM ALL NUCLIDE ADDITIONS?

Radionuclides may be added to bioassay standard samples using either calibrated glass micropipettes, uncalibrated glass micropipettes, fixed volume automatic pipettes, or adjustable automatic pipettes. Since the amount of nuclide specified for a sample is likely to require a volume of a radionuclide standard solution that does not correspond to a glass micropipette or fixed volume automatic pipette standard size, only an adjustable automatic pipette allows specified nuclide activity to be almost exactly approximated. Accuracy data for Eppendorf adjustable automatic pipettes of 2 ul-10 ul, 10 ul-100 ul, and 100 ul-1000 ul range is incorporated in this data processing module. The accuracy calculations are given in Appendix 3.

If an Eppendorf adjustable automatic pipette with one of the ranges specified above is used for all nuclide standard additions, enter Y followed by a <CR>. It is assumed that the pipette will be set to deliver the exact amount stated in the option selected from the NUCLIDE STANDARD ALIQUOT OPTION TABLE for each nuclide. A corresponding aliquot uncertainty is automatically calculated.

If glass micropipettes, fixed volume automatic pipettes, or adjustable automatic pipettes of other than Eppendorf manufacture are to be used, enter N followed by a <CR>. You will be prompted for input of the pipetted amount and the estimated accuracy at a later point.

Any entry other than Y or N will cause INVALID ENTRY to be printed to the terminal screen and the prompt to be repeated.

ENTER NUCLIDE

The request letter states specifications for the radionuclides to be present in each standard sample. Enter the code for the nuclide to be added to the current bioassay standard sample, followed by a <CR>. The natural uranium code is U[NAT]; all other nuclide codes are formatted as the chemical symbol followed by a hyphen and the mass number i.e., PU-239.

ENTER DESIRED ACTIVITY

Enter the activity specified for the current nuclide in the request letter, followed by a <CR>. Be sure to express this activity in the units stated in the prompt: U[NAT] in UG/SAMPLE, H-3 in DPM/GRAM SAMPLE, and all others in DPM/SAMPLE.

A table listing options for making the current nuclide addition is printed to the terminal screen.

The radionuclide data file BASTD.DAT is searched for standard solutions for which the current nuclide is listed as the principal nuclide, and the amount of each standard required to meet the activity specification is calculated. Serial number and the calculated amount for each nuclide standard solution are printed to the terminal screen as a table of consecutively numbered options.

If no nuclide standard record exists in the data file with the current nuclide listed as the principal nuclide, NO STANDARD OF THIS NUCLIDE AVAILABLE is printed to the terminal screen in place of the table, entry of the current nuclide is aborted, and the program options entry of another nuclide. Verify that the current nuclide was entered using the correct code format, and if not, enter it again correctly.

Select a listed option from the table using the following criteria priority:

1. Specified volume is at least 25 ul but less than 500 ul.
2. Specified volume is 10 ul to 25 ul or 500 ul to 1000 ul.
3. Specified volume is 2 ul to 10 ul or 1000 ul to 2000 ul.

Enter the number of the selected option, followed by a <CR>. If none of the options listed meet any of the above criteria, usually you should abort entry of the current nuclide by entering 0 followed by a <CR>. The IS THERE ANOTHER NUCLIDE TO BE ADDED prompt will be returned to the terminal screen. This abort option may also be used if an error has been made in entry of nuclide code or desired activity; the nuclide entry is then repeated from the beginning.

Any entry other than an integer within the range of the offered choices will cause INVALID ENTRY to be printed to the terminal screen and the prompt to be repeated.

If Y was entered in response to the WILL AN AUTOMATIC ADJUSTABLE PIPETTE BE USED TO PERFORM ALL NUCLIDE ADDITIONS? prompt, the pipette shall be set to deliver EXACTLY the amount stated in the option selected when the sample is prepared.

If N was entered in response to the WILL AN AUTOMATIC ADJUSTABLE PIPETTE BE USED TO PERFORM ALL NUCLIDE ADDITIONS? prompt, the ENTER ALIQUOT [UL] OF NUCLIDE STANDARD TO BE ADDED prompt will be printed to the terminal screen.

