U-003-303.13

3930

OPERABLE UNIT 1 MINIMUM ADDITIVE WASTE STABILIZATION REMEDIAL DESIGN BENCH-SCALE TREATABILITY STUDY WORK PLAN VOLUME II-APPENDICES NOVEMBER 1992

11/20/92

DOE-FN/EPA
~~100~~ 338
REPORT

[redacted]

U-003-303.13

3930

Operable Unit 1
Minimum Additive Waste Stabilization Remedial Design Bench-Scale Treatability Study Work Plan
Volume II - Appendices

Environmental Remedial Action Project
Fernald Environmental Management Project
Fernald, Ohio

November 1992
Rev. No. 0

United States Department of Energy

3930

Operable Unit 1
Minimum Additive Waste Stabilization Remedial Design Bench-Scale Treatability Study Work Plan
Volume II - Appendices

Environmental Remedial Action Project
Fernald Environmental Management Project
Fernald, Ohio

November 1992
Rev. No. 0

United States Department of Energy

2

Operable Unit 1
Minimum Additive Waste Stabilization
Remedial Design Bench-Scale Treatability Study Work Plan
Volume II - Appendices

CONTENTS

A Support Studies

B Analytical Methodology

C SOPs for the MAWS Bench-Scale Study

D Health and Safety Plan

3930

A

3-A

3930

APPENDIX A

SUPPORT STUDIES

APPENDIX A - SUPPORT STUDIES

Experimental Design Overview

Figure A-1 shows a flow-diagram overview of the experimental design used for the MAWS project. This appendix describes support studies that either have been performed or are currently being performed to support the MAWS Bench-Scale Treatability Study.

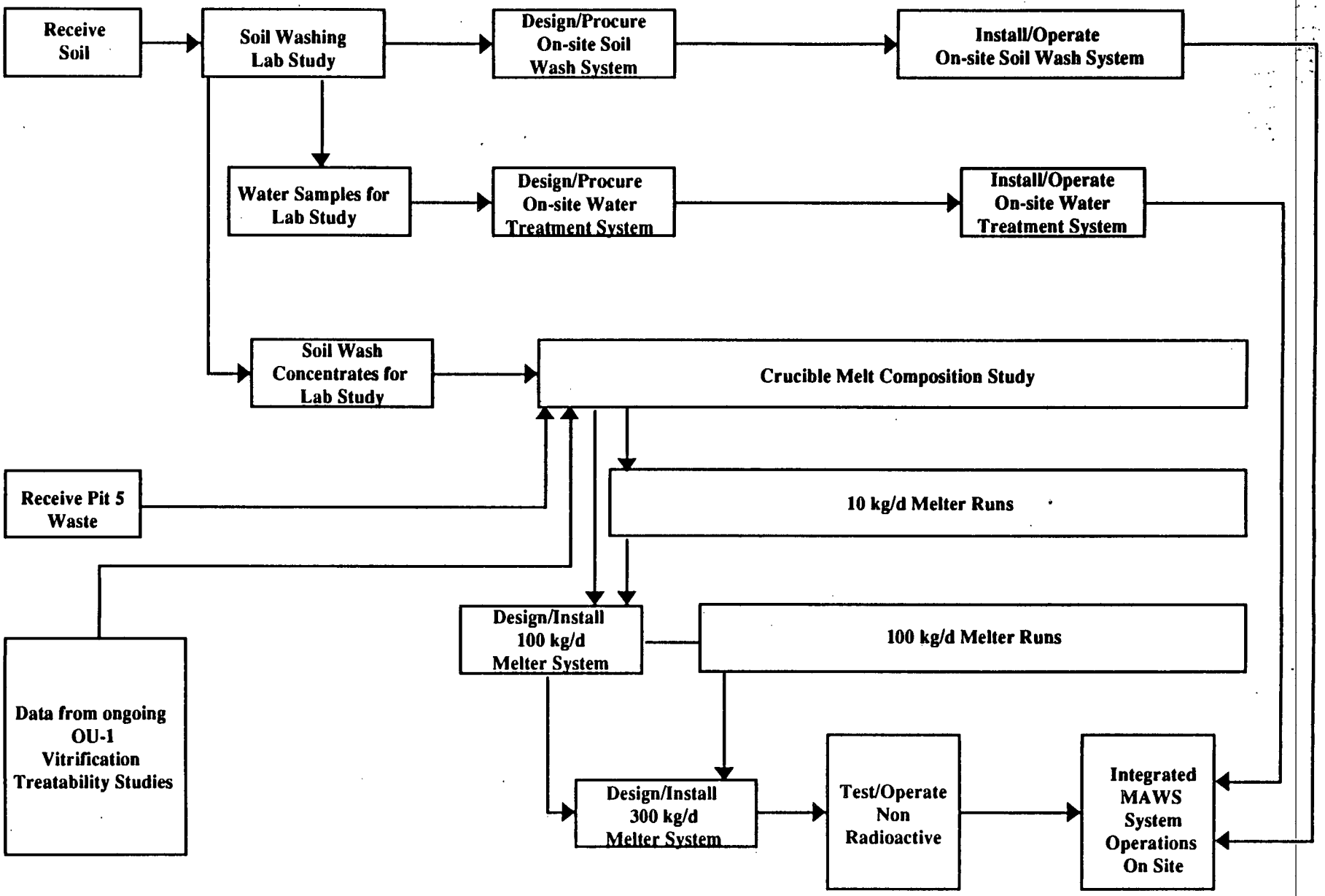


Figure A-1
Off-site Support Studies Experimental Design Overview

MAC\BILLUSDATA\OU-1\MAWS EXPERIMENTAL DESIGN

SECTION A1

SOIL WASHING

The following tasks will be performed at the Lockheed Analytical Laboratory (LAL):

Stage 1 - Physical-Only Separation

Physical-only separations studies in Stage 1 will focus on a qualitative and quantitative characterization of the distribution of uranium relative to specific soil size fractions. Stage 1 treatability testing amounts to bench-scale testing of small aliquots of the FEMP soils. The physical and chemical data obtained during the initial analysis will be used in a matrix of bench-scale tests designed to determine whether physical-only soil washing techniques will be effective in providing significant volume reductions of the FEMP soils. If the physical-only techniques are successful, no chemical testing will be performed. If the physical-only techniques are of limited success, a matrix of physical/chemical bench-scale tests will be performed.

The first series of tests during Stage 1 will use the sieve data and analytical data obtained in the initial analysis to determine if any of the soil size fractions can be separated as "clean" without further processing. If size fractionation alone is a possible remedy solution, a volume reduction will be calculated and recorded. Based on existing information (Lee and Marsh 1992), it is unlikely that simple size fractionation will provide significant volume reduction.

The second series of tests during Stage 1 will take several splits from individual 25-pound aliquots and process them in a bench-top attrition scrubber unit at various retention times and at the various rpm settings. After scrubbing, the soil will be wet sieved and the size fractions will be dried in a drying oven. When dry, three splits will be taken of the fractions and containerized. The soil in containers will be analyzed for uranium concentrations by laser phosphorimeter.

This data will be used to determine if the attrition scrubber was successful in reducing additional size fractions to below 35 pCi/g and, if so, at what rpm and retention time. This data will be used to calculate a volume reduction and will be recorded.

Stage 1 - Physical/Chemical Separation

The physical/chemical separation tests will use an oxidized bicarbonate/carbonate extraction fluid. This chemical extractant has been used successfully in the uranium mining industry for over 30 years. It is very selective for uranium. If this extractant is not effective on FEMP soils, other leaching agents (e.g.,

acids) will be evaluated.

Two series of leach tests will be conducted. In one series, the leach solution will be used in combination with an attrition scrubber. As described above, tests will be run at various retention times and rpm settings.

After scrubbing, the soil will be separated from the leach liquors and rinsed of residue leach liquor prior to being wet sieved. The extractant solution and rinse solutions will be analyzed using the laser phosphorimeter. Since we know the volume of extractant solution added to the soil by means of subtraction, we can calculate the uranium concentration of the extractant fluid minus the wet sieve solution.

The size fractions collected above will be dried in a drying oven. When dry, splits will be taken of the fractions and containerized. The soil in the containers will be analyzed by laser phosphorimeter, and the uranium concentration of the soil will be calculated. Additionally, splits of each size fraction will be taken for confirmatory analysis at LAL. This data will be used to determine if the attrition scrubber in combination with the extractant fluid was successful in reducing additional size fractions to below 35 pCi/g and, if so, at what rpm and retention time. These data will be used to calculate a volume reduction and will be recorded.

The second series of tests will evaluate chemical leaching effectiveness without an attrition scrubber. These tests will be conducted using various leach solution concentrations, retention times, and temperatures. The soil will be separated from the leach liquors and analyzed as described above.

Stage 2 - Physical/Chemical Testing

Stage 2 treatability testing incorporates the findings of Stage 1 physical separation and chemical extraction testing. The primary function of Stage 2 testing in the experimental design is to serve as a transition phase between Stage 1 testing and on-site Stage 3 testing. In this stage, tests will be conducted with equipment similar in scale to that used in the on-site testing system. These tests will be used to verify the performance of process units and to identify and resolve material processing issues.

Stage 2 testing will use the 500-pound batch samples of feed soil. These samples are composites of the individual aliquots which are representative of the soil as a whole and therefore, the batch soils are fully characterized. These batch samples will be mixed with the washing solution as defined in Stage 1 testing to form a thick slurry. The slurry will be delivered to a pilot-scale attrition scrubber at a rate consistent with the retention times defined in Stage 1 testing. The action of the slurry within the attrition scrubber will dislodge uranium particles and precipitate coatings from the sand- and silt-sized particles.

Upon exiting from the attrition scrubber, the slurry will be diluted and will pass over a vibrating screen (mesh size to be determined in Stage 1) and the "cleaned" soil fraction will be separated from the contaminated fine-grained material. The soil slurry will then enter a hydrocyclone sized to make an appropriate size cut. The underflow from the cyclone, plus the oversize from the vibrating screen will be dewatered and delivered to holding containers. An autosampling system will be used to collect representative soil samples for analysis. Again, laser phosphorimetry techniques will be used to determine if the coarse soil material meets the 35 pCi/g criteria and is able to be classified as "clean," if not, the soils will be diverted away from the "clean" soils and delivered to the melter 100 kg studies. The fine-grained soil fraction will be separated from the uranium-laden solution in the post-conditioning unit and aliquots of the process solution will be analyzed for uranium concentration. All process splits will be collected, split into aliquots, and analyzed for uranium concentration by laser phosphorimetry.

Additionally, selected duplicate aliquots will be analyzed at LAL to verify the findings of the in-house laser phosphorimeter. Those process splits which are found to be below 35 pCi/g release criteria will have TCLP tests performed on them to demonstrate that no hazardous components were added to the soils during the soil washing process.

SECTION A2
VITRIFICATION SUPPORT STUDIES

Soil wash concentrates (i.e., the contaminant-enriched fraction) from the laboratory studies will be shipped to VSL for use in the vitrification laboratory studies which will involve blending them with Pit 5 wastes. The vitrification study will be conducted in overlapping layers of increasingly large glass production rates. Data from ongoing OU-1 vitrification treatability studies will be used along with other relevant information to direct a composition variability study using crucible melts (about 500 g each). Suitable compositions will be tested on a 10 kg/day vitrification system and then progress to 100 kg/day system testing. Data from these tests will be used to finalize the design of the 300 kg/day system that will be installed at the FEMP. Major composition changes or other operating parameter changes will first be tested through the three laboratory scales before passing to on-site testing. This step approach is more efficient both in testing time and costs since both of these factors increase with the scale of the test.

The following sections provide a summary of the vitrification support studies.

A2.1 Chemical Characterization of Soil Fines

Soil will be separated into three fractions -- coarse, middle, and fine. Soil from the middle fraction will be fed to the melter by gravemetric means. Coarse and fine fractions will be leached, and the leachate will be sent to the water treatment.

A2.2 Vitrification Crucible Tests

A glass composition variability study will be designed for combinations of soil-wash concentrates, OU-1 sludges, and media from the water treatment system loaded with concentrated radioactive waste, with and without addition of chemical additives. At least twenty crucible melts, of about 500 g each, will be prepared on this basis and all of the glasses will be subjected to the glass characterization regimen outlined in Subsection 4.3.1.7. Approximately ten glasses will be made from combinations of soil-wash fines and OU-1 sludges, four from spent ion exchange media and OU-1 sludges, and five from all three waste streams, and one with OU1 sludge and purchased sand. The OU-1 sludge and sand mix will be used as a basis to judge the other glass mixes.

A2.3 Joule-Heated Melter Tests - 10 kg/day

Based on the results of the glass composition variability study using crucible melts a series of feed compositions will be selected for the 10 kg/day joule-heated melter tests. Six such tests will be conducted in order to acquire detailed process data including throughput rates, cold cap formation, foaming events, and off-gas characterization. At least one test will be carried out with a surrogate non radioactive feed.

A2.4 Joule-Heated Melter Tests - 100 kg/day

A melter capable of producing approximately 100 kg/day of vitrified waste will be installed at VSL. A total of four runs will be performed on the 100 kg/day melter vitrification system installed at Catholic University. The first two of these will use non-radioactive surrogate feeds for initial system tests. The second two runs will involve actual FEMP waste materials. These runs will provide the critical large-scale process data that will be necessary in the development of process controls and operating protocols for the 300 kg/day unit that will be installed at the FEMP. Process data will again include throughput rates, cold cap formation, and foaming events, as well as off-gas system performance evaluation. These data, collected on a series of units, will provide the basis for scale up to the larger pilot-scale and full-scale units if this approach proves to be optimal for the FEMP.

Laboratory vitrification activities will be directed toward the development of optimum compositions for vitrification of sludge/soil concentrate blends and definition of the operational process parameters. The characterization data obtained for the waste samples will be used for selecting the blends and calculating the raw-mix recipes. Previous experience and glass composition-property correlations that have been developed will be utilized while preparing these formulations. A further essential components is feed-back data from the glass characterization studies which will be used to refine the glass composition studies.

A flow diagram illustrating the sequential steps in glass preparation and glass characterization is shown in Figure A-2. As described previously, the MAWS program involves a stepwise scale up of the melter systems culminating in the 300 kg/day on-site unit. However, the general approach is as illustrated in Figure A-2.

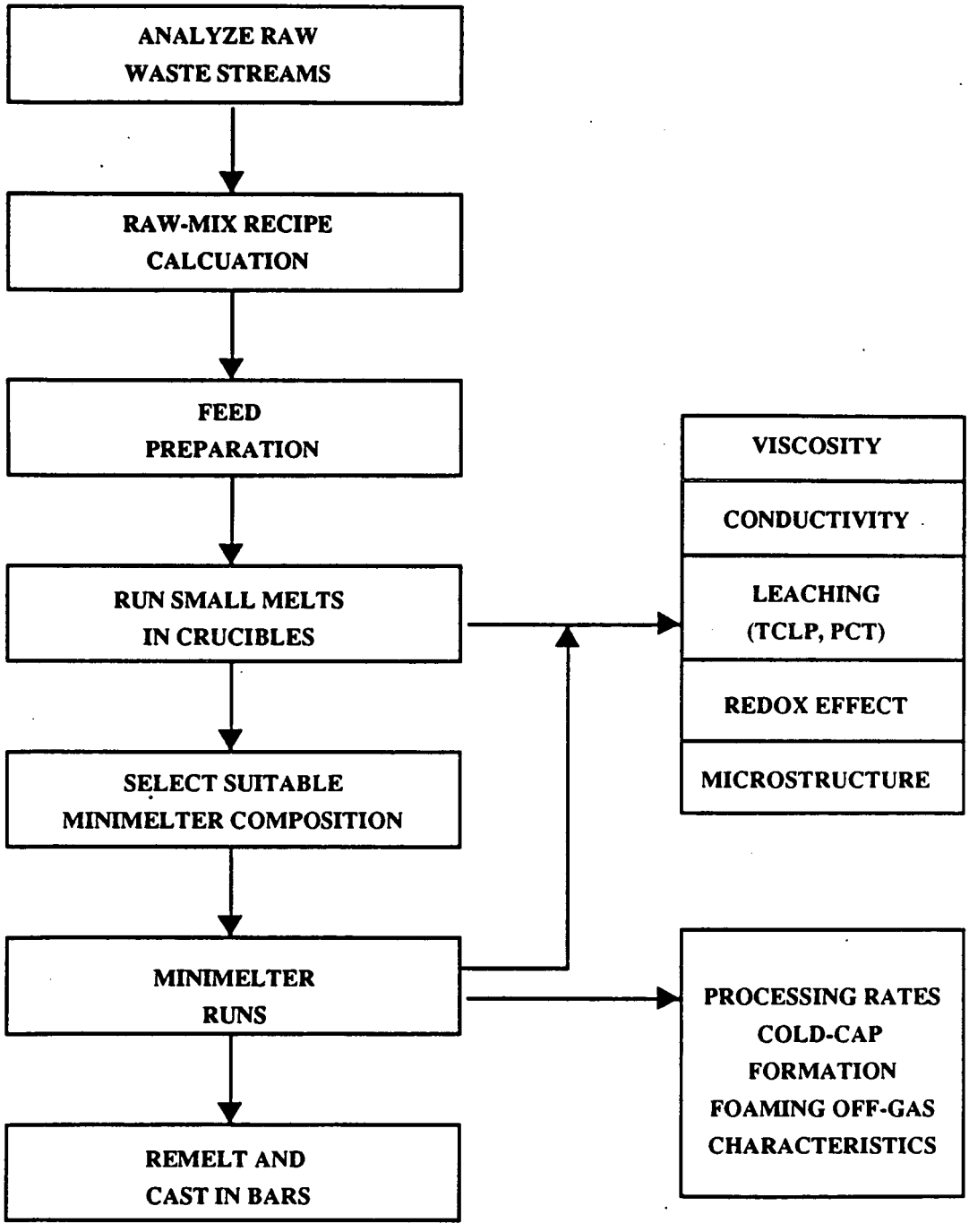


Figure A-2 - Sequential Steps in Glass Preparation

3930

B

12-A

APPENDIX B

The following analytical methodologies are presented in Appendix B:

Kinetic Phosphorescence Analysis (KPA)

TCLP Procedure (Modified)

Glass Characterization Methodology

1) Viscosity
2) Microstructural characterization
3) Scanning electron microscopy
4) Melt conductivity

Waste Characterization Procedure

1) Chemical composition/DC plasma
2) ICPMS

PCT Methodology

Physical Properties and Carbon Content

1) Thermogravemetric analysis
2) Analysis of carbon content
3) Specific gravity
4) Particle size analysis

PROCEDURES FOR GLASS CHARACTERIZATION

1) Viscosity
2) Microstructural characterization
3) Scanning electron microscopy
4) Melt conductivity

VSL Technical Procedure

Title: Glass Characterization

Document: TPI-GC.WVN

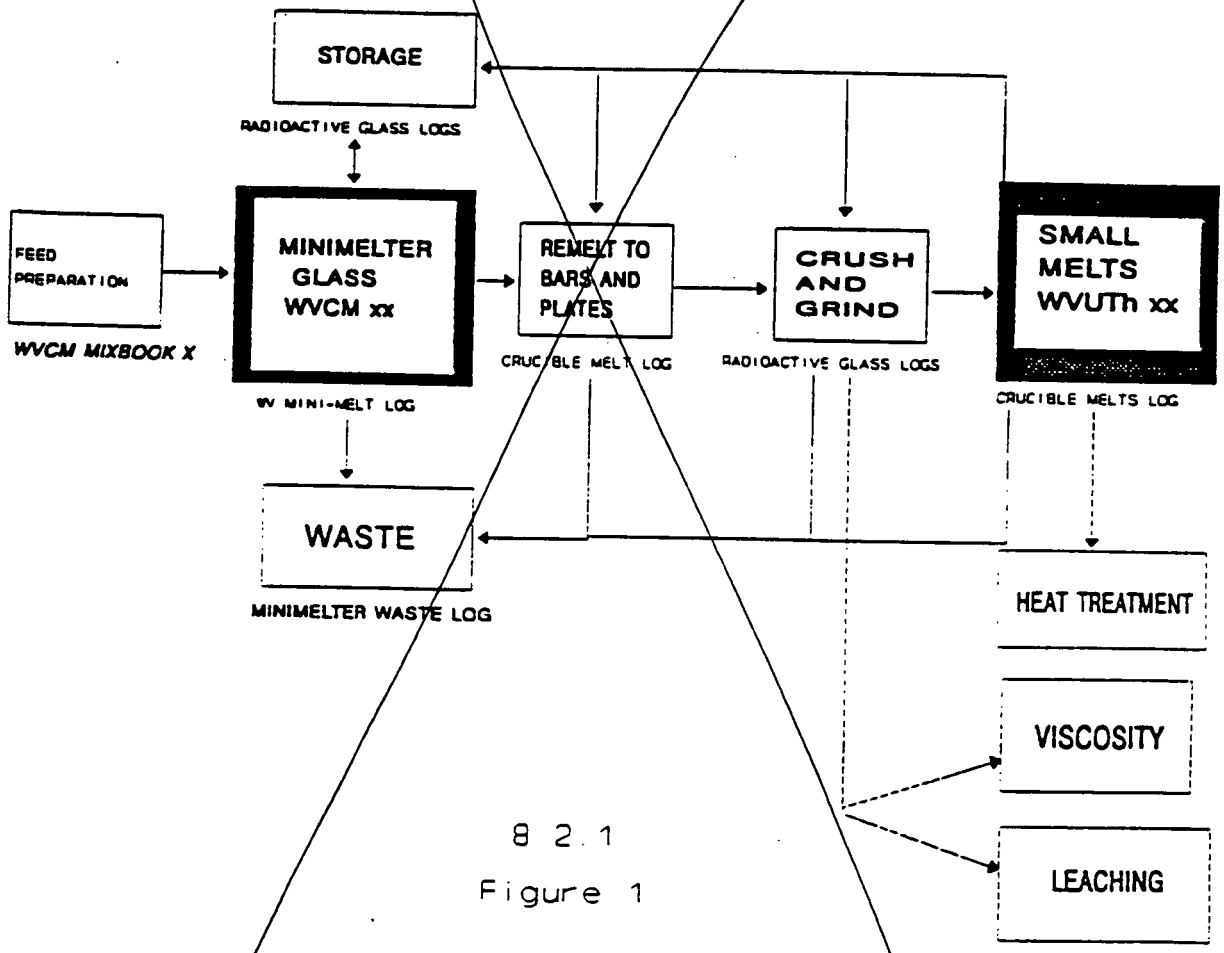
Issued: 10/91 Rev #0

Documents Incorporated:

TPI04.WVN	Rev #0
TPI-GC.WVN	Rev. # New

Date Issued: 10/91

Prepared by: Fr. Andrew Buechele Project Manager	Ian L. Pegg Project Manager
Approved by: Pedro B. Macedo Co-Director, VSL	C. Sivaprakash Quality Assurance Officer, VSL


STORAGE
RADIOACTIVE GLASS LOGS
FEED PREPARATION
WVCM MIXBOOK X
MINIMELTER GLASS WVCM xx
WV MINI-MELT LOG
REMELT TO BARS AND PLATES
CRUCIBLE MELT LOG
CRUSH AND GRIND
RADIOACTIVE GLASS LOGS
SMALL MELTS WVUTh xx
CRUCIBLE MELTS LOG
WASTE
MINIMELTER WASTE LOG
HEAT TREATMENT
VISCOSITY
LEACHING

8 2.1

Figure 1

GLASS CHARACTERIZATION

Table of Contents

1.0 PURPOSE

2.0 APPLICABILITY

3.0 SAFETY
- 3.1 Hazards
- 3.2 Hazard Mitigation
  - 3.2.1 Identification of Hazards
  - 3.2.2 Handling and Storage of Chemicals
  - 3.2.3 Emergencies
- 3.3 Personnel Protection

4.0 REQUIREMENTS

5.0 REFERENCES

6.0 PROCEDURES
- 6.1 Melt Viscosity Determination
  - 6.1.1 Equipment and Supplies
  - 6.1.2 Operating Procedures
  - 6.1.3 Calibrations
    - 6.1.3.1 Calibration of the Viscometer
    - 6.1.3.2 Calibration of the Spindle
  - 6.1.4 Computerized Data Analysis and Documentation
- 6.2 Microstructural Characterization of Glasses
  - 6.2.1 Heat Treatment of Glass Samples
    - 6.2.1.1 Equipment and Supplies
    - 6.2.1.2 Operating Procedures
  - 6.2.2 Preparation of Samples for Microscopic Examination
    - 6.2.2.1 Equipment and Supplies
    - 6.2.2.2 Operating Procedures
  - 6.2.3 Procedure for Operation of the Scanning Electron Microscope

7.0 Specimen and Data Traceability and Documentation

DOCUMENT REPLACEMENT RECORD

Glass Characterization

Procedure	Descriptions	Rev #	Replaced in this Manual by:
VSL-GC-1.WVN	Melt Viscosity Determination	1	Section 6.1
VSL-GC-2.WVN	Heat Treatment of Glass Samples	NEW	Section 6.2.1
VSL-GC-3.WVN	Preparation of Sample for Microscopic Examination	NEW	Section 6.2.2
VSL-GC-4.WVN	Procedure for Operation of the Scanning Electron Microscope	NEW	Section 6.2.3

10/91

1.0 PURPOSE

This procedure describes methods, materials, equipment and special conditions required to perform heat treatment, microstructural characterization, and melt viscosity characterization of nuclear waste glass. This procedure provides the means for obtaining verifiable, reproducible, documented data from tests and experiments.