Enter the aliquot, expressed in ul, selected from available pipettes to approximate the calculated amount of the selected option as closely as possible, followed by a <CR>. Multiple pipettings may be used and the sum entered here.

ENTER ESTIMATE OF UNCERTAINTY IN THE ALIQUOT

Enter an estimate of the uncertainty, expressed in ul, followed by a <CR>. If a calibrated or uncalibrated glass micropipette is used, obtain the estimate from the table in Appendix 2. The uncertainty of a multiple pipetting is calculated as the square root of the sum of the squares of the individual pipette uncertainties.

The ENTER ESTIMATE OF UNCERTAINTY IN THE ALIQUOT PROMPT also appears if the volume entered at the ENTER ALIQUOT [ul] OF NUCLIDE STANDARD TO BE ADDED prompt is greater than 1000 ul or less than 2 ul.

IS THERE ANOTHER NUCLIDE TO BE ADDED?

Enter Y, followed by a <CR>, if the request letter specified an additional nuclide for the current bioassay sample or sample set. The Y response is also used to re-enter a nuclide when the initial attempt was aborted due to the input error.

Enter N, followed by a <CR>, if all the specified nuclides have been entered.

Any response other than Y or N will cause INVALID ENTRY to be printed to the terminal screen and the prompt to be repeated.

DO YOU WISH TO ENTER MORE SAMPLES?

Enter Y, followed by a <CR>, if you wish additional samples to appear on the current report. The entry of an additional sample will be initialized and the IS A GROUP OF SAMPLES TO BE PREPARED AS A POOL prompt will be returned to the terminal screen.

Enter N, followed by a <CR>, if you have entered all the samples specified by the request letter or if you wish any further samples to appear as a separate report.

Any entry other than Y or N will cause INVALID RESPONSE to be printed to the terminal screen and the prompt to be repeated.

At this point REPORT PRINTOUT IN PROGRESS is printed to the terminal screen and output of the report containing the data entered for the current set of individual samples and groups is directed to the device designated as TXA2: by the system.

When printout is complete, REPORT PRINTOUT COMPLETE is printed to the terminal screen. Inspect the printed output. If the printed activity value for any radionuclide is not close to the value requested in the request letter, an error was made in data input at the ENTER DESIRED ACTIVITY prompt for that nuclide and the entire report production process shall be repeated.

DO YOU WISH TO PRINT ANOTHER COPY OF THIS REPORT [Y OR N]?

Enter Y, followed by a <CR>, if you wish an additional copy of the current report printed. This prompt is repeated after each printout so that any number of copies may be produced.

Enter N, followed by a <CR>, if no additional copies are required. The BAQC PROGRAM OPERATIONS MENU is returned to the terminal screen.

Any response other than Y or N will cause INVALID ENTRY to be printed to the terminal screen and the prompt to be repeated.

2. READ AND EDIT BIOASSAY STANDARDS DATA FILE

Data relating to radionuclide standards intended for use in preparation of bioassay program samples is contained in the BASTD.DAT data file. Each nuclide standard has one or more data records in that file - one record for each component nuclide in the standard for which activity data exists. Each record contains the serial number and principal nuclide of the nuclide standard together with the nuclide of the current record, its activity, its half life, and its reference date. Each record also contains a component number and the total number of components in that nuclide standard for which records exist. The record for the nuclide corresponding to the principal nuclide of the nuclide standard solution has a component number equal to 1. This file structure enables the program to automatically calculate and document multiple components or impurities present in a nuclide standard solution.

A nuclide standard solution index file, BAINDX.DAT, containing standard solution serial numbers and their respective index number, functions in some BASTD.DAT data management operations. The sole function of the index is to allow listing of nuclide standard solution in atomic number - mass number order. A nuclide standard must be indexed or it will not be listed during execution of Options 1 and 6 of the BIOASSAY PROGRAM NUCLIDE STANDARD DATA menu. BAINDX.DAT is not involved in data transfer between BASTD.DAT and the BAPRO.TSK module.

The BIOASSAY PROGRAM NUCLIDE STANDARD DATA menu is printed to the terminal screen. Seven numbered options are available:

1. READ THE DATA FILE prints the data for a specific nuclide standard serial number to the terminal screen, or optionally, lists data for all INDEXED nuclide standards in the BASTD.DAT data file on the printer.
2. ENTER A STANDARD RECORD allows entry of a nuclide standard solution into the BASTD.DAT data file.

3. EDIT A STANDARD RECORD allows changes to be made in the NUMERIC data contained in the file records for a specific serial numbered standard nuclide solution.

4. DELETE A STANDARD RECORD allows deletion of ALL records for a specific serial numbered standard nuclide solution from the BASTD.DAT data file.

5. TERMINAL PRINTOUT OF STANDARD DATA FILE prints to the terminal screen a listing, ordered in atomic number - mass number sequence and in a compressed format, or the INDEXED records in the BASTD.DAT data file. An unordered dump of ALL the records existing in the BASTD.DAT data file is optionally available.

6. TERMINAL PRINTOUT OF STANDARD INDEX FILE prints a sequential listing of INDEX NUMBERS, together with corresponding nuclide standard serial numbers and principal nuclides, to the terminal screen.

7. RETURN TO BIOASSAY PROGRAM OPERATIONS MENU transfers control to the BAQC.TSK program module and returns the OPERATIONS MENU to the terminal screen.

Enter the NUMBER of the selection option, followed by a <CR>, to execute the specific task. Any entry other than the integers 1 through 7 will cause INVALID RESPONSE to be printed to the terminal screen and the prompt to be repeated.

1. READ THE DATA FILE

   Selection of the READ THE DATA FILE option from the NUCLIDE STANDARDS DATA menu causes the NUCLIDE STANDARD DATA REVIEW menu to be printed to the terminal screen. Three numbered options are available:

   1. DISPLAY A SPECIFIC STANDARD ON TERMINAL SCREEN enables a data record for a specified nuclide standard to be printed to the terminal screen.

   2. OUTPUT ENTIRE DATA FILE TO PRINTER enables ALL INDEXED nuclide standard records in the BASTD.DAT data file to be outputed to the printer.

   3. RETURN TO NUCLIDE STANDARD DATA MENU causes that menu to be returned to the terminal screen.

   Enter the NUMBER of the selected option, followed by a <CR>, to execute the specific task. Any entry other than an integer 1 through 3 will cause INVALID RESPONSE to be printed to the terminal screen and the prompt to be repeated.

1. DISPLAY A SPECIFIC STANDARD ON THE TERMINAL SCREEN

ENTER SERIAL NO. OF NUCLIDE STANDARD

Enter the SERIAL NUMBER of the nuclide standard for which you wish to review the data record, followed by a <CR>. If you do not know the serial number, use Option 7 of the NUCLIDE STANDARD DATA menu, TERMINAL PRINTOUT OF STANDARD DATA FILE, instead.

The serial number and principal nuclide are printed, together with nuclide, reference date, activity, activity uncertainty, half life, and half life uncertainty, for EACH COMPONENT NUCLIDE of the designated standard.

If the amount of data exceeds the current display page, as indicated by the pagination label in the upper right of the display, you will be prompted to enter a <CR> to continue to additional pages of data.

If you enter a serial number that does not correspond to a record in the data file, UNRECOGNIZED SERIAL NO. ENTERED will be printed to the terminal screen. Entry of a <CR> will cause the NUCLIDE STANDARD DATA REVIEW menu to be returned to the terminal screen.

DO YOU WISH TO REVIEW ANOTHER STANDARD?

Enter Y, followed by a <CR>, to review another data record. The ENTER SERIAL NO. OF NUCLIDE STANDARD prompt is returned to the terminal screen.

Enter N, followed by a <CR>, if no more data records are to be reviewed. The NUCLIDE STANDARD DATA menu is returned to the terminal screen.

Any entry other than Y or N will cause INVALID RESPONSE to be printed to the terminal screen and the prompt to be repeated.

2. OUTPUT ENTIRE DATA FILE TO PRINTER

This option outputs ALL INDEXED records in the BASTD.DAT data file to the printer in INDEXED sequence (atomic number - mass number order); any UNINDEXED records existing in the data file are ignored. Serial number and principal nuclide are printed, together with nuclide, reference date, activity, activity uncertainty, half life, and half life uncertainty for EACH COMPONENT NUCLIDE present in EACH NUCLIDE STANDARD. BIOASSAY PROGRAM NUCLIDE STANDARD SUMMARY COMPLETED is printed at the end of the listing and the NUCLIDE STANDARD DATA menu is returned to the terminal screen.