2.0 APPLICABILITY

This procedure applies to all employees trained and authorized to perform heat treatment, microstructural characterization, and melt viscosity characterization of nuclear waste glass. Specific activities covered by this procedure include: (a) specimen preparation for heat treatment; (b) selection of container for heat treatment; (c) temperature measurement and control, thermocouple calibration; (d) control of redox state; (e) establishment of time-temperature schedule for heat treatments; (f) preparation of specimens for optical microscopy; (g) preparation of specimens for SEM examinations; (h) optical microscopy and photomicrography; (i) SEM examination and associated analytical procedures, namely:

1) X-ray EDS characterization, semi-quantitative and quantitative analysis, and elemental mapping.
2) X-ray WDS characterization, semi-quantitative and quantitative analysis, and elemental mapping.
3) Imaging techniques and photomicrography.

4) Image enhancement and processing.

5) Phase identification isolation and quantification through image analysis.

(j) documentation work, logging of images, photomicrographs, and analytical results in laboratory notebooks; (k) viscometer spindle calibration; (l) rotating spindle viscometer operation; (m) viscometer muffle furnace and temperature controller operation; (n) viscometer spindle cleaning procedure; (o) viscosity data analysis software.

This procedure will be implemented by personnel from the VSL.

3.0 SAFETY

3.1 HAZARDS

The definition of a hazardous chemical is given in Section 8.3 of the CUA Chemical Materials Safety Manual, adopted from the OSHA Hazard Communication Standard. The CUA Chemical Materials Safety Manual is hereafter referred to as the CCMSM. This Standard and its application to CUA facilities are described in Sections 8.1 of the CCMSM, with the exceptions noted in Section 8.28. The types of radioactive material encountered during heat treatment and specimen preparation for microstructural characterization include liquid, solid. and fine particulate. Materials used for viscosity determinations are generally monolithic glass bars but will from time to time include fine particulate samples.

3.2 HAZARD MITIGATION

3.2.1 Identification of Hazards

The identification of radioactive hazards shall be facilitated through an education program including the Radiation Health Physics course referred to in Section 4.1 and other specific directives.

All materials received by personnel in the heat treatment and microstructural characterization program shall be properly labeled and identified, if radioactive, by approved yellow radioactive hazard labels. A geiger counter shall be used regularly to monitor levels of radiation in the work area and identify any sources of radiation.

Viscosity measurements involve the use of hot, molten radioactive glass and all appropriate precautions should be exercised. Heat resistent gloves and tongs shall be used for handling furnace covers, spindles, crucibles, etc. Eye protection shall be worn at all times. A face mask is recommended during removal of the crucible from the furnace due to the potential for shattering. Personnel must ensure that the above-furnace exhaust system is operating over the course of all measurements.

Cleaning of the viscometer spindle involves the use of hydrofluoric acid (HF) solutions and personnel shall familiarize themselves with the particular hazards associated with that material (see Section 5.0). Acid resistent gloves, face protection. and aprons must be worn during this procedure. Personnel shall ensure that HF antidote gel is available near the work area before commencing work with HF.

3.2.2 Handling and Storage of Chemicals

Examination of liquid materials (solutions and suspensions) is not part of the microstructural or viscometric characterization program and shall not be carried out in areas designated for heat treatment, preparation, and examination of specimens. The only place where radioactive liquids will be encountered is in the cutting and polishing operations performed on solid specimens. All such work shall be carried out in a sealed glove box connected to an exhaust line through a HEPA filter. All solid materials resulting from such work shall be washed thoroughly in clean solvents and detergent solutions and dried prior to removal from the glove box to insure that no radioactive particulates or liquids are removed from the glove box with the samples. All radioactive wastes and materials contaminated with radioactivity during specimen preparations shall remain in the glove box until they can be removed for disposal or decontaminated using approved procedures.

Solid materials handled in this work shall not produce levels of radioactivity which create a serious danger to the personnel handling them. All standards set forth in the radiation safety manual of CUA by the radiation safety officer shall be adhered to at all times by those handling radioactive materials of any type. Cutting, grinding, polishing or pulverizing of solid radioactive materials shall only be carried out in a glove box using approved procedures.

Examination of particulate radioactive materials shall only be done if levels of radioactivity are low enough to permit handling without special precautions or if the particulates can be embedded in mounting resins or otherwise immobilized to prevent dispersion of such

materials in the environment and their ingestion or inhalation by handling personnel. Such embedding and immobilization and any further preparation likely to produce additional radioactive liquids or particulates shall be done in the glove box using the procedures outlined above for solid materials. Viscometric measurements made on initially particulate samples requires loading of the crucibles in a glove box and closing the crucible before removal to the viscometer furnace. The crucible should remain lightly covered until the sample has become molten.

3.2.3 Emergencies

Any accident which appears likely to release radioactivity in such a form that it can be ingested or inhaled by personnel, contaminate their person or clothing, or be dispersed in the environment shall be reported to supervisory personnel immediately and dealt with using approved techniques. The release must be confined and all contaminated items removed for decontamination or disposal by approved methods.

3.3 PERSONNEL PROTECTION

Personnel protection shall be effected through education in and familiarization with the hazards of and proper methods of handling radioactive materials. Approved radiation film or TLD badges shall be worn by personnel at all times when they are in areas where exposure to radioactivity above background levels is likely to occur, and these badges shall be collected and

processed monthly. A geiger counter or other approved means of detecting and monitoring levels of radiation shall be available to confirm that levels of radiation in the workplace are within acceptable limits and check for possible contamination of objects and surfaces in areas where radioactive materials are handled.

4.0 REQUIREMENTS

4.1 TRAINING

All glass characterization laboratory personnel are trained in the understanding and use of the technical methods that they will use by the laboratory supervisor or by a trained and experienced person designated by the laboratory supervisor. Upon completion of training for a method, a technician is qualified to use that method independent of direct supervision.

5.0 REFERENCES

Safe Handling of Radioactive Materials, National Bureau of Standards Handbook 92, National Committee on Radiation Protection Report No. 30, U. S. Government Printing Office: Washington, D. C., 1964.

Basic Radiological Health, Course Manual, Health Physics Society, Baltimore-Washington Chapter, 1988, (or most recent edition).

Scanning Electron Microscopy and X-ray Microanalysis, Goldstein, et al., Plenum Press: New York, 1981.

The Electron Microscope Handbook, M. W. Ladd, Ladd Research Industries, Burlington, Vermont: 1973.

Scanning Electron Microscopy, A Student's Handbook, Michael T. Postek, Ladd Research

Industries, Burlington, Vermont: 1980.

Advanced Scanning Electron Microscopy and X-ray Microanalysis. Newbury, et al., Plenum Press: New York, 1986.

Scanning Electron Microscopy, X-ray Microanalysis, and Analytical Electron Microscopy, A Laboratory Workbook, Lyman et al., Plenum Press: New York, 1990.

Principles of Analytical Electron Microscopy, Joy et al., Plenum Press: New York, 1986.

Operating and Maintenance Instructions, 11-1180 Isomet Low Speed Saw, A. Buehler Co.: Lake Bluff, Ill., 1987.

Operating and Maintenance Instructions, 69-1000 Minimet Polisher Grinder, A. Buehler Co.: Lake Bluff, Ill. 1985.

TN5500/5600 System Operation Manuals, Tracor-Northern (Noran Instruments, Inc.): Middleton, WI, 1986 and updates.

JEOL JSM-35C Operator's Manual Japan Electron Optics Ltd.: Tokyo, Japan 1978 and updates.

Radiation Safety Manual of the Catholic University of America, January 1980, W. E. Keene RSO.

Brookfield Viscometer Operation Manual, Brookfield Engineering Laboratories Inc., Stoughton, Mass. 02072.

Improved Apparatus for Rapid Measurement of Viscosity of Glass at High Temperatures, R. L. Tiede, J. Am. Ceram. Soc., paper presented at 61st Ann. meet., May 20, 1959.

Physical Properties of Multicomponent Borosilicate Glasses: A Study of Viscosity, Processing and Durability, E. E. Saad, Ph. D. Dissertation, The Catholic University of America, 1988.

Occupational Health Guideline for Hydrogen Fluoride, U. S. Dept. of Labor, OSHA, Sept., 1978.

Hydrofluoric Acid Dermal Exposure, Vet. Hum. Toxicol. 31, 243 (1989)

Comparative Effectiveness of Topical Treatments for Hydrofluoric Acid Burns, W. M. Bracken et al. Journal of Occupational Medicine, 27, 733 (1985).

6.0 PROCEDURE

6.1 MELT VISCOSITY DETERMINATION

6.1.1 Equipment and Supplies

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Viscometer	Brookfield	Synchralectic	I
1	Remelt Furnace			N.A.
1	Tube Furnace			I
1	Controller	Love	49	N.A.
1	Spindle		Iconel 754	II
	Spindle extensions	Brookfield		N.A.
1	Multimeter	Keithly	177	III
1	Compensator	Omega		N.A.
	Thermocouple	Chromel Alumel type K		N.A.
	Thermocouple	Pt/Pt-Rh type S		N.A.
	Thermocouple	Protection tubes		N.A.
	Crucible	U.S. Quartz		
1	Brass Cylinder			
1	Thermometer	Fisher		
	Standard Viscosity Oil	Cannon	S2000	
	Standard Reference Material	NBS	SRM711	

Calibration codes: I. Calibration frequency: Every six months or every fifteen uses; Calibration accuracy ± 7% (see later in this procedure); II. Calibration is performed prior to every viscosity measurement using a standard oil of known viscosity (see later in this procedure); III. Calibration: externally every two years.

6.1.2 OPERATING PROCEDURE

A. Viscosity Measurement

(1) Calibrate the spindle using the procedure given in Section 6.1.3.2.

(2) Weigh out accurately 85-110g of the glass sample into a quartz crucible and place it in the furnace.

(3) Turn on the power and set the controller temperature to 1150°C unless specified otherwise by the Project Manager.

(4) After attaining the set temperature, allow the furnace temperature to stabilize (i.e. until the change in the Keithly multimeter reading is less than +/-0.03 mV over a period of 10 minutes).

(5) Immerse the calibrated spindle into the melt and attach the spindle hook to the viscometer. Ensure that the spindle is completely immersed in the melt and the spindle tip is about 1 cm above the bottom of the crucible.

(6) Insert the Pt/Pt-Rh thermocouple with its sheath such that the tip of the thermocouple cover is at the top of the glass melt.

(7) Turn on the viscometer and set it to the lowest rotation speed.

(8) Allow the system to attain equilibrium (after a maximum of 70 seconds), and record the reading on the viscometer, the rotation speed in RPM and the temperature indicated by the Pt/Pt Rh thermocouple.

(9) Proceed to the next highest rotation speed of the viscometer and continue as in step (8) until either 50 RPM is reached or the viscometer reading is off scale.

(10) Set the viscometer RPM to the lowest value and cool the furnace by 50+/-10°C. Ensure that the furnace temperature has stabilized as in step (4).

(11) Repeat steps (7) through (10) until the furnace temperature reaches around 900°C.

(12) Remove the Pt/Pt-Rh thermocouple from the crucible and push the thermocouple sheath into the melt.

(13) At the end of the viscosity run continue as in Section C.

B. Cleaning of the Spindle

(1) Separate the spindle from the crucible and hang it in a tube furnace.

(2) Turn on the furnace and set the temperature to 1000 ± 50°C. Allow excess glass on the spindle to drip off.

(3) Turn off the furnace and allow the spindle to attain room temperature.

(4) Don safety equipment and place the spindle in an HF bath overnight.

(5) Inspect the spindle once a day and remove it from the bath when it is clean.

(6) Dip the spindle into the neutralizing solution, rinse it thoroughly and allow it to dry.

(7) Weigh the spindle after each run.

(8) Measure and record the dimensions of the spindle after every 5 runs.

(9) Ensure that the weight and dimension of the spindle fall within 1% of the previous data in order to check if any deterioration of the spindle has occurred. Report any larger deviations to the Project Manager.

C. Finishing the Viscosity Run

(1) Turn the viscometer off and set the furnace temperature to approximately 700°C.

(2) When the controller begins to cycle remove the top insulation using a glove.

(3) Remove the spindle extension by cranking the furnace upward and tilting the extension to the side until the extension falls off the spindle hook.

(4) Remove the extension from the spindle with repeated downward rocking movements.

(5) When the extension is free immediately hook the spindle with Nichrome wire and pull the spindle and crucible out of the furnace.

(6) Ensure that the black ring support falls off.

(7) Lower the spindle and crucible into the brass cylinder.

(8) Close the brass cylinder and let it cool.

(9) If the sample is not radioactive proceed to step (13), however, if the sample is radioactive open the brass cylinder in a glove box after putting on radiation badges and gloves.

(10) Empty the glass into one plastic bag and the spindle into another.

(11) Seal the plastic bags and the cylinder and remove them from the glove box.

(12) Discard the glass in the solid radioactive waste bucket.

(13) Proceed to clean the spindle according to the procedure given in section B.

6.1.3 Calibrations

6.1.3.1 Calibration of the Viscometer

(1) Weigh out accurately 120 ± 5g of the standard SRM-711 glass into a quartz crucible and place it in the furnace.

(2) Proceed as in section A, steps (3) through (12).

(3) Calculate the measure viscosity as in section 6.1.4 below for each temperature of the standard materials studied.

(4) Calculate the percentage error for each of the measured viscosity readings as compared to the nominal values.

(5) Examine the results and report deviation from the required accuracy of ± 7% to the Project Manager.

(6) Report the results in the viscosity calculation file.

6.1.3.2 Calibration of the Spindle

(1) Place the standard oil (Cannon Instrument Company S2000 viscosity oil) in a quartz crucible.

(2) Insert the spindle in the oil as described in step (5) of section A.

(3) Turn on the viscometer and record the viscometer readings at the various rotation speeds as in section A from step (7) to (9).

(4) Observe if there exists any eccentricity of the spindle and if necessary replace it.

(5) Measure the oil temperature using a partial immersion thermometer and note it down.

6.1.4 Computerized Data Analysis

(1) Calculate the value of the constant K_1 using the nominal value of the viscosity of the standard oil and record it in the viscosity calculation file.

(2) From the results of the calibration of the spindle perform a least squares fit on the equation:

$$\tau + \pi K_1 \omega + K_2 = 0$$

where τ is the viscometer reading,
K_1 and K_2 are instrument constants

n = shear viscosity of material under investigation

ω = rotation speed

and calculate the value of K_1.

(3) From the viscosity measurements, using the value of K_1 derived from the spindle calibration, determine values of n and K_2 from the above equation by performing a least squares fit on the data at each temperature.

(4) Using the data obtained in Step 3, perform a 3 - parameter least squares fit of the equation.

$$\text{Log } n = \frac{A}{T-T_0} + B$$

Where A, B and T_0 are fitting parameters.

(5) Record all the raw and analyzed data in the viscosity calibration file.

Procedure for Running the Viscosity
Data Reduction Programs

Equipment List				
Qty	Device	Manufacturer	Model	Calib. Req.
1	Computer	IBM Compatible	XT	NA
1	Monitor	Princeton Graphics Systems	MAX-12	NA
1	Keyboard	AT Style	0318483	NA
1	Printer	Epson	LX80	NA
1	Visco Software Package			

Procedure

Note: <CR> indicates the "enter" key on the keyboard.

(1) Turn the computer, monitor, and printer on.

(2) Type C:<CR>.

(3) CD\QBASIC <CR>.

(4) Type VISCO <CR>.

(5) Answer all the prompts and input the data as requested.

(6) Repeat the calculation with different values of To, varying To in steps of 10°, until the variance is a minimum.

(7) On answering no to the prompt of whether to perform another calculation, a printout of the latest set of data will be obtained and the program will be exited.

(8) Turn off the computer.

6.2 Microstructural Characterization of Glasses

6.2.1 Heat Treatment of Glass Samples

6.2.1.1 Equipment and Supplies

Qty	Device	Manufacturer	Model	Calib. Req.
1	Furnace	Lindberg	51848	NA
1	Annealing	Neytech	85M	NA
	Thermocouples		Type K	I
1	Digital Thermometer	Fluke	52	I
	Clay Combustion Crucibles	Leco		NA
	95% Platinum/5% Gold Crucible			NA
1	Crucible tongs			NA

Notes: I. Calibration to be carried out every six months or on every replacement with a new thermocouple. Calibration Accuracy: ± 10°C.

6.2.1.2 Procedure

Note: If the sample is radioactive steps 1-4 are to be carried out in the left hand glove box in Room 38

1. Place the glass sample in a plastic bag.

2. Break the glass into pieces small enough to enter the crucible by shattering the sample with a hammer.

3. If the sample comes in a crucible, remove pieces of the shattered crucible before continuing.

4. Transfer the glass pieces into the crucible by hand using a double pair of gloves.

5. Turn on the Lindberg Furnace.

6. Insert the thermocouple into the furnace through the hole in the door.

7. Set the controller on the front of the furnace to reach a temperature of 1100°C.

8. Wait for about 15 minutes for the temperature to reach 1100°C and stabilize.

9. Remove the thermocouple from the door of the furnace and open the door.

10. Place the crucible containing the glass sample into the oven, locate it in the proximity of the inserted thermocouple and close the door.

11. Replace the thermocouple in the furnace through the hole in the door.

12. Press the RECORD Button on the digital thermometer.

13. Wait for the required amount of time while the glass is remelted at 1100°C (Minimum 1 hour).

14. Press the VIEW button on the digital thermometer to check that the maximum and minimum temperatures fell in the range of 1125 to 1075°C. If not, consult the Project Manager.

15. Adjust the Lindberg Furnace controller to achieve the required temperature for heat treatment (this is generally in the range of 600 to 1000°C).

16. When the required temperature for heat treatment is reached record the time in the appropriate laboratory notebook.

17. Press the RECORD button on the digital thermometer.

18. Let the crucible remain in the furnace for the required time as determined by the Project Manager.

Thermoplastic cement,
hot plate, sample mounting
Fixtures for saw, 1" dia.
aluminum or brass polishing
stubs

Lubricants:

Dia-cut
Kerosene or isocut fluid
De-ionized water

Grinding/Polishing Media:

30μm Grid-abrade
12μm Grid-abrade
6μm Grid-abrade
15μm diamond paste on Texmet or nylon
6μm diamond paste on nylon
1μm diamond paste on nylon
0.05μm gamma alumina on microcloth

Cleaning supplies:

Ultrasonic clean, solution of Mr. Clean, tap water, deionized water, Methanol, acetone, tissue wipers.

Sample coating supplies:

Carbon electrodes, conductive paint.

6.2.2.2 Procedure

A. CUTTING AND POLISHING

Note: All cutting and polishing of radioactive samples must be performed in the two interconnected glove boxes located in Room 38.

1. If the sample is in a LECO clay crucible

   (a) Cement the crucible containing the glass sample using thermoplastic cement to the glass plate side of the sample holder.

   (b) Attach the mounted sample to the sample holding arm of the Buehler Isomet Saw.

   (c) Adjust the weights on the sample holding arm to produce moderate pressure of the sample against the saw blade.

   (d) Position the sample over the blade of the saw so that the cut will be made in the region of the sample from which the slice is to be taken.

   (e) Turn the power on and adjust the speed of rotation of the saw blade to produce the desired rate of cut.

   (f). Ensure that there is sufficient quantity of Dia-cut lubricant for the blade in the reservoir.

   (g) Gently lower the arm of the saw by hand until sample contacts the rotating blade.