3. RETURN TO NUCLIDE STANDARD DATA MENU.

This option returns the NUCLIDE STANDARD DATA menu to the terminal screen.

2. ENTER A STANDARD RECORD

Selection of the ENTER A STANDARD RECORD option from the NUCLIDE STANDARDS DATA menu allows records for a new nuclide standard to be entered into the BASTD.DAT data file and to be indexed in the BAINDX.DAT data file. A nuclide standard must be indexed before it can be listed by the READ THE DATA FILE- OUTPUT ENTIRE DATA FILE TO PRINTER or the TERMINAL OUTPUT OF STANDARD DATA FILE-INDEXED STANDARDS ORDERED IN INDEX SEQUENCE operations. Indexing is not involved in the READ THE DATA FILE- DISPLAY A SPECIFIC STANDARD ON THE TERMINAL SCREEN operation, nor in nuclide standard data transfer during PRODUCE BIOASSAY STANDARDS DATA REPORT operations.

Input of nuclide standard identification data is prompted first:

STANDARD SERIAL NO.

Enter the SERIAL NUMBER of the nuclide standard, followed by a <CR>. Serial numbers may consist of up to six (6) alpha-numeric characters, usually formatted as single alphabetic character followed by a hyphen and numeric characters. Entry of more than six (6) characters will cause the prompt to be repeated.

PRINCIPAL NUCLIDE

Enter the nuclide contained in the current standard for which the standard is named. In a standard containing multiple components or impurities, this is usually the nuclide highest in activity. Nuclide format consists of the chemical symbol followed by a hyphen and the mass number, excepting natural uranium which is formatted as U[NAT]. Six (6) characters maximum are allowed; entry of more than six (6) characters will cause the prompt to be repeated.

Input of data for the first component nuclide is now prompted. The sequence is repeated for each additional component nuclide present in the nuclide standard.

NUCLIDE

Enter the current nuclide, using the format described above, followed by a <CR>. If this is the FIRST nuclide entered for the current nuclide standard, the PRINCIPAL NUCLIDE is entered at this point. Six (6) characters maximum are allowed; entry of more than six (6) characters will cause the prompt to be repeated.

REFERENCE DATE

Input of the MONTH, DAY, and YEAR to which the current nuclide activity is referenced are prompted in sequence. Enter the appropriate NUMERIC data, followed by <CR>s. Month must be entered numerically [JAN=1 ... DEC=12]. Year may be entered in either full [1987] form or short [87] form. Entry of alphabetic characters will result in input error.

ACTIVITY

Enter the current nuclide activity, followed by a <CR>. Note that the U[NAT] MUST be expressed in MG/ML; all other nuclides MUST be expressed in D/M/ML.

ACTIVITY UNCERTAINTY

Enter the uncertainty in the current nuclide activity followed by a <CR>. Uncertainties are to be stated at the 95% CONFIDENCE LEVEL. If the uncertainty is not determined, enter 0 [zero]. Zero calculated uncertainties are not printed in a Bioassay Sample Data Report.

HALF LIFE

Enter the half life of the current nuclide, expressed in HOURS, DAYS, or YEARS, followed by a <CR>.

HALF LIFE UNCERTAINTY

Enter the uncertainty in the current nuclide half life, expressed in the SAME units as the half life, followed by a <CR>.

HALF LIFE AND UNCERTAINTY UNITS

Enter the single alphabetic character CODE corresponding to the units in which BOTH half life uncertainty were expressed, followed by a <CR>. Entries other than H, D, or Y will cause INVALID UNIT ENTERED to be printed to the terminal screen and both the half life and half life uncertainty prompts to be repeated.

This completes data input for the CURRENT NUCLIDE of the CURRENT NUCLIDE STANDARD SOLUTION. The record is written to the data file BASTD.DAT.

IS THERE ANOTHER NUCLIDE IN THE STANDARD?

Enter Y, followed by a <CR>, if the current nuclide standard contains nuclides additional to those already entered. The NUCLIDE prompt will be returned to the terminal screen and the data input sequence repeated for the new current nuclide.