   (h) Cut through the entire sample but do not allow the blade to pass through the glass plate to which it is cemented.

   (i) Lift the arm of the saw and repeat the cutting process after repositioning the sample for the desired thickness (2 or 3 turns of the micrometer screw).

   (j) Remove the slice and free it of all fragments of clay.

   (k) Proceed to Step 3.

2. If the sample is in a 95% Platinum - 5% gold crucible--

   (a) Turn the crucible upside down and tap it gently so that the sample drops out of the crucible.

   (b) Cement the sample using thermoplastic cement to the glass plate side of the sample holder.

   (c) Proceed as in steps 1 (b) through 1 (j).

3. Wash the slice and remainder of the sample together with the sample holder in clean water and wipe dry to remove any fine particles before taking out of the glove box.

4. Remove the remainder of the sample from the mounting plate by placing it on a hotplate to melt the thermoplastic cement.

5. Store the remainder of the sample in an appropriately marked bag.

6. Mount the glass slices on a 1" diameter aluminum or brass polishing stub using thermoplastic cement.

7. Polish the glass slices using the Buehler Minimet Polisher.

   Note: Each step of the polishing process should be carried on as long as required to remove the scratches from previous step. A typical polishing procedure is given below:

   (a) Grind the glass sample on a 30μm diamond Grid-abrade using water as the lubricant. Set the polisher to a speed setting of 6 and time setting of 5 and apply maximum pressure. Continue this process until the surface of the sample shows full contact with the grid surface.

   (b) Clean the glass sample in an ultrasonic cleaner first using a solution of Mr. Clean and water for 30 seconds to 1 minute and then using water alone.

   (c) Repeat step 7 (a) using a 12μm Grid-abrade, half pressure, speed setting of 5 and time setting of 5. Repeat 2-4 times until scratches from the previous step are removed.

   (d) Carry out the cleaning process as in step 7 (b).

   (e) Repeat the grinding/polishing process in step 7 (a) using a 6μm Grid-abrade, half pressure, a speed setting of 5 and a time setting of 5. Repeat 1-2 times to remove any scratches.

   (f) Clean the glass sample as in step 7 (b).

   (g) Polish the sample using 15μm diamond paste on Texmet or Nylon with kerosene or Isocut fluid as the lubricant. Apply full pressure, use a speed setting of 5-9, and a time setting of 5. Repeat as necessary until scratches from the previous

step are removed.

(h) Clean the sample with methanol or acetone using tissue wipers, and then in the ultrasonic cleaner using Mr. Clean and water. Again rinse with tap water in the ultrasonic cleaner before going to the next step.

(i) Repeat the polishing process in step 7 (g) using 6μm diamond paste on nylon with kerosene or Isocut fluid as the lubricant. Apply full pressure, speed 5 and a time setting of 9. Repeat till scratches from the previous step are removed.

(j) Clean as in step 7 (h).

(k) Repeat the polishing process in step 7 (i) using 1 μm diamond paste on nylon with kerosene or Isocut fluid as the lubricant. Apply full pressure, speed setting of 5 and a time setting of 9. Repeat till scratches from the previous step are removed.

(l) Repeat the cleaning process given in step 7 (h).

(m) Repeat the polishing process in step 7 (i) using 0.05μm gamma alumina on microcloth with deionized water a lubricant. Use a speed setting of 5 and a time setting of 4. Repeat till scratches from the previous step are removed.

(n) Repeat the cleaning process given in step 7 (h).

(o) Rinse the sample finally with tap water in the ultrasonic cleaner and wipe dry before removing the sample from the glove box.

B. <u>COATING WITH CARBON</u>

Note: I: If the evaporator system is in the shut down condition open the supply and return cooling water valves.

II: Specimens should be prepared for coating by painting the edge of the specimen and any remaining thermal cement with conductive paint so that a continuous conduction path will exist between the sample surface to be observed and the mounting stub.

1. Close the vent on the belljar.

2. Close the roughing valve.

3. Close the high vacuum valve.

4. Open the foreline valve.

5. Close the mechanical pump vent.

6. Start the mechanical pump.

7. Switch on the thermocouple gauge and note the foreline pressure.

8. Wait for the foreline pressure to reach 100 millitorr or less and then switch on the diffusion pump.

9. Wait for 15 minutes.

10. Switch on the high vacuum gauge and verify that the pressure is in 10^{-5} torr range.

11. Vent the belljar by opening the belljar vent valve.

12. Cautiously unseat the belljar from the base plate and lift it clear of the work area.

13. Loosen the spring-loaded electrode holder and swing it aside.

14. Insert a 1/8th inch flat-ended carbon electrode in a stationary electrode holder and tighten.

15. Insert a 1/8th inch carbon electrode with a sharpened point in the spring-loaded electrode holder and swing the holder back into its operating position adjusting the location of the sharpened carbon to meet with the flat surface of the opposite carbon electrode.

16. When proper positioning has been achieved tighten the sharpened carbon in its holder and tighten the holder.

17. Release the restraint on the spring-loaded electrode holder allowing the carbons to come into contact.

18. Place the samples to be coated directly under the point of contact.

19. Place the polished brass plate adjacent to specimens. This is to be used as an estimator for the coating thickness.

20. Lower the belljar and make sure it is firmly sealed against the base plate by applying downward pressure by hand from the top.

21. Close the belljar vent.

22. Close the foreline valve.

23. Switch on the thermocouple gauge to monitor belljar pressure.

24. Open the roughing valve.

25. Wait for pressure in the belljar to drop to 10 millitorr or less.

26. Close the roughing valve.

27. Open the foreline valve.

28. Switch the thermocouple gauge to read foreline pressure.

29. Open the high vacuum valve slowly (Do not allow the foreline pressure to rise above 50 millitorr).

30. At the same time monitor the high vacuum gauge and try to keep the pressure below 10^{-3} torr by controlling the rate of opening of the high vacuum valve.

31. When the high vacuum valve is fully opened wait at least one minute until the pressure on the high vacuum gauge reads well below 10^{-4} torr.

32. Ensure that the current control knob top of the evacuator is fully counter clockwise.

33. Turn on the Filament Transformer Switch on the lower panel of the vacuum system and advance the current control until a dull red glow is visible at the contact point of the carbons.

34. Allow the system to outgas at this current setting for about 1 minute.

35. Advance the current control knob while monitoring the system current on the top panel meter until the current reaches about 30 amps. (Avoid looking directly at the point of contact between carbons. Some slight sparking is normal when sufficient evaporating current has been reached.)

36. Evaporate for 15 to 30 seconds until reflection on the polished brass plate dims slightly.

37. Turn the current control fully counter clockwise and wait for a minute for the system to cool slightly.

38. Switch off the Filament Transformer.

39. Close the high vacuum valve and vent the belljar.

40. Remove specimens, replace belljar and evacuate the system as in steps 20-31.

<u>To Leave the System in Operating Condition Ensure that:</u>

(a) Belljar vent and roughing valve are closed.

(b) High vacuum valve is open.

(c) Foreline valve is open.

<u>To Shut down the System:</u>

(a) Switch off the diffusion pump

(b) Wait for 15 minutes

(c) Close the high vacuum valve

(d) Close the foreline valve

(e) Turn off the supply and return cooling water

(f) Turn off the mechanical pump

(g) Open the mechanical pump vent

(h) Switch off all gauges

6.2.3 Procedure for Operation of the Scanning Electron Microscope

Manufacturer: JEOL
Model: JSM-35(C)

X-RAY ANALYZER AND IMAGE ANALYSIS SYSTEM

Manufacturer: Tracor Northern (TN)
Model: TN5500

A. OPERATION PROCEDURE FOR SEM

Note: The main power key switch for the SEM is always left ON. When the instrument is not in use the white switch at the lower right on the front panel of the instrument is left in the "unattended operation" position.

1. Press the white toggle switch down from the "unattended operation" position to the normal position.

2. Mount the specimen in the appropriate stage and thread the stage onto the specimen exchange rod.

3. Withdraw the rod fully into the specimen exchange cap until it locks in place.

4. Introduce the mounted specimen into the SEM through the airlock as follows:

   (a) Go to standby setting as below:

      (i) Ensure SEI-BEI switch is in the middle position, and no lights on SEI unit are ON

      (ii) Ensure that Gun Filament knob is turned all the way counter-clockwise

      (iii) Ensure that HV is shut off

   (b) Put the specimen exchange cap on the airlock chamber.

   (c) Push the red button next to the airlock chamber.

(d) Wait until the light in the button goes OFF.

(e) Set the specimen stage control knobs to the following positions: (Tilt: 0 degrees, x: 7.5, Y: 12.5, Rotate: 000)

(f) Open the sliding door all the way.

(g) Push the specimen into the specimen chamber until the stage seats fully on the tapered mounting post.

(h) Unscrew the rod, and withdraw it to the locked position.

(i) Close the sliding door.

(j) Push the red button, remove the airlock chamber specimen exchange cap and store on its holder.

(k) Cover the airlock with the protective dust cover.

5. Select the working distance--15mm for high resolution work and 39mm for routine work and x-ray analysis.

6. Turn on the high voltage switch.

7. Select the KV required (Normally 25 KV is selected for most routine and x-ray work).

8. Turn SEI-BEI switch to SEI. Two red lights on the SEI unit come on.

9. Set the condenser lens knob according to the KV as below: (guidelines only--readjustment may be required)

KV	Lens Position
30 KV or higher	2:00
20 KV - 29 KV	1:00
10 KV - 19 KV	12:00
1 KV - 9 KV	10:00

10. Advance the brightness and contrast knobs on the display monitor to at least half-scale.

11. Switch magnification to minimum (10 or 20).

12. Push in "Rapid 2" and select "Line Profile" by turning the switch (▭. _) to ("___ ___").

    Note: If you do not see the line on the screen adjust the "Brightness" below the screen and then "Brightness" on SEI

13. Increase Gun Filament control until the filament is saturated. Watch the movement of "Line Profile".

    Note: i) If the movement of line profile is too little, increase the "contrast" on the SEI unit.

    ii) The lifetime of a filament will be shortened if the Gun Filament knob is turned beyond the saturation point.

14. Adjust "Gun Bias" until "Load Current" is around 100μA. Readjust the filament saturation. When 10KV or lower is used, use the maximum load current which is less than 100μA.

15. Adjust the two upper "Beam Alignment" knobs and bring the signal line upwards on the monitor as much as possible. (Gun tilt alignment).

16. Adjust the "Medium" objective lens knob until the "Line Profile" has sharp peaks. (Focusing the image).

17. Adjust the "Brightness" and "Contrast" knobs on the SEI unit until the magnitude of the line Profile is about 1½ inch and the bottom of the line Profile is about the middle of the monitor screen.

18. Turn the switch (▭. _) to " ▭ " (picture). An acceptable image should be observed on the monitor. If there is no image or the contrast of the image is too low, adjust the CONTRAST on the display monitor.

19. Go to 20x magnification at 15mm working distance (or 10x at 39mm.) Check the position of the oval shaped image on the monitor screen. Adjust the two lower "Beam Alignment" knobs until this oval image is approximately at the center of the screen.

Readjust the two upper "Beam Alignment" knobs for the maximum brightness.

Note: This step is usually necessary only after changing a filament.

20. An acceptable image should be observed on the monitor. In order to lessen the noise level at "Rapid 2", turn the condenser lens knob 1-2 settings counter-clockwise. In order to obtain a sharper image at a magnification higher than 10000x, turn the condenser lens knob 1-2 settings clockwise.

21. Examine the image on the monitor and identify features of interest.

B. PROCEDURE FOR OBTAINING A PHOTOGRAPH ON SEM

1. Select the area to be photographed.

2. Focus the image carefully by going to higher magnification and using the "Rapid 1" (10 times higher magnification for low magnification 2-3 time higher magnification for high magnification. For magnification above 20000x focus should be done at the magnification in use.

3. Return to the desired magnification for photographing.

4. Push in the "Wave Form Monitor" and "Slow 1" buttons. If nothing appears on the screen, adjust "Brightness" knob below the screen.

5. Adjust the "Brightness" and "Contrast" knobs on the SEI unit. Set the wave form between the top line (white) and the bottom line (black) for the maximum contrast. If the soft contrast is preferred, set the signal between the top line and the second line from the bottom (grey).

6. Push in the "Normal" button in order to return to the image.

7. Insert film in the camera.

8. Push "Photo" and wait for light in "Photo" button to go off.

9. Process the film.

C. STIGMATOR ADJUSTMENT FOR MAGNIFICATION ABOVE 2000x ON SEM

1. Rock the fine focus knob back and forth between under and over focus conditions. Observe that the flow (or striation) of the image will be in the directions at right angles to each other as one goes from under to over focus.

2. Adjust the focusing just to the focus where the flow cannot be seen. This focus is somewhere midway between under and over focus.

3. Increase the "Magnitude" knob of the stigmator by half a turn, then adjust the "orientation" knob until the image becomes sharper.

4. Adjust the "Magnitude" and the "Orientation" controls in order to make the image sharper and repeat this procedure until no improvement in image quality is apparent. At this point going to under or over focus should produce only an uniform smearing of the image rather than perpendicular directions of flow.

5. Adjust the "Fine" objective lens knob for the sharpest image.

D. TO APPLY CORRECTION FACTOR FOR MAGNIFICATION WHEN THE SPECIMEN SURFACE IS NOT FLAT

Note: The working distance remains constant while any of the specimen stage movements are made (x and y translation, tilting and rotation), for a specimen with a relatively flat surface. Therefore, the magnification is always calibrated. In cases when a specimen has no flat surface proceed as follows:

1. In the case that a specimen has a roughness up to about 3mm, adjust the fine-z on the specimen stage such that the area of interest ia at the same level as the top of the specimen holder which is the calibrated level.

2. In cases when the area of interest on a specimen is either much higher or lower than the calibrated level, (more than 3mm roughness), apply a correction factor to the magnification as below:

   a) Measure the vertical distance between the area of interest on a specimen and the top level of the specimen holder which is the calibrated level

   b) Read the correction factor from Figure 2 of section SEMINST-5 of the JSM-35C Scanning Microscope Operator's manual

E. PROCEDURE FOR X-RAY ANALYZER AND IMAGE ANALYSIS SYSTEM (TN)

Note: Normally the TN computer is left ON at all times. When not in use, the SYQUEST cartridges are removed, and the Monitor and Video Copy Processor (VCP) are left OFF. (The rear panel switch of the VCP is left on at all times).

(i) To Start the TN System:

1. Insert Master Cartridge in Drive 1, close the door, wait until the light on the front panel turns from red to green.

2. Turn on the Monitor.

3. Turn on the front panel power switch of the VCP.

4. Ensure that the VCP is configured for analog RGB operation, Frame Mode, and Monitor Mode.

5. If data is to be stored insert appropriate disks in Drives 2, 3, and/or 4.

6. If the TN system does not come ON, carry out the following steps:

   a) Ensure that the Printer in ON LINE

   b) Press the RESET Switch

   c) If still no response is obtained, turn the main power switch off, wait for 15 seconds, and turn it on again

   d) If still no response is obtained, contact the Project Manager

(ii) X-ray Analysis:

1. Ensure that the specimen is at a working distance of 39mm.

2. Insert the x-ray detector (EDS) to the position marked 45.7mm.

3. Center the object of interest in the field of view on the SEM unit.

4. Set up Pulse Processing as below:

a) Press the SET UP on the Soft-pad.

b) Use the Omni control knob to select the desired program.

c) Press the "Enter Dialogue" soft key.

d) If the spectrum is to be obtained in the half memory for a voltage range of 0-10 Kev, select 2048 for the number of channels. If the spectrum is to be obtained for a voltage range of 0 to 20 Kev select 4096 channels.

e) Press the "RETURN" key.

f) Select the amplifier count rate: for maximum resolution use "LOW," for minimum acquisition times use "MED," or "HIGH."

g) Press RETURN.

h) When "Set up Complete" appears on the screen, press the "RUN" button on the soft-pad.

5. Set up the Pulse Height Analyzer (PHA) as below:

a) On the TN press the ACQUIRE button on soft-pad.

b) Select Program 1 (Display PHA status).

c) Press the RUN key on the soft-pad.

d) Check the deadtime displayed and adjust the condenser lens current on the SEM until deadtime reads about 30%.

e) Press the EXIT soft key.

f) Refocus the image if necessary.

6. Acquire an x-ray spectrum as below:

a) Position the beam on the object of interest (SEM).

Note: If the object of interest is smaller than about 5μm in diameter or thickness, the spectrum collected will not be exclusively from the object of interest, but will include some of the adjoining matrix as well. Operator's discretion is required in interpreting such a spectrum.

b) Press the ACQUIRE key on the soft-pad.

c) Enter the parameters for spectrum acquisition.

d) When "Set up complete" appears on screen, press the RUN key on the soft-pad.

e) Note that spectrum acquisition will begin. Accumulated spectral data will be displayed and updated during acquisition.

f) To halt the acquisition prematurely press the STOP key on the soft-pad.

g) Note that acquisition will terminate automatically when the condition set in step 6 (c) is satisfied.

h) Identify peaks by pressing the MARKERS soft-key and the Z-SELECT soft key. Use omni control on keyboard to scan the periodic table.

7. To print the spectrum on C.ITOH printer carry out the following steps:

a) Press the OUTPUT key on the soft-pad.

b) Select the PLOT SPECTRUM program.

c) Select plot size (one half page is usual).

d) Press RETURN. "SET UP COMPLETE" should appear.

e) Set paper on printer at top of the page.

f) Press the RUN button on the soft-pad. A spectrum will be printed out on the printer.

8. For microanalysis carry out the following steps:

   a) Select the area to be analyzed.

   b) Collect the spectrum in the first half of memory.

   c) Load the SQ program.

   d) Identify elements present.

   e) Set up definitions.

   f) Select elements to be analyzed.

   g) Input the conditions of analysis. (Refer to the Tracor-Northern Operating Manual).

   h) Type the command "QUANTIFY" followed by RETURN.

   i) Results of analysis will be printed on the C.ITOH printer when complete.

iii) IMAGE ANALYSIS:

To acquire a Video Image on the TN System:

1. Press the upper sector of the "ENABLE" rocker switch on the trackball box.

2. Load the VISTA program.

3. Use the following soft-key sequence:

   - Acquire
   - Video
   - Image 1 (or 2) as desired
   - Select Resolution (128, 256, 512)

   The image will now be acquired and displayed.

To determine an AREA Fraction

1. Display the image to be analyzed.

2. Use the soft key sequence "Process," "Gray," "Segment."

3. Attach the cursor to one extreme of the video level of the feature or phase of interest.

4. As the cursor is moved, video levels on the image between the cursor and the "attach" point will be colored in. Continue until the entire feature or phase is just colored in.

5. Read the percent of the image colored in directly off the display.

TO ACQUIRE X-RAY MAPS:

1. Use the soft-key sequence "SETUP," X-RAY."

2. Input the parameters for x-ray map acquisition.

3. Redefine any regions of interest that may result in ambiguous results.

4. Acquire maps using the soft-key sequence: "Acquire," "Maps (x-ray)," "64" (or "128" for higher resolution.)

5. Maps will be displayed as acquired, one line at a time.

F. SHUT DOWN PROCEDURE
For SEM unit

1. Set the SEI detector to OFF position.

2. Set the magnification knob to maximum.

3. Set the Scan Generator knob to Slow 2.

4. Set the CONTRAST and BRIGHTNESS knobs on the display monitor to minimum.

5. Turn the Gun Filament knob fully counter-clockwise.

6. Switch off the Accelerating voltage.

7. Switch the SEM unit to "unattended operation" by pushing the white button up.

For the TN system

1. Press the "Drive 1" button, wait until the flashing red light on the unit goes out.

2. Remove disk.

3. If a disk is present in Drive 2, repeat steps 1 and 2 above for it.

4. Remove floppy disks (if any) from drives 3 and 4.

5. Turn off the monitor.

6. Turn off the Video Copy Processor at the front panel switch.

7. Leave the computer ON.

SECTION 7.0

SPECIMEN AND DATA TRACEABILITY AND DOCUMENTATION

Specimens for glass characterization are obtained from the Glass Preparation Laboratory. Samples are recorded in WVCM, UTh or Misc Radioactive glass logs while leaving the Glass Preparation Laboratory. The recipient of the glass dates and signs the log.

Viscosity data are recorded in the laboratory notebook "West Valley Viscosity Measurements." Calibration data and computer printouts are maintained in the "viscosity calculation file".

Details of heat treatment and sample preparation for Scanning Electron Microscope are recorded in the laboratory notebook "Heat Treatment and SEM Sample Preparation". Glass microstructural data and observations are recorded in a separate laboratory notebook.

Title: MELT CONDUCTIVITY DETERMINATION

Document: VSL-7.1-ANL

Issued: 11/90

Revisions

Rev. #	Date
NEW	11/90

Prepared by:

Robert K. Mohr
Project Manager

Approved by:

Pedro B. Macedo
Co-Director, VSL

Richard Sasson
Quality Assurance
Officer, VSL

MELT CONDUCTIVITY DETERMINATION

Equipment and Supplies

Qty	Device	Manufacturer	Model	# Cal.Rec
1	Controller	Love	49	N.A
1	Tube Furnace	VSL		I
1	Split Furnace	ATS Inc.	3320	I
1	Controller	Eurotherm	818P	N.A.
1	Multimeter	Keithly	177	II
1	Compensator	Omega		I
1	Thermocouple		Chromel/ Alumel type K	III
2	Thermocouple		Pt/Pt-Rh type S	I
	Thermocouple Protection tubes			N.A
	Crucible	U.S Quartz		
	Crucible	Engelhard	Platinum	N.A.
1	Thermometer	Fisher		
	Standard Ref. Mat.	NBS	SRM711	
1	Conductivity Probe	VSL	Pt	I
1	Impedance analyzer	Hewlett Packard	4194A	I

I. Calibration frequency: Every six months or sooner if required
Calibration accuracy +_ 7% (see later in this procedure)

II. Calibration: externally every two years

III. Replace after every third run in order to minimize oxidation.

PROCEDURE

A. Conductivity Measurement

(1) Perform instrument compensation using shorted and open terminals.

(2) Measure a precision resistor in the range of the glass resistance, the value to be within 1% of the quoted value.

(3) Perform instrument compensation using shorted and open probe.

(4) Weigh out enough glass to make up ~ 85 ml of melt (based on the density)

(5) Melt the sample at the upper temperature specified by the Project Manager

(6) Lower the probe electrodes into the melt (the electrode immersion depth is ~0.75 cm)

(7) Measure the resistance of the melt at a frequency of 100 Hz

(8) Lower the temperature and repeat step (7) at ~50°C intervals over the temperature range specified by the Project Manager

(9) Raise the temperature and repeat step (7) at ~100°C intervals over the measurement range

(10) Calculate the melt resistivity using the measured resistance and cell constant.

(11) Fit the data to a Fulcher equation. All data points should be within 20°C of the corresponding resistivity data point obtained from the Fulcher fit.

B. Cleaning of the Probe and Platinum Crucible

(1) Raise the probe above the melt and let the excess glass drip into the crucible

(2) Place the probe in a sealed can to cool to room temperature

(3) After the probe has cooled, place it in an HF bath to remove the remaining glass

(4) After the glass has been removed dip the probe in neutralizing solution, rinse it with deionized water and allow to dry

(5) Allow the furnace to cool to room temperature

(6) Remove the crucible and place it in a furnace at up to 1500°C

(7) After the glass temperature has stabilized pour out the glass into a clay crucible for disposal

(8) Place the platinum crucible in a sealed container to cool

(9) After the platinum crucible has reached room temperature place it in an HF bath to remove the remaining glass

(10) After the glass has been removed dip the crucible in neutralizing solution, rinse it with deionized water and allow it to dry

C. Calibration of the Conductivity Measurement System

(1) Perform instrument compensation using shorted and open terminals.

(2) Measure a precision resistor in the range of the glass resistance, the value to be within 1% of the quoted value.

(3) Perform instrument compensation using shorted and open probe.

(4) Measure the complex impedance of NaCl solutions of .01, .1 and .5 normality at 100, 200, 400 1000, 2000, 10,000, 40,000, and 100,000 Hz.

(5) Measure the temperature of the solutions using a thermometer.

(6) The probe immersion depth shall be 0.75 cm.

(7) Plot the real versus the imaginary impedance at each frequency and extrapolate to infinite frequency to obtain $R(\infty)$.

(8) Calculate the solution conductivities, σ, using the relations due to Stogryn (IEEE TRAN on MICROWAVE THEORY and TECH, Aug 1971 p733-736).

(9) Calculate the cell constant (L/A) from the relation:
$L/A = R(\infty)\sigma$.

(10) Perform procedures A. (4)-(10) using SRM 711 glass

(11) The difference between reported and calculated resistivities of SRM 711 shall be within $\pm$ 15%.

1.0 PURPOSE

This procedure describes methods, materials, equipment and special conditions required to perform heat treatment, microstructural characterization, and melt viscosity characterization of nuclear waste glass. This procedure provides the means for obtaining verifiable, reproducible, documented data from tests and experiments.

2.0 APPLICABILITY

This procedure applies to all employees trained and authorized to perform heat treatment, microstructural characterization, and melt viscosity characterization of nuclear waste glass. Specific activities covered by this procedure include: (a) specimen preparation for heat treatment; (b) selection of container for heat treatment: (c) temperature measurement and control, thermocouple calibration; (d) control of redox state; (e) establishment of time-temperature schedule for heat treatments: (f) preparation of specimens for optical microscopy: (g) preparation of specimens for SEM examinations; (h) optical microscopy and photomicrography; (i) SEM examination and associated analytical procedures, namely:

1) X-ray EDS characterization, semi-quantitative and quantitative analysis, and elemental mapping.
2) X-ray WDS characterization. semi-quantitative and quantitative analysis, and elemental mapping.
3) Imaging techniques and photomicrography.

4) Image enhancement and processing.

5) Phase identification isolation and quantification through image analysis.

(j) documentation work, logging of images, photomicrographs, and analytical results in laboratory notebooks; (k) viscometer spindle calibration; (l) rotating spindle viscometer operation; (m) viscometer muffle furnace and temperature controller operation; (n) viscometer spindle cleaning procedure; (o) viscosity data analysis software.

This procedure will be implemented by personnel from the VSL.

3.0 SAFETY

3.1 HAZARDS

The definition of a hazardous chemical is given in Section 8.3 of the CUA Chemical Materials Safety Manual, adopted from the OSHA Hazard Communication Standard. The CUA Chemical Materials Safety Manual is hereafter referred to as the CCMSM. This Standard and its application to CUA facilities are described in Sections 8.1 of the CCMSM, with the exceptions noted in Section 8.28. The types of radioactive material encountered during heat treatment and specimen preparation for microstructural characterization include liquid, solid, and fine particulate. Materials used for viscosity determinations are generally monolithic glass bars but will from time to time include fine particulate samples.

3.2 HAZARD MITIGATION

3.2.1 Identification of Hazards

The identification of radioactive hazards shall be facilitated through an education program including the Radiation Health Physics course referred to in Section 4.1 and other specific directives.

All materials received by personnel in the heat treatment and microstructural characterization program shall be properly labeled and identified, if radioactive, by approved yellow radioactive hazard labels. A geiger counter shall be used regularly to monitor levels of radiation in the work area and identify any sources of radiation.

Viscosity measurements involve the use of hot, molten radioactive glass and all appropriate precautions should be exercised. Heat resistent gloves and tongs shall be used for handling furnace covers, spindles, crucibles, etc. Eye protection shall be worn at all times. A face mask is recommended during removal of the crucible from the furnace due to the potential for shattering. Personnel must ensure that the above-furnace exhaust system is operating over the course of all measurements.

Cleaning of the viscometer spindle involves the use of hydrofluoric acid (HF) solutions and personnel shall familiarize themselves with the particular hazards associated with that material (see Section 5.0). Acid resistent gloves, face protection. and aprons must be worn during this procedure. Personnel shall ensure that HF antidote gel is available near the work area before commencing work with HF.

3.2.2 Handling and Storage of Chemicals

Examination of liquid materials (solutions and suspensions) is not part of the microstructural or viscometric characterization program and shall not be carried out in areas designated for heat treatment, preparation, and examination of specimens. The only place where radioactive liquids will be encountered is in the cutting and polishing operations performed on solid specimens. All such work shall be carried out in a sealed glove box connected to an exhaust line through a HEPA filter. All solid materials resulting from such work shall be washed thoroughly in clean solvents and detergent solutions and dried prior to removal from the glove box to insure that no radioactive particulates or liquids are removed from the glove box with the samples. All radioactive wastes and materials contaminated with radioactivity during specimen preparations shall remain in the glove box until they can be removed for disposal or decontaminated using approved procedures.

Solid materials handled in this work shall not produce levels of radioactivity which create a serious danger to the personnel handling them. All standards set forth in the radiation safety manual of CUA by the radiation safety officer shall be adhered to at all times by those handling radioactive materials of any type. Cutting, grinding, polishing or pulverizing of solid radioactive materials shall only be carried out in a glove box using approved procedures.

Examination of particulate radioactive materials shall only be done if levels of radioactivity are low enough to permit handling without special precautions or if the particulates can be embedded in mounting resins or otherwise immobilized to prevent dispersion of such

materials in the environment and their ingestion or inhalation by handling personnel. Such embedding and immobilization and any further preparation likely to produce additional radioactive liquids or particulates shall be done in the glove box using the procedures outlined above for solid materials. Viscometric measurements made on initially particulate samples requires loading of the crucibles in a glove box and closing the crucible before removal to the viscometer furnace. The crucible should remain lightly covered until the sample has become molten.

3.2.3 Emergencies

Any accident which appears likely to release radioactivity in such a form that it can be ingested or inhaled by personnel, contaminate their person or clothing, or be dispersed in the environment shall be reported to supervisory personnel immediately and dealt with using approved techniques. The release must be confined and all contaminated items removed for decontamination or disposal by approved methods.

3.3 PERSONNEL PROTECTION

Personnel protection shall be effected through education in and familiarization with the hazards of and proper methods of handling radioactive materials. Approved radiation film or TLD badges shall be worn by personnel at all times when they are in areas where exposure to radioactivity above background levels is likely to occur, and these badges shall be collected and

processed monthly. A geiger counter or other approved means of detecting and monitoring levels of radiation shall be available to confirm that levels of radiation in the workplace are within acceptable limits and check for possible contamination of objects and surfaces in areas where radioactive materials are handled.

4.0 REQUIREMENTS

4.1 TRAINING

All glass characterization laboratory personnel are trained in the understanding and use of the technical methods that they will use by the laboratory supervisor or by a trained and experienced person designated by the laboratory supervisor. Upon completion of training for a method, a technician is qualified to use that method independent of direct supervision.

5.0 REFERENCES

Safe Handling of Radioactive Materials, National Bureau of Standards Handbook 92, National Committee on Radiation Protection Report No. 30, U. S. Government Printing Office: Washington, D. C., 1964.

Basic Radiological Health, Course Manual, Health Physics Society, Baltimore-Washington Chapter, 1988, (or most recent edition).

Scanning Electron Microscopy and X-ray Microanalysis, Goldstein, et al., Plenum Press: New York, 1981.

The Electron Microscope Handbook, M. W. Ladd, Ladd Research Industries, Burlington, Vermont: 1973.

Scanning Electron Microscopy, A Student's Handbook, Michael T. Postek, Ladd Research

Industries, Burlington, Vermont: 1980.

Advanced Scanning Electron Microscopy and X-ray Microanalysis. Newbury, et al., Plenum Press: New York, 1986.

Scanning Electron Microscopy, X-ray Microanalysis, and Analytical Electron Microscopy, A Laboratory Workbook, Lyman et al., Plenum Press: New York, 1990.

Principles of Analytical Electron Microscopy, Joy et al., Plenum Press: New York, 1986.

Operating and Maintenance Instructions, 11-1180 Isomet Low Speed Saw, A. Buehler Co.: Lake Bluff, Ill., 1987.

Operating and Maintenance Instructions, 69-1000 Minimet Polisher Grinder, A. Buehler Co.: Lake Bluff, Ill. 1985.

TN5500/5600 System Operation Manuals, Tracor-Northern (Noran Instruments, Inc.): Middleton, WI, 1986 and updates.

JEOL JSM-35C Operator's Manual Japan Electron Optics Ltd.: Tokyo, Japan 1978 and updates.

Radiation Safety Manual of the Catholic University of America, January 1980, W. E. Keene RSO.

Brookfield Viscometer Operation Manual, Brookfield Engineering Laboratories Inc., Stoughton, Mass. 02072.

Improved Apparatus for Rapid Measurement of Viscosity of Glass at High Temperatures, R. L. Tiede, J. Am. Ceram. Soc., paper presented at 61st Ann. meet., May 20, 1959.

Physical Properties of Multicomponent Borosilicate Glasses: A Study of Viscosity, Processing and Durability, E. E. Saad, Ph. D. Dissertation, The Catholic University of America, 1988.

Occupational Health Guideline for Hydrogen Fluoride, U. S. Dept. of Labor, OSHA, Sept., 1978.

Hydrofluoric Acid Dermal Exposure, Vet. Hum. Toxicol. 31, 243 (1989)

Comparative Effectiveness of Topical Treatments for Hydrofluoric Acid Burns, W. M. Bracken et al. Journal of Occupational Medicine, 27, 733 (1985).

6.0 PROCEDURE

6.1 MELT VISCOSITY DETERMINATION

6.1.1 Equipment and Supplies

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Viscometer	Brookfield	Synchralectic	I
1	Remelt Furnace			N.A.
1	Tube Furnace			I
1	Controller	Love	49	N.A.
1	Spindle		Iconel 754	II
	Spindle extensions	Brookfield		N.A.
1	Multimeter	Keithly	177	III
1	Compensator	Omega		N.A.
	Thermocouple	Chromel Alumel type K		N.A.
	Thermocouple	Pt/Pt-Rh type S		N.A.
	Thermocouple	Protection tubes		N.A.
	Crucible	U.S. Quartz		
1	Brass Cylinder			
1	Thermometer	Fisher		
	Standard Viscosity Oil	Cannon	S2000	
	Standard Reference Material	NBS	SRM711	

Calibration codes: I. Calibration frequency: Every six months or every fifteen uses; Calibration accuracy ± 7% (see later in this procedure); II. Calibration is performed prior to every viscosity measurement using a standard oil of known viscosity (see later in this procedure); III. Calibration: externally every two years.

6.1.2 OPERATING PROCEDURE

A. Viscosity Measurement

(1) Calibrate the spindle using the procedure given in Section 6.1.3.2.

(2) Weigh out accurately 85-110g of the glass sample into a quartz crucible and place it in the furnace.

(3) Turn on the power and set the controller temperature to 1150°C unless specified otherwise by the Project Manager.

(4) After attaining the set temperature, allow the furnace temperature to stabilize (i.e. until the change in the Keithly multimeter reading is less than +/-0.03 mV over a period of 10 minutes).

(5) Immerse the calibrated spindle into the melt and attach the spindle hook to the viscometer. Ensure that the spindle is completely immersed in the melt and the spindle tip is about 1 cm above the bottom of the crucible.

(6) Insert the Pt/Pt-Rh thermocouple with its sheath such that the tip of the thermocouple cover is at the top of the glass melt.

(7) Turn on the viscometer and set it to the lowest rotation speed.

(8) Allow the system to attain equilibrium (after a maximum of 70 seconds), and record the reading on the viscometer, the rotation speed in RPM and the temperature indicated by the Pt/Pt Rh thermocouple.

(9) Proceed to the next highest rotation speed of the viscometer and continue as in step (8) until either 50 RPM is reached or the viscometer reading is off scale.

(10) Set the viscometer RPM to the lowest value and cool the furnace by 50+/-10°C. Ensure that the furnace temperature has stabilized as in step (4).

(11) Repeat steps (7) through (10) until the furnace temperature reaches around 900°C.

(12) Remove the Pt/Pt-Rh thermocouple from the crucible and push the thermocouple sheath into the melt.

(13) At the end of the viscosity run continue as in Section C.

B. Cleaning of the Spindle

(1) Separate the spindle from the crucible and hang it in a tube furnace.

(2) Turn on the furnace and set the temperature to 1000 ± 50°C. Allow excess glass on the spindle to drip off.

(3) Turn off the furnace and allow the spindle to attain room temperature.

(4) Don safety equipment and place the spindle in an HF bath overnight.

(5) Inspect the spindle once a day and remove it from the bath when it is clean.

(6) Dip the spindle into the neutralizing solution, rinse it thoroughly and allow it to dry.

(7) Weigh the spindle after each run.

(8) Measure and record the dimensions of the spindle after every 5 runs.

(9) Ensure that the weight and dimension of the spindle fall within 1% of the previous data in order to check if any deterioration of the spindle has occurred. Report any larger deviations to the Project Manager.

C. Finishing the Viscosity Run

(1) Turn the viscometer off and set the furnace temperature to approximately 700°C.

(2) When the controller begins to cycle remove the top insulation using a glove.

(3) Remove the spindle extension by cranking the furnace upward and tilting the extension to the side until the extension falls off the spindle hook.

(4) Remove the extension from the spindle with repeated downward rocking movements.

(5) When the extension is free immediately hook the spindle with Nichrome wire and pull the spindle and crucible out of the furnace.

(6) Ensure that the black ring support falls off.

(7) Lower the spindle and crucible into the brass cylinder.

(8) Close the brass cylinder and let it cool.

(9) If the sample is not radioactive proceed to step (13), however, if the sample is radioactive open the brass cylinder in a glove box after putting on radiation badges and gloves.

(10) Empty the glass into one plastic bag and the spindle into another.

(11) Seal the plastic bags and the cylinder and remove them from the glove box.

(12) Discard the glass in the solid radioactive waste bucket.

(13) Proceed to clean the spindle according to the procedure given in section B.

6.1.3 Calibrations

6.1.3.1 Calibration of the Viscometer

(1) Weigh out accurately 120 ± 5g of the standard SRM-711 glass into a quartz crucible and place it in the furnace.

(2) Proceed as in section A, steps (3) through (12).

(3) Calculate the measure viscosity as in section 6.1.4 below for each temperature of the standard materials studied.

(4) Calculate the percentage error for each of the measured viscosity readings as compared to the nominal values.

(5) Examine the results and report deviation from the required accuracy of ± 7% to the Project Manager.

(6) Report the results in the viscosity calculation file.

6.1.3.2 Calibration of the Spindle

(1) Place the standard oil (Cannon Instrument Company S2000 viscosity oil) in a quartz crucible.

(2) Insert the spindle in the oil as described in step (5) of section A.

(3) Turn on the viscometer and record the viscometer readings at the various rotation speeds as in section A from step (7) to (9).

(4) Observe if there exists any eccentricity of the spindle and if necessary replace it.

(5) Measure the oil temperature using a partial immersion thermometer and note it down.

6.1.4 Computerized Data Analysis

(1) Calculate the value of the constant K_1 using the nominal value of the viscosity of the standard oil and record it in the viscosity calculation file.

(2) From the results of the calibration of the spindle perform a least squares fit on the equation:

$$\tau + n K_1 \omega + K_2 = 0$$

where τ is the viscometer reading,
K_1 and K_2 are instrument constants

n = shear viscosity of material under investigation

ω = rotation speed

and calculate the value of K_1.

(3) From the viscosity measurements, using the value of K_1 derived from the spindle calibration, determine values of n and K_2 from the above equation by performing a least squares fit on the data at each temperature.

(4) Using the data obtained in Step 3, perform a 3 - parameter least squares fit of the equation.

$$\text{Log } n = \frac{A}{T-T_0} + B$$

Where A, B and T_0 are fitting parameters.

(5) Record all the raw and analyzed data in the viscosity calibration file.

Procedure for Running the Viscosity
Data Reduction Programs

Equipment List				
Qty	Device	Manufacturer	Model	Calib. Req.
1	Computer	IBM Compatible	XT	NA
1	Monitor	Princeton Graphics Systems	MAX-12	NA
1	Keyboard	AT Style	0318483	NA
1	Printer	Epson	LX80	NA
1	Visco Software Package			

Procedure

Note: <CR> indicates the "enter" key on the keyboard.

(1) Turn the computer, monitor, and printer on.

(2) Type C: <CR>.

(3) CD\QBASIC <CR>.

(4) Type VISCO <CR>.

(5) Answer all the prompts and input the data as requested.

(6) Repeat the calculation with different values of To, varying To in steps of 10°, until the variance is a minimum.

(7) On answering no to the prompt of whether to perform another calculation, a printout of the latest set of data will be obtained and the program will be exited.

(8) Turn off the computer.

6.2 Microstructural Characterization of Glasses

6.2.1 Heat Treatment of Glass Samples

6.2.1.1 Equipment and Supplies

Qty	Device	Manufacturer	Model	Calib. Req.
1	Furnace	Lindberg	51848	NA
1	Annealing	Neytech	85M	NA
	Thermocouples		Type K	I
1	Digital Thermometer	Fluke	52	I
	Clay Combustion Crucibles	Leco		NA
	95% Platinum/5% Gold Crucible			NA
1	Crucible tongs			NA

Notes: I. Calibration to be carried out every six months or on every replacement with a new thermocouple. Calibration Accuracy: ± 10°C.

6.2.1.2 Procedure

Note: If the sample is radioactive steps 1-4 are to be carried out in the left hand glove box in Room 38

1. Place the glass sample in a plastic bag.

2. Break the glass into pieces small enough to enter the crucible by shattering the sample with a hammer.

3. If the sample comes in a crucible, remove pieces of the shattered crucible before continuing.

4. Transfer the glass pieces into the crucible by hand using a double pair of gloves.

5. Turn on the Lindberg Furnace.

6. Insert the thermocouple into the furnace through the hole in the door.

7. Set the controller on the front of the furnace to reach a temperature of 1100°C.

8. Wait for about 15 minutes for the temperature to reach 1100°C and stabilize.

9. Remove the thermocouple from the door of the furnace and open the door.

10. Place the crucible containing the glass sample into the oven, locate it in the proximity of the inserted thermocouple and close the door.

11. Replace the thermocouple in the furnace through the hole in the door.

12. Press the RECORD Button on the digital thermometer.

13. Wait for the required amount of time while the glass is remelted at 1100°C (Minimum 1 hour).

14. Press the VIEW button on the digital thermometer to check that the maximum and minimum temperatures fell in the range of 1125 to 1075°C. If not, consult the Project Manager.

15. Adjust the Lindberg Furnace controller to achieve the required temperature for heat treatment (this is generally in the range of 600 to 1000°C).

16. When the required temperature for heat treatment is reached record the time in the appropriate laboratory notebook.

17. Press the RECORD button on the digital thermometer.

18. Let the crucible remain in the furnace for the required time as determined by the Project Manager.

Thermoplastic cement,
hot plate, sample mounting
Fixtures for saw, 1" dia.
aluminum or brass polishing
stubs

Lubricants:

Dia-cut
Kerosene or isocut fluid
De-ionized water

Grinding/Polishing Media:

30μm Grid-abrade
12μm Grid-abrade
6μm Grid-abrade
15μm diamond paste on Texmet or nylon
6μm diamond paste on nylon
1μm diamond paste on nylon
0.05μm gamma alumina on microcloth

Cleaning supplies:

Ultrasonic clean, solution of Mr. Clean, tap water, deionized water, Methanol, acetone, tissue wipers.

Sample coating supplies:

Carbon electrodes, conductive paint.

6.2.2.2 Procedure

A. CUTTING AND POLISHING

Note: All cutting and polishing of radioactive samples must be performed in the two interconnected glove boxes located in Room 38.

1. If the sample is in a LECO clay crucible

   (a) Cement the crucible containing the glass sample using thermoplastic cement to the glass plate side of the sample holder.

   (b) Attach the mounted sample to the sample holding arm of the Buehler Isomet Saw.

   (c) Adjust the weights on the sample holding arm to produce moderate pressure of the sample against the saw blade.

   (d) Position the sample over the blade of the saw so that the cut will be made in the region of the sample from which the slice is to be taken.

   (e) Turn the power on and adjust the speed of rotation of the saw blade to produce the desired rate of cut.

   (f) Ensure that there is sufficient quantity of Dia-cut lubricant for the blade in the reservoir.

   (g) Gently lower the arm of the saw by hand until sample contacts the rotating blade.

   (h) Cut through the entire sample but do not allow the blade to pass through the glass plate to which it is cemented.

   (i) Lift the arm of the saw and repeat the cutting process after repositioning the sample for the desired thickness (2 or 3 turns of the micrometer screw).

   (j) Remove the slice and free it of all fragments of clay.

   (k) Proceed to Step 3.

2. If the sample is in a 95% Platinum - 5% gold crucible--

   (a) Turn the crucible upside down and tap it gently so that the sample drops out of the crucible.