If you are entering a multi-component nuclide standard, have successfully entered at least one component nuclide, and then commit an error in subsequent entry which requires a CONTROL-C abort or otherwise results in exit from the program, the unsuccessfully entered component data records have been written to the BASTD.DAT data file but the nuclide standard will not be indexed. This means the DATA WILL NOT BE UNIVERSALLY READABLE by all the program modules. Such records should be deleted by means of the DELETE option. STD NOT LOCATED IN INDEX FILE will be written to the terminal screen following the deletion. The data must now be re-entered from the beginning.

Enter N, followed by a <CR>, if no additional nuclides are to be entered for the CURRENT nuclide standard.

Any entry other than Y or N will cause INVALID RESPONSE to be printed to the terminal screen and the prompt to be repeated.

The nuclide standard INDEX, consisting of the index numbers and their corresponding nuclide standard serial numbers and principal nuclides, is printed to the terminal screen.

ENTER THE NUMBER OF THE ELEMENT AFTER WHICH THIS ENTRY IS TO BE INDEXED

> Nuclide standards are indexed in order of ascending atomic number, mass number, and serial number. Locate the position in the INDEX where the current nuclide standard solution should be indexed, then enter the INDEX NUMBER of the standard PRECEDING ITS DESIRED POSITION, followed by a <CR>. The current standard will be indexed at the NEXT HIGHER NUMBER and all subsequent elements will be similarly re-indexed.

The NUCLIDE STANDARD DATA menu is returned to the terminal screen.

3. EDIT A STANDARD RECORD

Selection of the EDIT A STANDARD RECORD option from the NUCLIDE STANDARDS DATA menu enables most data contained in nuclide standards records in the BASTD.DAT data file to be changed. Nuclide standard serial numbers cannot be changed, nor can any record containing data for a component nuclide be deleted; a nuclide component record can be changed to contain data for a different nuclide.

ENTER THE SERIAL NUMBER OF THE NUCLIDE STANDARD TO BE EDITED

Enter the SERIAL NUMBER of the nuclide standard for which you wish to edit the data record, followed by a <CR>.

> The serial number and principal nuclide are printed to the terminal screen together with nuclide, reference date, activity, activity uncertainty, half life, and half life uncertainty, for EACH COMPONENT NUCLIDE of the designated standard.
>
> > If the amount of data exceeds the current display page, as indicated by the pagination label in the upper right of the display, you will be prompted to enter a <CR> to continue to additional pages of data.
>
> If you enter a serial number that does not correspond to a record in the BASTD.DAT data file, UNRECOGNIZED SERIAL NO. ENTERED will be printed to the terminal screen. Entry of a <CR> will cause the NUCLIDE STANDARD DATA menu to be returned to the terminal screen.

ENTER THE NUCLIDE IN THE STANDARD TO BE EDITED

Enter the nuclide for the record you wish to edit, followed by a <CR>. Nuclide format consists of the chemical symbol followed by a hyphen and the mass number, excepting natural uranium which is formatted as U[NAT].

> If you enter a nuclide for which no component record exists under the current nuclide standard serial number, or if the format of the entry is incorrect, UNRECOGNIZED SAMPLE COMPONENT NUCLIDE ENTERED will be printed to the terminal screen. Entry of a <CR> will cause the NUCLIDE STANDARD DATA menu to be returned to the terminal screen.

In subsequent dialogue, the corresponding EXISTING record data will be printed to the terminal screen together with each prompt for input. To RETAIN the current data enter only a <CR>; to REPLACE the current data enter the desired data followed by a <CR>.

CURRENT REFERENCE DATE: MONTH

> Enter the corrected MONTH, followed by a <CR>; otherwise enter only a <CR> to retain the entire current reference date. Reference date data must be entered in numerical form [JAN=1 ... DEC=12]; entry of alphabetic characters will result in input error.
>
> > If reference date MONTH has changed, input of DAY and YEAR will be prompted in sequence. Enter the appropriate NUMERICAL data, followed by <CR>s. YEAR may be entered in full [1987] form or short [87] form.