   (b) Cement the sample using thermoplastic cement to the glass plate side of the sample holder.

   (c) Proceed as in steps 1 (b) through 1 (j).

3. Wash the slice and remainder of the sample together with the sample holder in clean water and wipe dry to remove any fine particles before taking out of the glove box.

4. Remove the remainder of the sample from the mounting plate by placing it on a hotplate to melt the thermoplastic cement.

5. Store the remainder of the sample in an appropriately marked bag.

6. Mount the glass slices on a 1" diameter aluminum or brass polishing stub using thermoplastic cement.

7. Polish the glass slices using the Buehler Minimet Polisher.

   Note: Each step of the polishing process should be carried on as long as required to remove the scratches from previous step. A typical polishing procedure is given below:

   (a) Grind the glass sample on a 30μm diamond Grid-abrade using water as the lubricant. Set the polisher to a speed setting of 6 and time setting of 5 and apply maximum pressure. Continue this process until the surface of the sample shows full contact with the grid surface.

   (b) Clean the glass sample in an ultrasonic cleaner first using a solution of Mr. Clean and water for 30 seconds to 1 minute and then using water alone.

   (c) Repeat step 7 (a) using a 12μm Grid-abrade, half pressure, speed setting of 5 and time setting of 5. Repeat 2-4 times until scratches from the previous step are removed.

   (d) Carry out the cleaning process as in step 7 (b).

   (e) Repeat the grinding/polishing process in step 7 (a) using a 6μm Grid-abrade, half pressure, a speed setting of 5 and a time setting of 5. Repeat 1-2 times to remove any scratches.

   (f) Clean the glass sample as in step 7 (b).

   (g) Polish the sample using 15μm diamond paste on Texmet or Nylon with kerosene or Isocut fluid as the lubricant. Apply full pressure, use a speed setting of 5-9, and a time setting of 5. Repeat as necessary until scratches from the previous

step are removed.

(h) Clean the sample with methanol or acetone using tissue wipers, and then in the ultrasonic cleaner using Mr. Clean and water. Again rinse with tap water in the ultrasonic cleaner before going to the next step.

(i) Repeat the polishing process in step 7 (g) using 6μm diamond paste on nylon with kerosene or Isocut fluid as the lubricant. Apply full pressure, speed 5 and a time setting of 9. Repeat till scratches from the previous step are removed.

(j) Clean as in step 7 (h).

(k) Repeat the polishing process in step 7 (i) using 1 μm diamond paste on nylon with kerosene or Isocut fluid as the lubricant. Apply full pressure, speed setting of 5 and a time setting of 9. Repeat till scratches from the previous step are removed.

(l) Repeat the cleaning process given in step 7 (h).

(m) Repeat the polishing process in step 7 (i) using 0.05μm gamma alumina on microcloth with deionized water a lubricant. Use a speed setting of 5 and a time setting of 4. Repeat till scratches from the previous step are removed.

(n) Repeat the cleaning process given in step 7 (h).

(o) Rinse the sample finally with tap water in the ultrasonic cleaner and wipe dry before removing the sample from the glove box.

B. <u>COATING WITH CARBON</u>

Note: I: If the evaporator system is in the shut down condition open the supply and return cooling water valves.

II: Specimens should be prepared for coating by painting the edge of the specimen and any remaining thermal cement with conductive paint so that a continuous conduction path will exist between the sample surface to be observed and the mounting stub.

1. Close the vent on the belljar.

2. Close the roughing valve.

3. Close the high vacuum valve.

4. Open the foreline valve.

5. Close the mechanical pump vent.

6. Start the mechanical pump.

7. Switch on the thermocouple gauge and note the foreline pressure.

8. Wait for the foreline pressure to reach 100 millitorr or less and then switch on the diffusion pump.

9. Wait for 15 minutes.

10. Switch on the high vacuum gauge and verify that the pressure is in 10^{-5} torr range.

11. Vent the belljar by opening the belljar vent valve.

12. Cautiously unseat the belljar from the base plate and lift it clear of the work area.

13. Loosen the spring-loaded electrode holder and swing it aside.

14. Insert a 1/8th inch flat-ended carbon electrode in a stationary electrode holder and tighten.

15. Insert a 1/8th inch carbon electrode with a sharpened point in the spring-loaded electrode holder and swing the holder back into its operating position adjusting the location of the sharpened carbon to meet with the flat surface of the opposite carbon electrode.

16. When proper positioning has been achieved tighten the sharpened carbon in its holder and tighten the holder.

17. Release the restraint on the spring-loaded electrode holder allowing the carbons to come into contact.

18. Place the samples to be coated directly under the point of contact.

19. Place the polished brass plate adjacent to specimens. This is to be used as an estimator for the coating thickness.

20. Lower the belljar and make sure it is firmly sealed against the base plate by applying downward pressure by hand from the top.

21. Close the belljar vent.

22. Close the foreline valve.

23. Switch on the thermocouple gauge to monitor belljar pressure.

24. Open the roughing valve.

25. Wait for pressure in the belljar to drop to 10 millitorr or less.

26. Close the roughing valve.

27. Open the foreline valve.

28. Switch the thermocouple gauge to read foreline pressure.

29. Open the high vacuum valve slowly (Do not allow the foreline pressure to rise above 50 millitorr).

30. At the same time monitor the high vacuum gauge and try to keep the pressure below 10^{-3} torr by controlling the rate of opening of the high vacuum valve.

31. When the high vacuum valve is fully opened wait at least one minute until the pressure on the high vacuum gauge reads well below 10^{-4} torr.

32. Ensure that the current control knob top of the evacuator is fully counter clockwise.

33. Turn on the Filament Transformer Switch on the lower panel of the vacuum system and advance the current control until a dull red glow is visible at the contact point of the carbons.

34. Allow the system to outgas at this current setting for about 1 minute.

35. Advance the current control knob while monitoring the system current on the top panel meter until the current reaches about 30 amps. (Avoid looking directly at the point of contact between carbons. Some slight sparking is normal when sufficient evaporating current has been reached.)

36. Evaporate for 15 to 30 seconds until reflection on the polished brass plate dims slightly.

37. Turn the current control fully counter clockwise and wait for a minute for the system to cool slightly.

38. Switch off the Filament Transformer.

39. Close the high vacuum valve and vent the belljar.

40. Remove specimens, replace belljar and evacuate the system as in steps 20-31.

<u>To Leave the System in Operating Condition Ensure that:</u>

(a) Belljar vent and roughing valve are closed.

(b) High vacuum valve is open.

(c) Foreline valve is open.

<u>To Shut down the System:</u>

(a) Switch off the diffusion pump

(b) Wait for 15 minutes

(c) Close the high vacuum valve

(d) Close the foreline valve

(e) Turn off the supply and return cooling water

(f) Turn off the mechanical pump

(g) Open the mechanical pump vent

(h) Switch off all gauges

6.2.3 Procedure for Operation of the Scanning Electron Microscope

Manufacturer: JEOL
Model: JSM-35(C)

X-RAY ANALYZER AND IMAGE ANALYSIS SYSTEM

Manufacturer: Tracor Northern (TN)
Model: TN5500

A. OPERATION PROCEDURE FOR SEM

Note: The main power key switch for the SEM is always left ON. When the instrument is not in use the white switch at the lower right on the front panel of the instrument is left in the "unattended operation" position.

1. Press the white toggle switch down from the "unattended operation" position to the normal position.

2. Mount the specimen in the appropriate stage and thread the stage onto the specimen exchange rod.

3. Withdraw the rod fully into the specimen exchange cap until it locks in place.

4. Introduce the mounted specimen into the SEM through the airlock as follows:

   (a) Go to standby setting as below:

      (i) Ensure SEI-BEI switch is in the middle position, and no lights on SEI unit are ON

      (ii) Ensure that Gun Filament knob is turned all the way counter-clockwise

      (iii) Ensure that HV is shut off

   (b) Put the specimen exchange cap on the airlock chamber.

   (c) Push the red button next to the airlock chamber.

(d) Wait until the light in the button goes OFF.

(e) Set the specimen stage control knobs to the following positions: (Tilt: 0 degrees, x: 7.5, Y: 12.5, Rotate: 000)

(f) Open the sliding door all the way.

(g) Push the specimen into the specimen chamber until the stage seats fully on the tapered mounting post.

(h) Unscrew the rod, and withdraw it to the locked position.

(i) Close the sliding door.

(j) Push the red button, remove the airlock chamber specimen exchange cap and store on its holder.

(k) Cover the airlock with the protective dust cover.

5. Select the working distance--15mm for high resolution work and 39mm for routine work and x-ray analysis.

6. Turn on the high voltage switch.

7. Select the KV required (Normally 25 KV is selected for most routine and x-ray work).

8. Turn SEI-BEI switch to SEI. Two red lights on the SEI unit come on.

9. Set the condenser lens knob according to the KV as below: (guidelines only--readjustment may be required)

KV	Lens Position
30 KV or higher	2:00
20 KV - 29 KV	1:00
10 KV - 19 KV	12:00
1 KV - 9 KV	10:00

10. Advance the brightness and contrast knobs on the display monitor to at least half-scale.

11. Switch magnification to minimum (10 or 20).

12. Push in "Rapid 2" and select "Line Profile" by turning the switch (▭. _) to ("___ ___").

    Note: If you do not see the line on the screen adjust the "Brightness" below the screen and then "Brightness" on SEI

13. Increase Gun Filament control until the filament is saturated. Watch the movement of "Line Profile".

    Note: i) If the movement of line profile is too little, increase the "contrast" on the SEI unit.

    ii) The lifetime of a filament will be shortened if the Gun Filament knob is turned beyond the saturation point.

14. Adjust "Gun Bias" until "Load Current" is around 100μA. Readjust the filament saturation. When 10KV or lower is used, use the maximum load current which is less than 100μA.

15. Adjust the two upper "Beam Alignment" knobs and bring the signal line upwards on the monitor as much as possible. (Gun tilt alignment).

16. Adjust the "Medium" objective lens knob until the "Line Profile" has sharp peaks. (Focusing the image).

17. Adjust the "Brightness" and "Contrast" knobs on the SEI unit until the magnitude of the line Profile is about 1½ inch and the bottom of the line Profile is about the middle of the monitor screen.

18. Turn the switch (▭. _) to " ▭ " (picture). An acceptable image should be observed on the monitor. If there is no image or the contrast of the image is too low, adjust the CONTRAST on the display monitor.

19. Go to 20x magnification at 15mm working distance (or 10x at 39mm.) Check the position of the oval shaped image on the monitor screen. Adjust the two lower "Beam Alignment" knobs until this oval image is approximately at the center of the screen.

Readjust the two upper "Beam Alignment" knobs for the maximum brightness.

Note: This step is usually necessary only after changing a filament.

20. An acceptable image should be observed on the monitor. In order to lessen the noise level at "Rapid 2", turn the condenser lens knob 1-2 settings counter-clockwise. In order to obtain a sharper image at a magnification higher than 10000x, turn the condenser lens knob 1-2 settings clockwise.

21. Examine the image on the monitor and identify features of interest.

B. PROCEDURE FOR OBTAINING A PHOTOGRAPH ON SEM

1. Select the area to be photographed.

2. Focus the image carefully by going to higher magnification and using the "Rapid 1" (10 times higher magnification for low magnification 2-3 time higher magnification for high magnification. For magnification above 20000x focus should be done at the magnification in use.

3. Return to the desired magnification for photographing.

4. Push in the "Wave Form Monitor" and "Slow 1" buttons. If nothing appears on the screen, adjust "Brightness" knob below the screen.

5. Adjust the "Brightness" and "Contrast" knobs on the SEI unit. Set the wave form between the top line (white) and the bottom line (black) for the maximum contrast. If the soft contrast is preferred, set the signal between the top line and the second line from the bottom (grey).

6. Push in the "Normal" button in order to return to the image.

7. Insert film in the camera.

8. Push "Photo" and wait for light in "Photo" button to go off.

9. Process the film.

C. STIGMATOR ADJUSTMENT FOR MAGNIFICATION ABOVE 2000x ON SEM

1. Rock the fine focus knob back and forth between under and over focus conditions. Observe that the flow (or striation) of the image will be in the directions at right angles to each other as one goes from under to over focus.

2. Adjust the focusing just to the focus where the flow cannot be seen. This focus is somewhere midway between under and over focus.

3. Increase the "Magnitude" knob of the stigmator by half a turn, then adjust the "orientation" knob until the image becomes sharper.

4. Adjust the "Magnitude" and the "Orientation" controls in order to make the image sharper and repeat this procedure until no improvement in image quality is apparent. At this point going to under or over focus should produce only an uniform smearing of the image rather than perpendicular directions of flow.

5. Adjust the "Fine" objective lens knob for the sharpest image.

D. TO APPLY CORRECTION FACTOR FOR MAGNIFICATION WHEN THE SPECIMEN SURFACE IS NOT FLAT

Note: The working distance remains constant while any of the specimen stage movements are made (x and y translation, tilting and rotation), for a specimen with a relatively flat surface. Therefore, the magnification is always calibrated. In cases when a specimen has no flat surface proceed as follows:

1. In the case that a specimen has a roughness up to about 3mm, adjust the fine-z on the specimen stage such that the area of interest ia at the same level as the top of the specimen holder which is the calibrated level.

2. In cases when the area of interest on a specimen is either much higher or lower than the calibrated level, (more than 3mm roughness), apply a correction factor to the magnification as below:

   a) Measure the vertical distance between the area of interest on a specimen and the top level of the specimen holder which is the calibrated level

   b) Read the correction factor from Figure 2 of section SEMINST-5 of the JSM-35C Scanning Microscope Operator's manual

E. PROCEDURE FOR X-RAY ANALYZER AND IMAGE ANALYSIS SYSTEM (TN)

Note: Normally the TN computer is left ON at all times. When not in use, the SYQUEST cartridges are removed, and the Monitor and Video Copy Processor (VCP) are left OFF. (The rear panel switch of the VCP is left on at all times).

(i) To Start the TN System:

1. Insert Master Cartridge in Drive 1, close the door, wait until the light on the front panel turns from red to green.

2. Turn on the Monitor.

3. Turn on the front panel power switch of the VCP.

4. Ensure that the VCP is configured for analog RGB operation, Frame Mode, and Monitor Mode.

5. If data is to be stored insert appropriate disks in Drives 2, 3, and/or 4.

6. If the TN system does not come ON, carry out the following steps:

   a) Ensure that the Printer in ON LINE

   b) Press the RESET Switch

   c) If still no response is obtained, turn the main power switch off, wait for 15 seconds, and turn it on again

   d) If still no response is obtained, contact the Project Manager

(ii) X-ray Analysis:

1. Ensure that the specimen is at a working distance of 39mm.

2. Insert the x-ray detector (EDS) to the position marked 45.7mm.

3. Center the object of interest in the field of view on the SEM unit.

4. Set up Pulse Processing as below:

a) Press the SET UP on the Soft-pad.

b) Use the Omni control knob to select the desired program.

c) Press the "Enter Dialogue" soft key.

d) If the spectrum is to be obtained in the half memory for a voltage range of 0-10 Kev, select 2048 for the number of channels. If the spectrum is to be obtained for a voltage range of 0 to 20 Kev select 4096 channels.

e) Press the "RETURN" key.

f) Select the amplifier count rate: for maximum resolution use "LOW," for minimum acquisition times use "MED," or "HIGH."

g) Press RETURN.

h) When "Set up Complete" appears on the screen, press the "RUN" button on the soft-pad.

5. Set up the Pulse Height Analyzer (PHA) as below:

a) On the TN press the ACQUIRE button on soft-pad.

b) Select Program 1 (Display PHA status).

c) Press the RUN key on the soft-pad.

d) Check the deadtime displayed and adjust the condenser lens current on the SEM until deadtime reads about 30%.

e) Press the EXIT soft key.

f) Refocus the image if necessary.

6. Acquire an x-ray spectrum as below:

a) Position the beam on the object of interest (SEM).

Note: If the object of interest is smaller than about 5μm in diameter or thickness, the spectrum collected will not be exclusively from the object of interest, but will include some of the adjoining matrix as well. Operator's discretion is required in interpreting such a spectrum.

b) Press the ACQUIRE key on the soft-pad.

c) Enter the parameters for spectrum acquisition.

d) When "Set up complete" appears on screen, press the RUN key on the soft-pad.

e) Note that spectrum acquisition will begin. Accumulated spectral data will be displayed and updated during acquisition.

f) To halt the acquisition prematurely press the STOP key on the soft-pad.

g) Note that acquisition will terminate automatically when the condition set in step 6 (c) is satisfied.

h) Identify peaks by pressing the MARKERS soft-key and the Z-SELECT soft key. Use omni control on keyboard to scan the periodic table.

7. To print the spectrum on C.ITOH printer carry out the following steps:

a) Press the OUTPUT key on the soft-pad.

b) Select the PLOT SPECTRUM program.

c) Select plot size (one half page is usual).

d) Press RETURN. "SET UP COMPLETE" should appear.

e) Set paper on printer at top of the page.

f) Press the RUN button on the soft-pad. A spectrum will be printed out on the printer.

8. For microanalysis carry out the following steps:

   a) Select the area to be analyzed.

   b) Collect the spectrum in the first half of memory.

   c) Load the SQ program.

   d) Identify elements present.

   e) Set up definitions.

   f) Select elements to be analyzed.

   g) Input the conditions of analysis. (Refer to the Tracor-Northern Operating Manual).

   h) Type the command "QUANTIFY" followed by RETURN.

   i) Results of analysis will be printed on the C.ITOH printer when complete.

iii) IMAGE ANALYSIS:

To acquire a Video Image on the TN System:

1. Press the upper sector of the "ENABLE" rocker switch on the trackball box.

2. Load the VISTA program.

3. Use the following soft-key sequence:

   - Acquire
   - Video
   - Image 1 (or 2) as desired
   - Select Resolution (128, 256, 512)

   The image will now be acquired and displayed.

89

To determine an AREA Fraction

1. Display the image to be analyzed.

2. Use the soft key sequence "Process," "Gray," "Segment."

3. Attach the cursor to one extreme of the video level of the feature or phase of interest.

4. As the cursor is moved, video levels on the image between the cursor and the "attach" point will be colored in. Continue until the entire feature or phase is just colored in.

5. Read the percent of the image colored in directly off the display.

TO ACQUIRE X-RAY MAPS:

1. Use the soft-key sequence "SETUP," X-RAY."

2. Input the parameters for x-ray map acquisition.

3. Redefine any regions of interest that may result in ambiguous results.

4. Acquire maps using the soft-key sequence: "Acquire," "Maps (x-ray)," "64" (or "128" for higher resolution.)

5. Maps will be displayed as acquired, one line at a time.

F. SHUT DOWN PROCEDURE
For SEM unit

1. Set the SEI detector to OFF position.

2. Set the magnification knob to maximum.

3. Set the Scan Generator knob to Slow 2.

4. Set the CONTRAST and BRIGHTNESS knobs on the display monitor to minimum.

5. Turn the Gun Filament knob fully counter-clockwise.

6. Switch off the Accelerating voltage.

7. Switch the SEM unit to "unattended operation" by pushing the white button up.

For the TN system

1. Press the "Drive 1" button, wait until the flashing red light on the unit goes out.

2. Remove disk.

3. If a disk is present in Drive 2, repeat steps 1 and 2 above for it.

4. Remove floppy disks (if any) from drives 3 and 4.

5. Turn off the monitor.

6. Turn off the Video Copy Processor at the front panel switch.

7. Leave the computer ON.

SECTION 7.0

SPECIMEN AND DATA TRACEABILITY AND DOCUMENTATION

Specimens for glass characterization are obtained from the Glass Preparation Laboratory. Samples are recorded in WVCM, UTh or Misc Radioactive glass logs while leaving the Glass Preparation Laboratory. The recipient of the glass dates and signs the log.

Viscosity data are recorded in the laboratory notebook "West Valley Viscosity Measurements." Calibration data and computer printouts are maintained in the "viscosity calculation file".

Details of heat treatment and sample preparation for Scanning Electron Microscope are recorded in the laboratory notebook "Heat Treatment and SEM Sample Preparation". Glass microstructural data and observations are recorded in a separate laboratory notebook.

MELT CONDUCTIVITY DETERMINATION

Equipment and Supplies

Qty	Device	Manufacturer	Model	# Cal.Rec
1	Controller	Love	49	N.A
1	Tube Furnace	VSL		I
1	Split Furnace	ATS Inc.	3320	I
1	Controller	Eurotherm	818P	N.A.
1	Multimeter	Keithly	177	II
1	Compensator	Omega		I
1	Thermocouple		Chromel/ Alumel type K	III
2	Thermocouple		Pt/Pt-Rh type S	I
	Thermocouple Protection tubes			N.A
	Crucible	U.S Quartz		
	Crucible	Engelhard	Platinum	N.A.
1	Thermometer	Fisher		
	Standard Ref. Mat.	NBS	SRM711	
1	Conductivity Probe	VSL	Pt	I
1	Impedance analyzer	Hewlett Packard	4194A	I

I. Calibration frequency: Every six months or sooner if required
Calibration accuracy +_ 7% (see later in this procedure)

II. Calibration: externally every two years

III. Replace after every third run in order to minimize oxidation.

Title: MELT CONDUCTIVITY DETERMINATION

Document: VSL-7.1-ANL

Issued: 11/90

Revisions

Rev. #	Date
NEW	11/90

Prepared by:

Robert K. Mohr
Project Manager

Approved by:

Pedro B. Macedo
Co-Director, VSL

Richard Sasson
Quality Assurance
Officer, VSL

PROCEDURE

A. Conductivity Measurement

(1) Perform instrument compensation using shorted and open terminals.

(2) Measure a precision resistor in the range of the glass resistance, the value to be within 1% of the quoted value.

(3) Perform instrument compensation using shorted and open probe.

(4) Weigh out enough glass to make up ~ 85 ml of melt (based on the density)

(5) Melt the sample at the upper temperature specified by the Project Manager

(6) Lower the probe electrodes into the melt (the electrode immersion depth is ~0.75 cm)

(7) Measure the resistance of the melt at a frequency of 100 Hz

(8) Lower the temperature and repeat step (7) at ~50°C intervals over the temperature range specified by the Project Manager

(9) Raise the temperature and repeat step (7) at ~100°C intervals over the measurement range

(10) Calculate the melt resistivity using the measured resistance and cell constant.

(11) Fit the data to a Fulcher equation. All data points should be within 20°C of the corresponding resistivity data point obtained from the Fulcher fit.

B. Cleaning of the Probe and Platinum Crucible

(1) Raise the probe above the melt and let the excess glass drip into the crucible

(2) Place the probe in a sealed can to cool to room temperature

(3) After the probe has cooled, place it in an HF bath to remove the remaining glass

(4) After the glass has been removed dip the probe in neutralizing solution, rinse it with deionized water and allow to dry

(5) Allow the furnace to cool to room temperature

(6) Remove the crucible and place it in a furnace at up to 1500°C

(7) After the glass temperature has stabilized pour out the glass into a clay crucible for disposal

(8) Place the platinum crucible in a sealed container to cool

(9) After the platinum crucible has reached room temperature place it in an HF bath to remove the remaining glass

(10) After the glass has been removed dip the crucible in neutralizing solution, rinse it with deionized water and allow it to dry

C. Calibration of the Conductivity Measurement System

(1) Perform instrument compensation using shorted and open terminals.

(2) Measure a precision resistor in the range of the glass resistance, the value to be within 1% of the quoted value.

(3) Perform instrument compensation using shorted and open probe.

(4) Measure the complex impedance of NaCl solutions of .01, .1 and .5 normality at 100, 200, 400 1000, 2000, 10,000, 40,000, and 100,000 Hz.

(5) Measure the temperature of the solutions using a thermometer.

(6) The probe immersion depth shall be 0.75 cm.

(7) Plot the real versus the imaginary impedance at each frequency and extrapolate to infinite frequency to obtain $R(\infty)$.

(8) Calculate the solution conductivities, σ, using the relations due to Stogryn (IEEE TRAN on MICROWAVE THEORY and TECH, Aug 1971 p733-736).

(9) Calculate the cell constant (L/A) from the relation:
$L/A = R(\infty)\sigma$.

(10) Perform procedures A. (4)-(10) using SRM 711 glass

(11) The difference between reported and calculated resistivities of SRM 711 shall be within $\pm$ 15%.

PROCEDURE FOR KINETIC ANALYSIS METHODOLOGY (KPA)

Lockheed KPA Analytical Method (for use on-site at Fernald)

Uranium in Water, Soil/Sediment, and Air Filters
by Pulsed-Laser Phosphorimetry

Working Linear Range:	Greater than 50 ng/L, infinite with dilution
Reporting Limit:	50 ng/L Water; TBD for other matricies
Reporting Units:	Water, mg/L; Solids
Matricies:	Water, soil/sediment

1.0 Scope and Application

1.1 The method covers the determination of uranium in water and soil/sediment in the range of 50mg/L or greater. Samples with uranium levels above the laser phosphorimeter dynamic range may be diluted to bring the concentration to a measurable level. The minimum detectable concentration is approximately 50 ng U/L of water. The nominal sensitivity that may be obtained by this exact method for the other media requires additional performance data.

1.2 The method applies to Analytical Support Level C.

2.0 Method Summary

2.1 The method is based on the use of commercially available laser phosphorimeters to analyze uranium in the sample media.

2.2 The method is useful for the analysis of water either directly, following dilution, or following wet-ashing as required by the sample media.

3.0 Interferences

3.1 Possible interference modes in uranium assays will consist of four types:

3.1.1 Absorption (Inner Filter Effect): Absorption of ultraviolet excitation light (337 nm) is more severe than visible excitation because many prevalent compounds have pi-bonding and absorb strongly in that region. Ferric iron and oxy-anions such as nitrate and organic acids are examples. Visible excitation (425 nm) may be absorbed by yellow solutions; e.g., chromate. Interferences may cause reduced signals and low results.

3.2.1 Lumiphors: Many organic substances, such a humic acids and organic degradation products from incomplete ashing, emit luminescence of varying lifetimes after excitation. Such effects are handled according to the manufacturer's instructions.

3.1.3 Quenching: Shortened triplet-state lifetime and reduced phosphorescence intensities of the excited uranyl complex result when quenching occurs. Reliable result can not be obtained when quenching exceeds 80 to 90%. Reducing agents, such as alcohols, halides except fluoride, and metals with electronic energy levels overlapping those of uranyl ion, are strong quenching agents. Examples are silver, lead, iron (II), manganese (II), and thallium. Results from single time-gated instruments are particularly sensitive to even mild quenching agents such as Al (II), Mg (II), Ca(II), and Sr(II). See the manufacturer's literature for more specific information.

3.1.4 Competing Reactions: For the method to perform well, the uranyl ion must be protected from various intermolecular mechanisms that rapidly quench the uranyl luminescence.

Complexation fulfills this need, an examples of effective agents are phosphoric acid, polyphosphates for uranium analysis is patented by Scintrex, Ltd.; they are very acid sensitive. Nitric acid as low as one molar concentration suppresses complexation of uranyl ion with phosphoric acid which permits increased quenching effects. Uraplex is a stronger complexing agent and is effective in samples containing up to two molar nitric acid.

4.0 Safety Precautions

4.1 The analyst must practice standard laboratory safety procedures as outlined in the laboratory-specific hygiene plan as specified by OSHA regulation 29 CFR Part 1910.1450. Any hazardous waste generated during the procedure, or samples determined to be hazardous, will be disposed of in accordance with applicable federal, state, and local regulations.

4.2 Because hazardous chemicals are used during the method, procedures for handling low level radioactive materials, acids, and/or solvents must be practiced. Personal protective equipment must include goggles for eye protection, gloves for skin protection, and lab coat or apron for clothing protection.

5.0 Sample Collection and Handling

Sample size, container, and preservative requirements are detailed in Section 6.7 and Appendix K of the FEMP SCQ, and they are summarized in Appendix A, Table 6-1.

6.0 Apparatus

6.1 Laser phosphorimeter, meeting the following criteria:

6.1.1 Detection limit: The detectable level for uranium must be 50 mg/L or less.

6.1.2 Dynamic range: The phosphorimeter must handle an analytical range from 50 to 20,000 ng/L. Samples with higher concentrations may be diluted.

6.1.3 Instrumental precision: The precision of repetitive measurements must be within 15% R.S.D.

6.2 Beakers, pipettes, funnels, and volumetric flasks: Class A volumetric glassware is used for standard preparation unless otherwise specified. If samples containing less than 100 ng/L uranium are to be analyzed, digestion vessels (both Teflon and glassware) if used, should be leached in hot, dilute nitric acid to reduce sample contamination from leachable uranium. Liquid scintillation vials, for example, should be hot-acid leached for at least 3 days before use in digestions.

6.3 Ceramic or Vycor containers (casseroles).

6.4 Drying oven: Gravity convection type is recommended, having thermostatic controls to maintain desired temperature and able to reach at least 125 C and able to maintain temperatures within +/-5 C.

6.5 Hot Plate

6.6 Muffle furnace: Able to reach at least 150°C and able to maintain temperatures within +/-15 C.

6.7 Analytical balance: Scale readability of +/- 0.01 g.

6.8 Centrifuge capable of 5000 rpm with timer.

6.9 Electric hot plate/magnetic stirrer: Apparatus should have built in stirrer and stepless temperature controls that can be changed as heating requirements demand.

7.0 Routine Preventive Maintenance

7.1 Perform routine preventive maintenance for the laser phosphorimeter according to the manufacturer's directions.

7.2 All instrument maintenance must be documented in the instrument-specific maintenance logbook, as specified in Section 13 of the SCQ.

7.3 Examine Class A glassware before each use for scratches and cracks and replace as necessary.

8.0 Reagents

8.1 Chemicals must be reagent grade, meeting American Chemical Society (ACS) specifications. In all cases, acids or bases are added to water.

8.2 Water: All references to water, unless otherwise specified, assume the use of ASTM Type II water.

8.3 Nitric acid (HNO_3), 16 M: Concentrated.

8.4 Nitric acid (HNO_3), 1 M: Dilute 60 mL of concentrated HNO_3, to 1 L with water.

8.5 Nitric acid (HNO_3), 3 M: Dilute 189.5 mL of concentrated HNO_3, to 1 L with water.

8.6 Uranium complexant. The source of phosphoric acid, if used, must be selected with care because it has varying levels of uranium impurity. Reagents supplied by laser phosphorimeter manufacturers are recommended because of lower uranium background. Use of URAPLEX can produce better precision and lower detection limits because of the longer phosphorescence lifetimes of the uranyl complex as well as stronger complexes for resistance to quenching.

8.7 Uranium standard: From NIST, or NIST-traceable, or from another nationally recognized agency.

8.8 Hydrogen peroxide (H_2O_2), 30%: Reagent.

9.0 Calibration Procedures

Follow the manufacturer's instructions to calibrate the laser phosphorimeter.

9.1 The laser phosphorimeter must be calibrated annually over the entire calibration range.

9.2 The calibration must be verified weekly or prior to each use with three standards, one each at the extremes and another at the center of the concentration range.

9.3 A single point calibration check must be made with each batch of samples.

10.1 **Sample Preparation**

10.1 Samples may be analyzed with any of three levels of pretreatment. The choice depends on desired detection limit, what is known about the sample source, and the content of quenchers and lumiphors. General guidelines below are followed by specific sample media preparation steps.

10.1.1 Direct: Clear water from municipal supplies or streams can usually be analyzed without dilution. Follow the instructions provided by the phosphorimeter manufacturer.

10.1.2 Dilution: If the desired lower level of determination permits a large dilution, this may be the only sample treatment necessary. Both quenching agents and lumiphors can be diluted to levels of negligible effect. Analyze the dilution according to the instructions provided by the phosphorimeter manufacturer.

10.1.3 Ashing: Most quenching agents are either volatilized or oxidized, and lunimizing substances can be decomposed.

10.2. Water: If sample cannot be analyzed directly or by dilution, wet ash the sample as follows.

10.2.1 Transfer desired aliquot of sample to a beaker and add at least 10% by volume of concentrated nitric acid. Record volume of sample used.

10.2.2 Record comment if presence of any undissolved material is noted.

10.2.3 Carefully evaporate the sample solution to dryness. Caution: Rapid boiling will cause spattering and poor precision.

Note: Substantial organic material will require addition of hydrogen peroxide as a second oxidant. The nitric acid/oxidant may need to be replenished to complete the ashing.

10.2.4 Dissolve residue with 1 M nitric acid and warm; transfer to volumetric flask and dilute to the desired final volume using 1 M nitric acid. Record final volume.

10.3 Glass Fiber Filters

10.3.1 Remove filter from shipping envelope or bag and hold filter over 125 mL platinum dish while cutting it into pieces about 1" by 2" with a cleaned pair of scissors. Transfer any material remaining inside bag to platinum dish.

10.3.2 Place dish with sample in muffle furnace. Ash sample for about 16 hours at 500 C +/- 15 C.

10.3.3 Remove dish and allow to cool.

10.3.4 Completely dampen the sample with a minimum amount of but no more than 10 mL of concentrated HNO_3.

10.3.5 Add 15 mL of concentrated HF in 5 mL portions. Evaporate on hot plate until moist residue remains. Remove dish and allow to cool.

10.3.6 Add 10 mL of concentrated HF and evaporate until residue is almost completely dry.

Remove dish and allow to cool.

10.3.7 Add 10 mL of concentrated HNO_3 and evaporate until sample is lightly fuming and just moist. Remove dish and allow to cool.

10.3.8 Repeat above step (step 10.3.7).

10.3.9 Moisten residue on sides and bottom of dish with 3 M HNO_3. Scrape residue from sides and bottom of dish, and break it up with a Teflon rod. Wash down sides of dish and Teflon rod thoroughly using 3 M HNO_3.

10.3.10 *Return dish to hot plate and evaporate until about 5 mL of solution remains.* Remove dish and allow to cool.

10.3.11 Filter sample using a funnel and Whatman No. 42 filter paper into 50 mL volumetric flask.

10.3.12 Wash out dish using three small portions (less than 5 mL each) of 3 M HNO_3.

10.3.13 Wash down filter and residue with three small portions (less than 5 mL each) of 3 M HNO_3.

10.3.14 Make up contents of volumetric flask to 50 mL with 3 M HNO_3, stopper, and mix thoroughly.

10.3.15 Continue with Sample Analysis, Section 11.0

10.4 Soil/Sediment

10.4.1 Dry sample at 100 C /- 5 C until visible dry.

Note: Use FEMP procedure FM-CON-0190 to determine percent moisture (soils) or percent solids (sediment), if requested.

10.4.2 Weigh an appropriate amount of the dried soil/sediment sample to meet the required sensitivity and transfer to casserole. Record exact (dry) weight used.

Heat casserole containing sample in oven. Muffle for 2 hours at 200 C +/- 15 C. Remove and cool.

10.4.3 Transfer sample to 250 mL beaker, rinsing casserole with 10 mL portions of 16 M HNO_3, to a final volume of 60 mL of nitric acid.

10.4.4 Carefully add 30 mL each of 16 M HNO_3 and digest on a hot plate with some stirring for an additional hour.

10.4.5 Remove from hot plate and cool to room temperature. Slowly add 20 mL of 16 M HNO_3, and heat on hot plate with some stirring until solution has evaporated to liquid volume of approximately 10 mL.

10.4.6 Add 50 mL of water, and digest on hot plate with stirring for 10 minutes to dissolve soluble salts.

10.4.7 Cool and centrifuge sample at 5000 rpm for 5 minutes. Pour off liquid into 100 mL volumetric flask with minimum of 3 M HNO_3. Wash residue with 3 M HNO_3.

If any residue remains, repeat steps 10.4.3 through 10.4.7, combining filtrates in the 100 mL volumetric flask.

10.4.8 Make volume up to 10 mL with 3 M HNO_3. Proceed to Sample Analysis Section 11.0 Sample may require additional dilution before analysis.

11.0 Sample Analysis

Analyze the solution according to the instructions provided by the laser phosphorimeter manufacturer.

12.0 Calculations

12.1 Refer to the laser phosphorimeter manual for appropriate calculation, which varies depending on the instrument model and brand.

12.2 Final results are automatically calculated by computerized instruments.

13.0 Data Package Deliverables

Data package deliverables are determined by the Analytical Support Level and are outlined in the FEMP SCQ or specified in the project specific Sampling and Analysis Plan or the analytical laboratory services contract.

14.0 Quality Control Requirements

Quality Control requirements are determined by the Analytical Support Level and the project specific plan. A specific discussion of each type of QC sample is presented in the SCQ.

Analytical Support Level C and D

Requirement	Frequency*	Acceptance Range	Corrective Action
Blank	1/20	<MDA	Qualify data
LCS	1/20	70 - 130%	Qualify data
Duplicate	1/20	0 - 20% RPD	Qualify data

* or per batch or fraction thereof
\- per matrix

Where LCS Laboratory Control Sample
MDA Minimum Detectable Amount
RPD Relative Percent Difference

15.0 References

Standard Test Method for Trace Uranium in Water by Pulsed-Laser Phosphorimetry, (Draft) ASTM Standard D19.04.005RO. 1992.[1]

Uranium in water, soil/sediment, and air filters by Pulsed-Laser Phosphorimetry, Fernald Laboratory Analytical Method FM-RAD-0120.[1]

[1]This procedure differs from the above referenced procedures with respect to digestion of soils in

HNO_3/HF. The Fernald and ASTM methods call for heated concentrated HNO_3/HF digestion. This method will remove occluded uranium from refractory silicates and surficial contamination. Use of HF ensures removal of occluded uranium from refractory silicates. Since existing data or Fernald soils and Lockheed's analysis of Fernald soils indicates that the contamination is surficial use of HF is not necessary to obtain accurate measurements of total uranium. Consequently this procedure calls for a heated HNO_3 digestion.

PROCEDURE FOR CHARACTERIZATION OF PHYSICAL PROPERTIES AND CARBON CONTENT OF WASTES AND GLASS

1) Thermogravemetric analysis
2) Analysis of carbon content
3) Specific gravity
4) Particle size analysis

Procedure for Characterization of Physical Properties and Carbon Content of Wastes and Glass

Table of Contents

1.0 Purpose

2.0 Applicability

3.0 Safety

- 3.1 Hazards
- 3.2 Hazard Mitigation
  - 3.2.1 Identification of Hazards
  - 3.2.2 Handling and Storage of Chemicals
  - 3.2.3 Emergencies
- 3.3 Personnel Protection

4.0 Requirements

- 4.1 Training

5.0 Prerequisites

6.0 Operational Procedures

- 6.1 Thermogravimetric Analysis
- 6.2 Analysis of Carbon Content
- 6.3 Specific Gravity
- 6.4 Particle-Size Analysis

7.0 Specimen Control/Traceability

8.0 Record Keeping

9.0 References

10.0 Appendix

1.0 PURPOSE

This procedure describes the characterization of feed materials such as soil, sludge or fly ash in terms of its thermogravimetric properties, carbon content, specific gravity and particle size distribution. This procedure also provides the means for obtaining verifiable, reproducible, documented data from all tests performed.

2.0 APPLICABILITY

This procedure applies to all VSL personnel trained and authorized to handle radioisotope-containing samples. Activities covered by this procedure include:

(a) Thermogravimetric analysis
(b) Analysis of total carbon or total organic carbon
(c) Specific gravity determination
(d) Particle-size analysis - sieving
(e) Sample accounting for traceability

3.0 SAFETY

3.1 Hazards

3.1.1 Chemical Hazards

The definition of a hazardous chemical is given in Section 8.3 of the CUA Chemical Materials Safety Manual, adapted from the OSHA Hazard Communication Standard. The CUA Chemical Materials Safety Manual is hereafter referred to as the CCMSM. This Standard and its application to CUA facilities are described in Sections 8.1 of the CCMSM with the exceptions noted in Section 8.28.

3.1.2 Radioactive Hazards

The radioactive isotopes present in the sample (sludge, soil or fly ash) are the source of radioactive hazard.

3.2 Hazard Mitigation

3.2.1 Identification of Hazards

The identification of chemical hazards should include an education program (Section 8.2 of the CCMSM). This program should include familiarization with the CCMSM as a whole, including the toxic properties of chemicals according to Sections

8.22, 8.23, 8.24 and 8.25 of the CCMSM, other hazards of chemicals classified under Sections 8.9, 8.10, 8.11, 8.12, 8.13, and 8.14 of the CCMSM, chemical handling and storage procedures (see paragraph 3.2.2 below), and emergencies (see paragraph 3.2.3 below). The education program will also include familiarization with the CUA Chemical Hygiene Program (CCHPP) when the document describing this Program is finalized and approved for distribution by the University.

Other elements of hazard identification include the proper use of labels (Section 8.4 of the CCMSM) and of Material Safety Data Sheets (Sections 8.25, 8.26, and 8.27 of the CCMSM). Workplace chemical lists should be compiled, maintained, and made available for employees in accordance with Section 8.31. In addition, a copy of the CCMSM should be kept in the laboratory and its use should be included in the education program cited above. The same should apply to the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University.

3.2.2 Handling and Storage of Chemicals

Handling of chemicals should be conducted according to Section 8.6 of the CCMSM. Storage of chemicals should follow Section 8.8 of the CCMSM. Special precautions should be taken in handling and storage of incompatible chemicals, solvents, compressed gases, and radioactive materials according to Section 8.10, 8.12, 8.13, and 8.14 of the CCMSM, respectively.

Waste disposal of hazardous chemicals should follow procedures established by the CUA Environmental Safety Office according to Section 8.16 of the CCMSM.

3.2.3 Emergencies

Chemical spills should be dealt with according to Section 8.17 of the CCMSM. Fire and fire-related emergencies should be controlled according to Section 8.21 of the CCMSM. Cases of personal contamination should be treated according to Section 8.19 of the CCMSM, cases of injury and illness according to Section 8.18, and cases requiring minor first aid according to Section 8.20.

3.2.4 Radioactive Hazard Mitigation

All rules for control and monitoring of personnel exposure and environmental radiation are described in Chapter 3 of the radiation safety manual of The Catholic

University of America. Application of these rules is the responsibility of each user working in the restricted area (rooms 37 to 40 of Hannan Hall) and the project managers, under the guidance of Dr. Warren E. Keene, Radiation Safety Officer of CUA.

3.3 Personnel Protection

Personnel protection from hazardous chemicals should consist of two elements. The first is familiarization and compliance with the instructions of the CUA Chemical Materials Safety Manual (CCMSM), including identification of hazards (see paragraph 3.2.1 above), handling and storage of chemicals (see paragraph 3.2.2 above), and dealing with emergencies (see Paragraph 3.2.3 above). The second element is familiarization and compliance with the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University. The overall chemical hygiene program (section 8.34 of the CCHP), based on the OSHA Regulation on Occupational Exposure to Hazardous Chemicals in Laboratories, should be followed. In detail, exposure reduction measures (Section 8.35 of the CCHP) will include environmental monitoring (8.35.1), inspections, maintenance and housekeeping (8.35.2), use of protective apparel and equipment (8.35.3), posting of signs and labels (8.35.4) and dealing with accidents and spills (8.35.5). Ventilation of both general laboratory spaces and of special areas and local devices such as chemical fume hoods and glove boxes should follow the instructions of Section 8.36 of the CCHP. Employees should take part in the safety information and training program which exists in the University according to Section 8.37 of the CCHP, and should be informed about the medical program provided by the University in cases of work with hazardous substances according to Section 8.39 of the CCHP. Responsibility for chemical hygiene rests with all employees.

In addition to compliance with the general instructions described in the CUA radiation safety manual, the following rules apply to the protection of personnel working in the restricted area of the Vitreous State Laboratory:

1) All personnel working in the restricted area shall routinely undergo radiation safety training given by the radiation safety officer of CUA or in off-campus courses approved by the CUA RSO (see Section 4.1).

2) The restricted area should remain locked and only workers assigned to this area and project managers should have access to this section. All other persons who need temporary access to the radioactive laboratory shall be accompanied by authorized personnel.

3) Film badges shall be worn by operation personnel upon entering the restricted area. Ring badges and disposable gloves shall be worn when handling radioactive material.

4) Shoe covers are to be worn in the melter room at all times.

5) Any radioactive spill must be cleaned up immediately, checked after cleaning with a survey meter, and the radiation safety officer shall be notified as soon as possible so that wipe tests may be performed. Immediately notify RSO of any unenclosed spills greater than about 100 ml.: phone x 5206, home [redacted]

6) All samples shall be labeled with sample name, date and notebook/page of record indicating sample preparation. All new materials shall be entered into the inventory control file. Any material not in current use must be returned to the storage area in Room 40.

7) Respirators are to be worn as backup protection for operations involving the possible release of contaminated dust.