ACTIVITY

> Enter the corrected ACTIVITY, followed by a <CR>; otherwise enter only a <CR> to retain the current activity and activity uncertainty values. U[NAT] activity must be expressed in MG/ML; all other nuclides must be expressed in D/M/ML.
>
> > If ACTIVITY was changed, input of ACTIVITY UNCERTAINTY will be prompted. Enter the uncertainty in the corrected ACTIVITY, expressed in the same units, followed by a <CR>. Uncertainties are to be stated at the 95% CONFIDENCE LEVEL. If the uncertainty is not determined, enter 0 [zero]. Zero calculated uncertainties are not printed in a Bioassay SAMPLE DATA Report.

HALF LIFE

Enter the corrected HALF LIFE, expressed in HOURS, DAYS, or YEARS, followed by a <CR>; otherwise enter only a <CR> to retain the current half life and half life uncertainty.

If HALF LIFE was unchanged, input of HALF LIFE UNCERTAINTY and HALF LIFE AND UNCERTAINTY UNITS will be prompted in sequence.

In response to the HALF LIFE UNCERTAINTY prompt enter the HALF LIFE UNCERTAINTY, expressed in the same units at the half life, followed by a <CR>.

In a response to the UNITS prompt, enter the single alphabetic character corresponding to the units in which BOTH half life and half life uncertainty were expressed, followed by a <CR>. Entries other than H, D, or Y will cause INVALID UNIT ENTERED to be printed to the terminal screen and the uncertainty units prompt to be repeated.

The record as edited is written to the data file BASTD.DAT.

DO YOU WISH TO EDIT ANOTHER COMPONENT OF THIS STANDARD?

Enter Y, followed by a <CR>, if you wish to edit the record for another COMPONENT nuclide in the CURRENT nuclide standard. The ENTER THE NUCLIDE IN THE STANDARD TO BE EDITED prompt will be returned to the terminal screen and the data edit sequence repeated for the new current nuclide.

Enter N, followed by a <CR>, if no additional nuclide records are to edited for the CURRENT nuclide standard. The NUCLIDE STANDARD DATA MENU is returned to the terminal screen.

4. DELETE A STANDARD RECORD

Selection of the DELETE A STANDARD RECORD option from the NUCLIDE STANDARDS DATA menu enables deletion of data records with a designated serial number from the BASTD.DAT data file. The corresponding record in the index file BAINDX.DAT is automatically deleted and the records remaining in the file re-indexed.

TO DELETE A NUCLIDE STANDARD ENTER SERIAL NO.

Enter the SERIAL NUMBER of the nuclide standard to be deleted, followed by a <CR>. All the component nuclide records are deleted for the designated serial number, not selected individual components.

If you enter a serial number that does not correspond to a record in the BASTD.DAT data file, UNRECOGNIZED SERIAL NO. ENTERED will be printed to the terminal screen and the serial number prompt will be repeated.

Enter the NUMBER of the selected option, followed by a <CR>, to execute the specified task. Any entry other than the integers 1 or 2 will cause INVALID RESPONSE ENTERED to be printed to the terminal screen and the prompt to be repeated.

1. INDEXED STANDARDS ORDERED IN INDEX SEQUENCE

   Data is printed to the terminal screen in INDEX sequence. If the amount of data exceeds the current display page, you will be prompted to enter a <CR> to continue to additional pages of data.

   When all the data has been displayed, STANDARDS LISTING COMPLETE is printed to the terminal screen. Enter a <CR>; control is transferred to the BASTD.TSK program module and the NUCLIDE STANDARD DATA menu is returned to the terminal screen.

2. DUMP OF ALL DATA RECORDS IN UNORDERED SEQUENCE

   Control is transferred to the BADATDMP.TSK program module and the data is printed to the terminal screen in UNORDERED sequence. This option is useful for detecting duplicate and other undesirable records produced by entry errors and poor deletion practices.

   If the amount of data exceeds the current display page, you will be prompted to enter a <CR> to continue to additional pages of data.

   When all the data has been displayed, STANDARDS LISTING COMPLETE is printed to the terminal screen. Enter a <CR>; control is transferred to the BASTD.TSK program module and the NUCLIDE STANDARD DATA menu is returned to the terminal screen.