8) Repairs to equipment involving hazardous operations should not be performed unless under the direction and in the presence of one or more of the following: R. Mohr, H. Hojaji, I. Muller, W. Keene, P.B. Macedo. If alone and a hazardous situation occurs do only what is necessary to prevent a further hazard, and report the problem promptly to your supervisor.

Refer to previous section 3.2.3 for emergency response. Notify Bob Mohr [redacted] Hamid Hojaji [redacted] Isabelle Muller [redacted] or Pedro Macedo [redacted] to obtain assistance. Notify Campus security and or the fire department of fire or serious accident. Security, x 5111. Fire and emergency, dial 9 for outside line, then 911.

4.0 REQUIREMENTS

4.1 Training

All radioactive restricted area workers shall be trained both by the laboratory supervisor regarding their specific duties and by the CUA radiation safety officer.

Documents 10CFR19 and 10CFR20 are available to all restricted area workers. Each restricted area worker must attend a course in radiation safety given by or approved by the CUA RSO.

Training on each technical method and equipment used in radioactive counting is given by the laboratory supervisor and/or by a trained and experienced person designated by the laboratory supervisor until the technician shows competence to use that method without direct supervision.

5.0 PREREQUISITES

5.1 Equipment/Materials List

Thermogravimetric Analysis:

QTY	EQUIPMENT/MATERIAL	MANUFACTURER/MODEL
1	Furnace	Deltech/DT-28-12
1	Furnace	Deltech/DT-28-06
1	Laboratory box furnace	Neytech
1	Balance, 100g	Sartorius/B120S
1	Balance, 1.2kg	Mettler/PL1200
1	Crucible, Pt-Au, 430g	
1	Crucible, Inconel, 500g	
	Fireclay crucibles, 400g	
	Fireclay crucibles, 1.4kg	
	Disposable latex gloves or	
	Disposable vinyl gloves	
	Desiccator	
	Crucible tongs	
	Green goggles	
	Glovebox	

Carbon Content Analysis:

QTY	EQUIPMENT/MATERIAL	MANUFACTURER/MODEL
1	Total organic carbon analyzer	Dohrmann/DC-80
1	Boat sampling module	Rosemount Analytical/183
3	Platinum boat, P/N 511-793	Rosemount Analytical
1	Stopwatch/Timer	
	Soap film bubble meter	
	Tweezers	
	20mL Glass or polystyrene vials	
	250mL Amber bottles	
	Spatula	
	Mortar and pestle, Diamonite	
	Quartz wool	
	Oxygen gas cylinder	

Note: Refer to the ASTM procedures in the appendix for the rest of the apparatus/equipment required in the specific gravity and particle-size analysis. For the calibration of the above listed equipment refer to the prerequisites section of the Glass Preparation and Minimelter procedure, TPI-GP.WVN.

6.0 Operational Procedures

6.1 Thermogravimetric Analysis of Soils, Sludges and Fly Ash

Note: The analysis should normally be performed in a platinum crucible (Pt-Au or Pt-Rh) but clay or inconel crucibles may be used at the direction of the Project Manager. If using a platinum crucible, ensure that no metallic objects come into contact with the hot crucible.

1. Sampling

Soil and fly ash are sampled by the method of quartering. Spread out the contents of the soil or fly ash from its bucket on a large plastic sheet

(obtain approval from Project Manager whether this can be done outside or inside the glovebox or laboratory hood, if outside the glovebox, wear the proper mask to avoid inhalation of hazardous particles), mark off quarters, and take scoop-fulls from each quarter collecting the desired sample volume. The samples obtained may contain large rocks, stones, soil aggregates, roots or vegetation. Consult the Project Manager whether these components are to be included or discarded from the samples for analysis.

For sludges, thoroughly mix the sludge in the drum until homogeneous to ensure that a representative sample is taken.

2. Weigh a clean dry crucible and record the weight in laboratory notebook, VSL #289-92.

3. Place crucible into a plastic bag, pass into glovebox and transfer into it the soil, sludge or fly ash to be analyzed.

4. Remove the crucible with sample from the glovebox, weigh and record the weight. Calculate the weight of the total sample removed and record this value in its corresponding "Daily Removal/Treatment and Chain-of-Custody Record", (Form VSL #19) compiled in laboratory notebook VSL #328-92.

5. Place the crucible with the sample into a furnace.

6. Drying of the samples is done in stages given in the table below unless otherwise specified by the Project Manager.

Temperature	Drying Time
110°C	18 hrs
450°C	4 hrs
850°C	4 hrs
1150°C	4 hrs

7. At each drying stage,

   (a) Set the furnace to the selected temperature and hold for the specified period of time.

   (b) At the conclusion of each drying time, shut off the furnace and allow the sample to cool inside the furnace.

   (c) When the furnace has cooled to around 200°C, (except for the first stage) remove the sample from the furnace and place in a desiccator to cool to room temperature.

   (d) Remove the sample from desiccator, weigh, and record the total mass of dry sample plus crucible.

   (e) Calculate and record the percent weight loss of the sample after drying.

8. After each drying stage, it may be necessary to take a sample of the dried material for analysis, e.g. 5 grams for chemical analysis, (per instruction of Project Manager). In this case, weigh and record the final mass of sample plus the crucible before proceeding to the next drying stage.

9. After completing the last drying stage, the dried material is transferred from the crucible to a clean sealable plastic jar and label indicating sample name (see section 7.0 below), and reference VSL Laboratory Notebook Number.

6.2 Analysis of Carbon Content

The measurement of the carbon content of sludge, flyash or soil samples is done using the Dohrmann DC-80 Carbon Analyzer attached with the 183 Boat Sampling Module (BSM). This system is capable of measuring the total carbon (TC), total organic carbon (TOC), and the inorganic carbon (IC) contents of wastewater, slurries, sludges and solid samples. Refer to the DC-80 Carbon Analyzer Equipment Manual and the Operation Manual of the Boat Sampling Module for additional information on the features and operation of the system.

1. Start-up and calibration

Before attempting operation, verify and check the following:

- the IR detector has been on for at least 2 hours, for temperature stabilization. Ultimate stability is attained after 24 hours.

- the carrier gas (oxygen) is flowing at the detector "out" port in the range of 180-220 mL/min. This is checked using a soap film bubble meter. See Appendix E, page 10-1 of the DC-80 Manual.

- the TOC/POC mode switch on the DC-80 unit is in the TOC position.

- the detector/ppm switch on the DC-80 unit is in the ppm position.

- the disperser at the bottom of the sparger of the BSM is well submerged in acidified (with phosphoric acid, to pH 2) deionized water.

- the mist trap of the BSM should not be more than half filled with water. Empty out if necessary.

- inspect the tin/copper scrubber for presence of water. Replace if necessary.

(a) Turn on the combustion furnace of the Boat Sampling Module (BSM) by switching the power on located on the front panel of the module. Wait for about 15 minutes for furnace to stabilize at 800°C, factory preset temperature.

(b) Turn on the white power switch of the DC-80 unit. The readout will display "----" (indicates no printer connected) and the red indicator (error) is lit. Pressing the start button twice clears the readout to 0.0000 and lights up the green (ready) indicator.

(c) When the green LED indicator on the front panel of the BSM becomes lit, the furnace is stable at about 800°C. (Verify this temperature by following the test procedure specified on page 5 of the BSM Operation Manual).

(d) With the furnace at the desired operating temperature, advance the platinum boat into the furnace to bake for about 2 minutes. This eliminates any

carbonaceous material residing in the boat. Then, retract the boat until it is at the hatch port.

(e) Place tufts of quartz wool in the sample boat, then bake as described in step d. The wool helps promote even vaporization of sample while in the furnace.

(f) Calibrate the system by injecting 40 uL of Potassium Hydrogen Phthalate ($C_8H_5O_4K$, KHP) standard containing 2000 ppm C. This standard is prepared by dissolving 425 mg of KHP in 100 mL deionized water and 0.1 mL of concentrated phosphoric acid (refer to Appendix A, page 6-1 of the DC-80 Manual). Record this calibration data in logbook VSL #329-92.

2. Sample pretreatment

a) Samples containing particulates, such as slurries and suspensions, must be treated for the solids to pass through the needle of the syringe or the tip of a micropipette (consult the Project Manager if the particulates are to be included in the analyses). When the particulates must be included in the analyses, pulverize the sample using a mortar and pestle, or a Tissuemizer or any kind of homogenizer, if available. Samples which can not be pulverized must be analyzed as solid samples. After homogenization, proceed to acidify the sample.

b) For solid samples, pulverization results in greater homogeneity which allows efficient vaporization of the sample in the furnace. Weigh about 50 mg of the pulverized sample and add in 5 mL of deionized water in a 20 mL vial. Thoroughly mix the solution, then proceed to acidify the sample.

c) Acidify the sample with a few drops of concentrated phosphoric or sulfuric acid to pH 2-3, if analyzing for TOC. (For TC analyses, no acidification is necessary. Proceed to sample analysis.)

d) Sparge the acidified sample for 6 minutes in the sample sparging station of the BSM.

3. Sample analysis

a) Check the system calibration by injecting 40uL of 2000 ppm C KHP standard. Recalibrate the system if necessary. (Refer to page 3-5 to 3-9 of the DC-80 Manual).

b) Situate the sample boat at the hatch port.

c) Lift the hatch and transfer the sample to the boat using a micropipette or syringe. (Samples can also be transferred via the septum syringe port of the race tube near the hatch port.) Ensure complete transfer of sample from the syringe or micropipette by touching the needle or pipet tip to the quartz wool. If the boat was recently retracted from the furnace, allow at least 30 seconds for cooling before injecting the sample into it.

d) Close the hatch and wait for 1-2 minutes to allow detector baseline to stabilize.

e) Press the START button of the DC-80 unit and advance the boat into the furnace at about 2 inches per second.

f) Wait 2-8 minutes for the analysis to finish. When the detector signal is essentially back to original base line, the analysis terminates automatically and a beeping sound is activated. If the red (error) light did not come on, the analysis is successful. Record the reading on the display panel in logbook VSL #329-92. If the red light comes on, the analysis is erroneous. Refer to pages 3-9 and 3-10 in the DC-80 Manual for comments on error messages.

g) Retract the boat back to the hatch port when the analysis is finished. Allow the boat to cool down for at least 30 seconds before injecting another sample.

h) Do at least 5 trials per sample.

i) Correct the panel reading given in ppm C (by volume) to ppm C (by weight) in solid samples by correlating the amount of carbon and the concentration of the standard used in the calibration, to the reading obtained on a known weight of sample. (Refer to the sample calculation on pages 9 and 10 of the BSM Operation Manual).

j) Calculate the average of the corrected values and the standard deviation. Record all results in logbook VSL #329-92.

6.3 Specific Gravity

The specific gravity of soil, sludge and fly ash is determined by following ASTM D854-83 - Standard Test Method for Specific Gravity of Soils (see Attachment III

in the Appendix). To determint the specific gravity of glass, the glass sample is crushed to pass No. 10 (2.00 mm) sieve, and then ASTM D854-83 followed.

6.4 Particle Size Analysis

Particle size analysis of soil, sludge and fly ash is done using the ASTM D422-63 - Standard Test Method for Particle-Size Analysis of Soils, and ASTM D421-85 - Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants (see Attachments II and I, respectively, in the Appendix).

7.0 Specimen Control/Traceability

Thermogravimetric Analysis: When a sample of sludge is taken from the drum or soil or fly ash is taken from its bucket for thermogravimetric analysis, the sample removed is recorded in their corresponding "Daily removal/treatment and chain of custody form", (Form VSL #19), compiled in the loose leaf binder, VSL #328-92. This sample removal is also documented in the users laboratory notebook, VSL #289-92 or VSL #300-92. After undergoing the final drying stage, the dried material is transferred to a container with a label indicating its sample name and the process the sample underwent. For example, FE1-D450 in the label, will stand for:

FE1 - Fernald Pit 5
D1150 - D for Dried, 1150 for 1150°C drying temperature

The label will also include the reference VSL laboratory notebook number and page where the process was recorded. This container with the dried sample is stored in the Fernald processed sample storage area temporarily located in room 39.

Carbon Content: All samples for analysis of carbon content (TOC or TC) will be logged in the logbook VSL #329-92 with a description of the sample, name, originator and its reference VSL laboratory notebook #. Any pretreatment process that the sample undergoes e.g. grinding or pulverization, or dissolution in water, shall be recorded in the logbook and the processed samples shall be labeled to reflect its name and reference logbook (VSL #329-92) and page number. All leftover and processed samples are saved and stored temporarily near the Dohrmann Carbon Analyzer while the originator or the responsible

person is notified. All samples are to be returned to the originator who must sign out the samples in the log book, VSL #329-92.

Specific Gravity: Sampling of materials for specific gravity test and its documentation is the same as stated above. Processed samples are not saved and are directly disposed of to a Fernald waste container.

Particle Size Analysis: Sampling of materials for particle size analysis and its documentation is the same as stated above. After sieving the samples, the fractions retained and passing each of the sieves used are collected and placed in a container with a label indicating the sample name and the sieve used, FEa-Sbxxx (a=1 for Pit 5, 2 for Pit 6, 3 for Clearwell, 4 for Fly ash RMIC 877, and 5 for Fly ash RMIC 878. For soils, FEa is replaced with their RMIC #. b=P for fraction passing, R for fraction retained; xxx=the mesh or sieve number.) For example, FE1-SP200 in the label will stand for:

FE1 - Fernald Pit 5
SP200 - Sieved Passing #200 mesh size sieve

or 815-SR10

- 815 - Fernald Soil with RMIC #815
SR10 - Sieved Retained at #10 mesh size sieve (passed the next coarser sieve used in the analysis)

The label has to include the reference laboratory notebook VSL # and page where the process was recorded. The samples generated from particle size analysis are stored in the Fernald processed samples storage area temporarily located in room 39.

8.0 Record Keeping

The following is a list of laboratory notebooks and forms currently in use where all data and activities pertaining to all of the analyses performed on Fernald samples described above are recorded.

1. VSL #289-92 - Thermogravimetric analysis
2. VSL #300-92 - Specific gravity and particle size analysis

3. VSL #328-92 (Loose Leaf Binder) - Daily Removal/Treatment and Chain-of-custody record
4. VSL #329-92 - Carbon content (TOC/TC) analysis logbook
5. VSL #306-92 - Gamma counting record
6. VSL #305-92 - Detector calibration record
7. VSL #326-92 - Sample for radioactive counting logbook
8. VSL Form #19 - Daily Removal/Treatment and Chain-of-custody form

9.0 References

1) Radiation Safety Manual of the Catholic University of America; Warren Keene, RSO, Washington, DC, January 1992

2) 1991 Annual Book of ASTM Standards, Section 4, Volume 04.08, ASTM Philadelphia, PA, 1991

3) Dohrmann DC-80 Total Organic Carbon Analyzer Equipment Manual, Edition 11, July 1986, P/N 915-121

4) Installation and Operation of the 183 Boat Sampling Module, Rosemount Analytical Inc., P/N 915-240, January 1991

10.0 Appendix

List of Attachments

Attachment I - ASTM D421-85 - Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants.

Attachment II - ASTM D422-63 - Standard Test Method for Particle-Size Analysis of Soils.

Attachment III - ASTM D854-83 - Standard Test Method for Specific Gravity of Soils.

Standard Test Method for Specific Gravity of Soils[1]

This standard is issued under the fixed designation D 854; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense. Consult the DoD Index of Specifications and Standards for the specific year of issue which has been adopted by the Department of Defense.

$^{\epsilon 1}$ NOTE—Section 11 was added editorially in September 1990.

1. Scope

1.1 This test method covers determination of the specific gravity of soils by means of a pycnometer. When the soil is composed of particles larger than the No. 4 (4.75-mm) sieve, the method outlined in Test Method C 127 shall be followed. When the soil is composed of particles both larger and smaller than the No. 4 sieve, the sample shall be separated on the No. 4 sieve and the appropriate test method used on each portion. The specific gravity value for the soil shall be the weighted average of the two values (Note 1). When the specific gravity value is to be used in calculations in connection with the hydrometer portion of Method D 422, it is intended that the specific gravity test be made on that portion of the soil which passes the No. 10 (2.00-mm) sieve.

NOTE 1—The weighted average specific gravity should be calculated using the following equation:

$$G_{avg} = \frac{1}{\frac{R_1}{100G_1} + \frac{P_1}{100G_2}}$$

where:

G_{avg} = weighted average specific gravity of soils composed of particles larger and smaller than the No. 4 (4.75-mm) sieve,

R_1 = percent of soil particles retained on the No. 4 sieve,

P_1 = percent of soil particles passing the No. 4 sieve,

G_1 = apparent specific gravity of soil particles retained on the No. 4 sieve as determined by Test Method C 127, and

G_2 = specific gravity of soil particles passing the No. 4 sieve as determined by this test method.

1.2 The values stated in acceptable metric units are to be regarded as the standard.

1.3 *This standard does not purport to address the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 127 Test Method for Specific Gravity and Absorption of Coarse Aggregate[2]

C 670 Practice for Preparing Precision and Bias Statements for Test Methods for Construction Materials[3]

D 422 Method for Particle-Size Analysis of Soils[3]

E 12 Definitions of Terms Relating to Density and Specific Gravity of Solids, Liquids, and Gases[4]

3. Definition

3.1 *specific gravity*—the ratio of the mass of a unit volume of a material at a stated temperature to the mass in air of the same volume of gas-free distilled water at a stated temperature (per Definitions E 12).

4. Significance and Use

4.1 The specific gravity of a soil is used in almost every equation expressing the phase relationship of air, water, and solids in a given volume of material.

4.2 The term "solid particles," as used in geotechnical engineering, is typically assumed to mean naturally occurring mineral particles that are not very soluble in water. Therefore, the specific gravity of materials containing extraneous matter (such as cement, lime, etc.), water-soluble matter (such as sodium chloride), and soils containing matter with a specific gravity of less than one, typically require special treatment or a qualified definition of specific gravity.

5. Apparatus

5.1 *Pycnometer*—Either a volumetric flask having a capacity of at least 100 mL or a stoppered bottle having a capacity of at least 50 mL (Note 2). The stopper shall be of the same material as the bottle, and of such size and shape that it can be easily inserted to a fixed depth in the neck of the bottle, and shall have a small hole through its center to permit the emission of air and surplus water.

NOTE 2—The use of either the volumetric flask or the stoppered bottle is a matter of individual preference, but in general, the flask should be used when a larger sample than can be used in the stoppered bottle is needed due to maximum grain size of the sample.

5.2 *Balance*—Either a balance sensitive to 0.01 g for use with the volumetric flask, or a balance sensitive to 0.001 g for use with the stoppered bottle.

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 28, 1983. Published January 1984. Originally issued as D 854 – 45. Last previous edition D 854 – 58 (1979).

[2] *Annual Book of ASTM Standards*, Vol 04.02.

[3] *Annual Book of ASTM Standards*, Vol 04.08.

[4] *Annual Book of ASTM Standards*, Vol 15.05.

PCT METHODOLOGY

VSL Technical Procedure

Title: Leach Test Procedures

Document: TPI-LT.WVN

Issued: 10/91 Rev #0

Documents Incorporated:

TPI-02.WVN	Rev #0
TPI-LT.WVN	Rev #4
TPI-DP.WVN	Rev #1

Date Issued: 10/91

Prepared by: Aaron Barkatt Aaron Barkatt Project Manager	Shantao Lai Shantao Lai Project Manager
Approved by: Pedro B. Macedo Pedro B. Macedo Co-Director, VSL	C. Sivaprakash C. Sivaprakash Quality Assurance Officer, VSL

This book, in addition to the maintenance/troubleshooting information (as described in paragraph 2 above), should contain the following records:

(a) Calibration chromatograms and curves

(b) Summary of analytical results (the table showing sample designation along with the concentrations of the analyzed anions)

(5) Maintenance/Troubleshooting Book for ICP-MS

This book should contain information on daily maintenance/troubleshooting or corrective action performed.

(6) Calibration of Pipettes

All records of calibration data for pipettes, percentage of error detected should be maintained.

(7) Colorimetry Data

SiO_2 colorimetry data, verification of spectrophotometer accuracy and the spectral records obtained should be documented in addition to maintenance/troubleshooting log book of spectrophotometer.

(8) Other Records

Any round robin tests performed should be documented in a record book. Any general analysis performed in addition to above instrumental analysis should also be recorded in a separate book.

All the above laboratory record books are subjected to periodic surveillances as part of the Quality Assurance Program.

Table of Contents

1.0 Purpose

2.0 Applicability and Characteristics to be Tested

3.0 Safety
- 3.1 Hazards
- 3.2 Hazard Mitigation
  - 3.2.1 Identification of Hazards
  - 3.2.2 Handling and Storage of Chemicals
  - 3.2.3 Emergencies
- 3.3 Personnel Protection

4.0 Requirements
- 4.1 Training
- 4.2 Definitions
- 4.3 Reagents and Standards
- 4.4 Acceptance/Rejection Criteria

5.0 References

6.0 Operational Procedures
- 6.1 Sample Preparation
  - 6.1.1 Ground Sample Preparation
  - 6.1.2 Monolithic Sample Preparation
- 6.2 Leachant Preparation
  - 6.2.1 Procedure for Preparation of DI Water
  - 6.2.2 Procedure for Preparation of Grande Ronde
  - 6.2.3 Procedure for Preparation of EJ-13
- 6.3 Cleaning Procedure
  - 6.3.1 Procedure for Cleaning Monolithic Samples
  - 6.3.2 Cleaning Procedure for Teflon and Steel
  - 6.3.3 Cleaning Ross Type pH Electrodes
- 6.4 Test Procedures
  - 6.4.1 Pulsed Flow Tests
  - 6.4.2 PCT
  - 6.4.3 IAEA
- 6.5 Calibration Procedures
  - 6.5.1 Balance

6.5.2 Pipettes
6.5.3 pH Meter
6.5.4 Oven Thermometers
7.0 Specimen and Data Traceability

8.0 Data Processing
8.1 Pulsed Flow
8.2 PCT
8.3 IAEA

9.0 Accuracy and Reliability of Test Results

10.0 Record Keeping

DOCUMENT REPLACEMENT RECORD

Leaching Tests

Procedure	Description	Rev #	Replaced in this Manual by:
VSL-LT-1.WVN	Ground Sample Preparation	4	Section 6.1.1
VSL-LT-2.WVN	Monolithic Sample Preparation	2	Section 6.1.2
VSL-LT-3.WVN	Procedure for Cleaning Monolithic Samples	1	Section 6.3.1
VSL-LT-4.WVN	Cleaning Procedure for Teflon and Stainless Steel Parts	4	Section 6.3.2
VSL-LT-5.WVN	Procedure for Pulsed Flow Tests	4	Section 6.4.1
VSL-LT-6.WVN	Procedure for IAEA (High Dilution) Tests	4	Section 6.4.3
VSL-LT-7.WVN	Procedure for Cleaning Ross-Type pH Electrodes	4	Section 6.3.3
VSL-LT-8.WVN	Procedure for MCC-3 Tests	5	Dropped
VSL-LT-9.WVN	Procedure for MCC-1 Tests	3	Dropped
VSL-LT-10.WVN	Balance Calibration Check Procedure	5	Section 6.5.1
VSL-LT-11.WVN	Pipette Calibration Check Procedure	5	Section 6.5.2
VSL-LT-12.WVN	pH Meter Calibration Procedure	5	Section 6.5.3
VSL-LT-13.WVN	Procedure for Preparation of Deionized (DI) Water	5	Section 6.2.1
VSL-LT-14.WVN	Procedure for Preparation of Reference Grande Ronde Water (Synthetic Ground Water)	NEW	Section 6.2.2

VSL-LT-15.WVN	Procedure for Preparation of EJ-13 Water	NEW	Section 6.2.3
VSL-LT-16.WVN	Procedure for PCT Tests	5	Section 6.4.2
VSL-LT-17.WVN	Procedure for Calibration of Oven Thermometers	NEW	Section 6.5.4
VSL-DP.3.WVN	Procedure for Running Pulsed Flow Data Analysis Programs	NEW	Section 8.1
VSL-DP-4.WVN	Procedure for Running MCC-3 Data Analysis Programs	NEW	Section 8.2
VSL-DP-5.WVN	Procedure for Running IAEA Data Analysis Programs	NEW	Section 8.3

Rev #0
10/91

1.0 PURPOSE AND OBJECTIVES

These procedures describe methods, materials, equipment and special conditions required to perform leach testing on glasses and other solids. These procedures provide the means for obtaining verifiable, reproducible, documented data from tests and experiments.