6. TERMINAL PRINTOUT OF STANDARD INDEX FILE

Selection of the TERMINAL PRINTOUT of standard index file option from the NUCLIDE STANDARD DATA menu prints the contents of the BAINDX.DAT data file to the terminal screen. The sole function of indexing is to provide a mechanism for listing nuclide standards in atomic number - mass number order of the principal nuclides. The index is a convenient means of identifying serial numbers of nuclide standards containing a specific principal nuclide.

INDEX NUMBER, SERIAL NUMBER, AND PRINCIPAL NUCLIDE are printed to the terminal screen for each nuclide standard solution in INDEX sequence. When review is completed, enter a <CR>; control is transferred to the BASTD.TSK program module and the NUCLIDE STANDARD DATA menu is returned to the terminal screen.

7. RETURN TO BIOASSAY PROGRAM OPERATIONS MENU

Control is transferred to the BAQC.TSK program module and the BIOASSAY PROGRAM OPERATIONS MENU is returned to the terminal screen.

3. GENERATE RANDOM H20 ADDITION VOLUMES

Specification letters submitted by the Health Physics Section often request the addition of 100 ml to 500 ml water to individual test samples. The usual purpose of this addition is to disguise the otherwise identical weights of test samples. Selection of this program option generates truly random numbers between 100 and 500 that are multiples of five which can be used to establish volumes of water to be added.

HOW MANY RANDOM NUMBERS ARE TO BE GENERATED?

Determine the number of individual test samples to which water is to be added, as specified in the specification letter for the Bioassay test sample set. Enter this number, followed by a <CR>.

The requested number of random volumes will be printed to the terminal screen. Record these numbers, in sequence, in the column of the specification letter titled ADD WATER. These numbers will be entered during execution of the PRODUCE BIOASSAY STANDARDS DATA REPORT program module in response to the ENTER ANY ADDITIONAL COMMENT prompt.

```
HIT <CR> TO CONTINUE
```

ENTER A <CR>. Execution of the random number generating module will be terminated and the BAQC OPERATIONS MENU is returned to the terminal screen.

4. TERMINATE PROGRAM

Selection of this option causes the system to terminate execution of the BAQC.EXE program module and returns control to Digital Control Language (DCL) level.

When the DCL $ prompt is printed to the terminal screen, sign off the terminal by entering LO (LOGOFF), followed by a <CR>. A message confirming a successful sign off will be printed to the terminal screen.

APPENDIX 2

TABLE OF UNCERTAINTY FOR CALIBRATED AND UNCALIBRATED GLASS MICROPIPETTES

		UNCERTAINTY [95%CI]
PIPETTE (ul)	SPECIFICATION	CALIBRATED
5	±0.100 ul	±0.010 ul
10	0.150	0.020
15	0.150	0.030
20	0.200	0.040
25	0.075	0.050
30	0.090	0.060
35	0.105	0.070
40	0.120	0.080
45	0.135	0.090
50	0.150	0.100
60	0.180	0.199
65	0.195	0.127
75	0.225	0.144
100	0.300	0.177
125	0.375	0.197
150	0.450	0.206
175	0.525	0.223
200	0.400	0.215
250	0.500	0.170
300	0.600	0.142
350	0.700	0.166
400	0.800	0.190
450	0.900	0.213
500	1.000	0.237
600	1.200	0.284
700	1.400	0.331
800	1.600	0.379
900	1.800	0.427
1000	2.000	0.474
1500	3.000	0.711
2500	5.000	1.185
5000	10.000	2.370

Uncertainty data for calibrated glass micropipettes is adapted from manufacturers specifications.

Uncertainty data for calibrated glass micropipettes is calculated from mercury calibration data.

APPENDIX 3

UNCERTAINTIES FOR EPPENDORF ADJUSTABLE AUTOMATIC PIPETTERS

Manufacturers specifications state the following accuracies:

digital pipette 2ul-10ul range:	6% at 2ul	1.2% at 10ul

accuracy(ul) = [ul set][0.576-(0.048)(ul set)]/8

digital pipette 10ul-100ul range:	1.5% at 10ul	0.6% at 100ul

accuracy(ul) = [ul set][1.44-(0.009)(ul set)]/90

digital pipette 100ul-1000ul range:	1.0 at 100ul	0.5% at 1000ul

accuracy(ul) = [ul set][9.5-(0.005)(ul set)]/900

END

DATE FILMED

10/13/93