The objectives of the leach tests are for: 1) evaluating the chemical durability of glasses; 2) evaluating the radionuclide release properties of nuclear waste glasses; and 3) evaluating whether the glass durability or radionuclide release properties have been consistently controlled during long-term production. Accordingly, its applicability is widespread throughout manufacturing, research, and development. These tests can be used for specification acceptance.

These test methods may be applicable to the evaluation of the chemical durability of glasses and the radionuclide release properties of nuclear waste glasses in natural environments.

2.0 APPLICABILITY AND CHARACTERISTICS TO BE TESTED

These procedures apply to all employees trained and authorized to perform leach testing on glasses and other solids in the VSL. Specific activities covered by these procedures include: (a) Ordering, assembly and cleaning of leach containers; (b) calibration, standardization and monitoring of environmental chambers, balances, volume measurement devices (pipettes), spectrophotometers and pH meters; (c) selection and ordering of chemicals to assure a sufficiently high grade of purity; (d) Operation, maintenance and testing of water purification

system; (e) preparation, storage, pH testing and sampling of leachants (including groundwater); (f) preparation and handling of test specimens, including crushing, sieving, washing, weighing and loading into the leach container in the cases of non-radioactive powdered samples only, and washing, measuring the dimensions, weighing and loading into the leach container in the cases of non-radioactive as well as radioactive monolithic specimens; (g) placing the necessary volume of leachant in the leach container, closing and weighing the leach container, and placing it in an environmental chamber; (h) removing all or part of the leachate at specified intervals and replacing it with fresh leachant; (i) measuring the pH of the leachate; (j) diluting the leachate whenever required with water or acid; (k) sending the leachate for chemical analysis, with a filled Request for Analysis form, for analysis in the analytical chemistry facility and/or the ICP-MS laboratory; (l) checking and compilation of analytical results; (m) documenting all operations in laboratory notebooks.

These procedures will be implemented by personnel from the VSL.

3.0 SAFETY

3.1 HAZARDS

The definition of a hazardous chemical is given in Section 8.3 of the CUA Chemical Materials Safety Manual, adopted from the OSHA Hazard Communication Standard. The CUA Chemical Materials Safety Manual is hereafter referred to as the CCMSM. This Standard and its application to CUA facilities are described in Sections 8.1 of the CCMSM. with the exceptions noted in Section 8.28.

3.2 HAZARD MITIGATION

3.2.1 Identification of Hazards

The identification of chemical hazards should include an education program (Section 8.2 of the CCMSM). This program should include familiarization with the CCMSM as a whole, including the toxic properties of chemicals according to Sections 8.22, 8.23, 8.24 and 8.25 of the CCMSM, other hazards of chemicals classified under Sections 8.9, 8.10, 8.11, 8.12, 8.13 and 8.14 of the CCMSM, chemical handling and storage procedures (see paragraph 3.2.2 below), and emergencies (see paragraph 3.2.3 below). The education program will also include familiarization with the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University.

Other elements of hazard identification include the proper use of labels (Section 8.4 of the CCMSM) and of Material Safety Data Sheets (Sections 8.5, 8.26 and 8.27 of the CCMSM). Workplace chemical lists should be compiled, maintained, and made available for employees in accordance with Section 8.31. In addition, a copy of the CCMSM should be kept in the laboratory and its use should be included in the education program cited above. The same should apply to the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University.

3.2.2 Handling and Storage of Chemicals

Handling of chemicals should be conducted according to Section 8.6 of the CCMSM. Storage of chemicals should follow Section 8.8 of the CCMSM. Special precautions should be

taken in handling and storage of incompatible chemicals, solvents, compressed gases, and radioactive materials according to Sections 8.10, 8.12, 8.13, and 8.14 of the CCMSM, respectively. Unstable chemicals according to Section 8.9 should be excluded from the leach testing laboratory except in cases where the introduction of such a material is required by the project manager. Such a requirement should be made in writing and specify the maximum quantity of the material and the maximum period it may be stored before being discarded. Shock-sensitive chemicals according to Section 8.11 should never be introduced into the laboratory under any circumstances. No work requiring the use of restricted areas according to Section 8.15 should be performed within the leach testing laboratory.

Waste disposal of hazardous chemicals should follow procedures established by the CUA Environmental safety Office according to Section 8.16 of the CCMSM.

3.2.3 Emergencies

Chemical spills should be dealt with according to Section 8.17 of the CCMSM. Fire and fire-related emergencies should be controlled according to Section 8.21 of the CCMSM. Cases of personal contamination should be treated according to Section 8.19 of the CCMSM, cases of injury and illness according to Section 8.18, and cases requiring minor first aid according to Section 8.20.

3.3 PERSONNEL PROTECTION

Personnel protection should consist of two elements. The first is familiarization and

compliance with the instructions of the CUA Chemical Materials Safety Manual (CCMSM), including identification of hazards (see paragraph 3.2.1 above), handling and storage of chemicals (see paragraph 3.2.2 above), and dealing with emergencies (see paragraph 3.2.3 above). The second element is familiarization and compliance with the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University. The overall chemical hygiene program (Section 8.34 of the CCHP), based on the OSHA Regulation on Occupational Exposure to Hazardous Chemicals in Laboratories, should be followed. In detail, exposure reduction measures (Section 8.35 of the CCHP) will include environmental monitoring (8.35.1), inspections, maintenance and housekeeping (8.35.2), use of protective apparel and equipment (8.35.3), posting of signs and labels (8.35.4), and dealing with accidents and spills (8.35.5). Ventilation of both general laboratory spaces and of special areas and local devices such as chemical fume hoods and glove boxes should follow the instructions of Section 8.36 of the CCHP. Employees should take part in the safety information and training program which exists in the University according to Section 8.37 of the CCHP. The leaching laboratory should not conduct operations with hazardous substances which require a special review of laboratory activities under Section 8.38 of the CCHP, viz. reproductive toxins, chemicals which have a high degree of acute toxicity, and chemicals considered select carcinogens. Employees should be informed about the medical program provided by the University in cases of work with hazardous substances according to Section 8.39 of the CCHP. Responsibility for chemical hygiene rests with all employees. Specific chemical hygiene responsibilities as applied to the leach testing laboratory are specified

in Section 8.40 of the CCHP. Leach testing laboratory workers should be familiar with the basic rules and procedures for working with chemicals included in Section 8.41 of the CCHP and should work in full compliance with these rules and procedures. No work with chemicals of high chronic toxicity according to Section 8.41.4 of the CCHP should be carried out in the leach testing laboratory. Animal work, whether involving chemicals of high chronic toxicity according to Section 8.41.5 of the CCHP or not involving chemicals of this type, should not be carried out in the leach testing laboratory.

4.0 REQUIREMENTS

4.1 TRAINING

All leach testing laboratory personnel are trained in the understanding and use of the technical methods that they will use by the laboratory supervisor or by a trained and experienced person designated by the laboratory supervisor. Upon completion of training for a method, a technician is qualified to use that method independent of direct supervision.

4.2 DEFINITIONS

Leachant - The solution that is being used, or is intended for use in leaching. [3]

Leachate - The solution resulting from a leach test. [3]

ASTM Type I water - Purified water with a maximum total matter content of 0.1 mg/L, and electrical conductivity of 0.06 μmho/cm at 25°C, a minimum electrical resistivity of 16.67

MΩ*cm at 25°C, and no detectable soluble silica (consult ASTM D 1193). [1]

Open system tests - A system is closed if during the process under consideration, transfer of matter either into or out of the system takes place, e.g. O_2 and/or CO_2 diffusion into or out of the leach vessel. [6]

Closed system tests - A system is closed if during the process under consideration no transfer of matter either into or out of the system takes place. [6]

Set of samples - Those which have been tested simultaneously in the same oven.

Sample blank - A cleaned test vessel which has been filled with the same amount of leachant as the sample vessels but contains not glass sample.

Pipettes - Calibrated and precleaned pipette tips.

Syringes and Syringe Filters - Precleaned syringes and 0.45 μM syringe filters (for example Gelman #4497).

Sample Vials - Presterilized sample vials and caps.

pH Meter - pH meter with an accuracy of ± 0.2 pH units.

Milli-Q Water Purification System - Water purification system for producing ASTM-Type I water.

Ultrasonic Cleaner - Size to be compatible with cleaning of several leach vessels simultaneously.

High Pressure Air or Freon Pressurized Canister - Pressure to be sufficient to dry sieves after washing.

Ion Selective Electrode - Ion selective electrode for F determination.

CALIBRATIONS

Calibrations - Initially calibrate all instruments used in this test. Perform periodic calibrations during use of the instrument to minimize possible errors due to instrumental drift.

Calibration and Standardization Schedule:

Thermister or thermocouple - Calibrate annually with NIST Standards or ice/boiling water.

Balance - Have the balance calibrated on a monthly basis.

pH meter - Initially and after with commercial buffer solutions that bracket the solution pH being measured.

4.3 Reagents and Standards

Reference Glass - A reference glass of choice, similar in composition to the glass being tested, is to be run in triplicate along with each batch of glasses tested. The reference glass should be traceable to NIST, or a comparable equivalent used.

Multi-element Solution Standard - A reference solution of choice. containing the major elements of the composition of the leachate being tested, is to be submitted along with each batch of leachates for multi-element analysis. The reference solution standard should be traceable to NIST, or a comparable equivalent used and a certified shelf life.

pH Buffers - Commercial pH buffers to bracket the measured pH range of the leachant and leachate.

Ion Standard Solution - The reference solution standard should be traceable to NIST, or a comparable equivalent used.

Reagent Grade Acids - Reagent grad HNO_3 and HF for cleaning of leach vessels.

High Purity Acid - Ultrex high purity concentrated HNO_3 for acidification of leachates.

Solvents - Ethyl Alcohol - 95% pure, reagent grade acetone.

ASTM Type I Water - Type I water shall have a minimal electrical resistivity of 16.67 M Ohm cm at 25°C and a maximum of 20.0 M Ohm cm at 25°C (consult ASTM D 1193).

The source water shall be passed through Milli-RO15 System which contains 6 cartridges (Ful-Flow, Teel, Lifegard, Rogard Prefilter and Milli-Ro-20 Spiral-Wound Reverse Osmosis) and Milli-Q System that consists of five cartridges (Lifegard, Super-C, two of Ion-Exchanger, and Millipore DI-12). Pass the purified water through an in-line conductivity cell to verify its purity.

CHOICE OF LEACH VESSEL

Stainless Steel Vessels - Stainless steel vessels made of 304L are to be used in all tests.

PREPARATION OF VESSELS

Identification of Vessels - A unique identifying number should be permanently etched on each vessel.

Identification of Vessel Cleaning History - Each batch of cleaned leach vessels will be labeled with a unique batch number. A log book of the leach vessel number and date the cleaning is completed shall be kept.

Cleaning of New Stainless Steel Vessels - New 304L stainless steel vessels shall be cleaned by

the following procedure:

Clean the vessels and lids (without the gaskets) ultrasonically in reagent grade acetone for 5 minutes. Clean the vessels and lids ultrasonically in 95%

5.0 REFERENCES

Waste Acceptance Preliminary Specifications (WAPS)

Leach Testing of Immobilized Radioactive Waste Solids, E.D. Hespe, At. Ener. Rev., 9, 195-207 (1971).

Static and Dynamic Tests for the Chemical Durability of Nuclear Waste Glass, Aa. Barkatt et al., Nucl. Chem. Waste Manage., 2, 151-164 (1981).

MCC-1P Static Leach Test Method, in Nuclear Waste Materials Handbook, Materials Characterization Center, J.E. Mendel, Manager, DOE/TIC-11400, Pacific Northwest Laboratory, Richland, WA, September 1983.

MCC-3S Agitated Powder Leach Test Method, in Test Methods Submitted for Nuclear Waste Materials Handbook, Materials Characterization Center, J.E. Mendel, Manager, PNL-3990, Pacific Northwest Laboratory, Richland, WA, May 1984.

The Use of a Flow Test and a Flow Model in Evaluating the Durability of Various Nuclear Waste-Form Materials, Nucl. Chem. Waste Manage., 4, 153-169 (1983).

Development of QC and Predictive Leach Tests for West Valley Glasses, Aa. Barkatt et al., Waste Management '88, Vol. 2, ed. R.G. Post, University of Arizona Board of Regents, Tucson, AZ, 1988, pp. 473-481.

Nuclear Waste Glass Product Consistency Test (PCT) Method, Version 3.0, C. M. Jantzen and N. E. Bibler, Savannah River Laboratory.

The Catholic University of America Chemical Materials Safety Manual, January 1989.

The Catholic University Chemical Hygiene Program, in preparation.

6.0 PROCEDURE

6.1 SAMPLE PREPARATION

6.1.1 GROUND SAMPLE PREPARATION

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Grinder	Retsch	ZM-1	N.A.
1	Sieves			I
1	Mortar & Pestle			N.A.
1	Balance	Mettler	AE160	II
1	Sieve shaker	Tyler		N.A.

Calibration codes: I: See TPI-GP.WVN, Section 5.2.2. Calibration to be performed once. II: Calibration accuracy: ± 1 mg. Calibration frequency: monthly.

Procedure

A. Non-radioactive samples

(1) Break glass sample received from the glass preparation group or the Project Manager into smaller pieces which will fit into the grinder.

(2) Grind the sample using a Retsch ZM-1 grinder.

(3) Fractionate the ground sample according to particie size -40 +60 mesh, <60 mesh, <325 mesh - using a stack of U.S. Standard Brass sieves which are placed

in a Tyler Portable Sieve Shaker.

(4) Store the powders in a glass vials and identify each vial.

B. Radioactive samples (Alternative procedure: Sectopm 6.9 in TPI-GP.WVN)

Note: Work must be performed inside designated glove box in Room 39 following procedures to handle radioactive materials as per instructions of CUA's RSO.

(1) Obtain bar sample from Glass Preparation group.

(2) Place bar into a plastic bag and break up into small pieces using a hammer.

(3) Grind glass pieces with a mortar and pestle.

(4) Fractionate the ground sample according to particle size - 40 + 60 mesh, < 60 mesh, < 325 mesh - using a set of U.S. Standard Brass sieves.

(5) Store the powders in plastic vials and identify each vial with a radioactive label. Keep loaded vials in Room 39.

6.1.2 Monolithic Sample Preparation

Procedure

A. Blocks

(1) Prepare a flat surface on bulk glass using a 360 grit diamond polishing lap. This provides adequate stability for cutting. This step is not necessary if bars are available.

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Faceting Machine	Graves	Mark IV	N.A.
1	Cutting Saw	Graves		N.A.
	Cutting Blades		Red Blazer	N.A.
	Cutting Blades	Felker	D200-L50-MBI/8	N.A.
	Diamond Laps	Various		N.A.
1	Hot plate			N.A.
	Mounting wax			N.A.
	Acetone			N.A.

(2) Shape a parallel piped out of bulk sample using a diamond saw blade (Red Blazer) and smooth surface with a 360 grit diamond polishing lap.

(3) Using a diamond saw blade cut out blocks with dimensions about 15% - 20% greater then those required to give a surface area of 400 mm^2, (e.g. 9.5mm x 9.5mm x 9.5mm).

(4) Smooth out all surfaces using a 600 grit diamond polishing lap mounted on a MARK IV faceting machine, taking care that the end dimensions give a total surface area of $400 \pm 40 mm^2$. Parallelicity is insured by proper use of the faceting machine.

(5) Clean samples with acetone.

(6) Store sample in an envelope or vial identifying it with all pertinent information, i.e., source, sample I.D., dimensions and surface area. Include deviations if calculated.

(7) Document in the appropriate L.N. the preparation of the sample including deviations

from this procedure. Record all pertinent information about the sample, i.e. source, sample I.D., dimensions and surface area, and the laboratory to which it was delivered and the person who received it.

B. Slides

(1) Prepare a flat surface on bulk glass using a 360 grit diamond polishing lap.

(2) Using a diamond saw blade prepare a surface perpendicular to the first one.

(3) Using mounting wax, attach the sample to the cutting jig and set stop such that slices ~ 1 mm thick are produced.

(4) Mount 200 grit diamond cutting blade (Felker D200-L50-MBI/8) on saw.

(5) Mount jig with sample on cutting table and carefully cut slides insuring that feed is slow (~0.3mm/sec.) and smooth.

(6) Using mounting wax, attach individual slices onto a microscope slide.

(7) Using the 200 grit diamond saw blade, cut out samples from the slices such that their total surface area is $400 \pm 40 mm^2$ (e.g. 17mm x 10mm x 1mm).

(8) Detach samples from glass slide by heating up gently, and clean with acetone.

(9) Store sample in an envelope identifying it with all pertinent information, i.e., source, sample I.D., dimensions and surface area. Include deviations if calculated.

(10) Document in the appropriate L.N. the preparation of the sample including deviations from this procedure. Record all pertinent information about the sample, i.e. source, sample I.D., dimensions and surface area, and the laboratory to which it was delivered and the person who received it.

6.2 LEACHANT PREPARATION

6.2.1 Procedure for Preparation of Deionized (DI) Water

A. Specifications for Deionized Water

The definition of deionized water is that it must pass the following specifications.

(1) The resistivity of the water should be greater than 16 MΩ cm. This should be checked at least once a day and recorded on the sign-up sheet in Room 332.

(2) The concentration of silicon in the water should be not greater than 10 parts per billion. This should be checked by carrying out the procedure for silicon analysis (See Analytical Procedures Manual) once a month and the results should be recorded in the "Si Colorimetric Analysis" LN.

(3) The minimum color retention time of potassium permanganate should be 60 minutes. This test should be performed once a month according to the procedure given below.

(a) Prepare a potassium permanganate solution by dissolving 0.0316 g of $KMnO_4$ in 100 ml of water.

(b) Determine the consumption of potassium permanganate by adding 0.20 ml of $KMnO_4$ solution to a mixture of 500 ml of the reagent water and 1 ml of H_2SO_4 in a stoppered bottle. Consider the reagent water as having passed the test if the permanganate color does not disappear completely after standing for one hour at room temperature and record this information in the "Millipore Records" Laboratory Notebook.

Equipment and Supplies

Qty	Device	Manufacturer	Model	Calib. Req.
1	Milli-RO15 System - Containing the following cartridges	Millipore		
	1 Ful-Flow		RWS-5	I
	1 Teel			II
	1 Lifegard		CP20-010-03	III
	1 Rogard Prefilter		CDPR-012-F4	IV
	1 Milli-RO-20 Spiral Wound Reverse Osmosis Cartridge		CDRO-025-SI	V
1	Milli-Q System Containing the following cartridges	Millipore		
	1 Lifegard Prefilter		CP15-010-03	VI
	1 Super-C		CDFC-012-04	VII
	2 Ion-Ex		CDMB-012-02	VIII
	1 Millipore DI-12		CWDI-012-03	IX
1	Conductivity meter	Amber Science		X
	Polyethylene containers			N/A

Calibration notes:

I: Replace when the whole column turns from white to yellow (usually about every two weeks); II: Replace when the Ful-Flow cartridge is replaced; III: Replace when the pressure gauge reads less than 60 psi; IV: Replace when the pressure gauge reads more than 10 psi less than the pressure gauge of the RO cartridge; V: Replace once a year or when the percentage of divalent cations (Mg^{2+}, Ca^{2+}) removed falls below 80% and the percentage of monovalent cations (Na^{+}, K^{+}) removed falls below 65%; VI: Replace when the pressure differential between the first and second cartridge housings is greater than 10 psi; VII: Replace when the permanganate test given in section A.3 fails; VIII: Replace when the resistivity of the Meg-O-Meter falls below 16 M Ω cm; IX: Replace every 3-6 months when on output flow from Milli-Q system drops below 0.5 lit/min; ***(NOTE: All cartridge replacement must be recorded both in "Millipore Records" LN and on labels on the cartridge housings)***X: Self check prior to each use.

B. Operation of the Millipore Water System

(1) Check the water level in the storage reservoir:

(a) If the water level in the tygon tube is lower than the mark on the tube, wait until the water level passes above the mark and then proceed to step 2.

(b) If the water level in the tygon tube is higher than the mark proceed to step 2.

(2) Turn on the pump.

(3) Wait for approximately 5-10 minutes.

(4) Check the resistivity on the resistivity meter:

(a) If the reading is greater than 16 MΩ cm go to step 5.

(b) If the reading is less than 16 M cm consult project manager concerning replacement of cartridges.

(5) Open the final valve and let 1-2 litres of water flow to be sure the line is clean.

(6) Rinse a clean conventional polyethylene container with a small quantity of fresh deionized water.

(7) Collect the required volume of deionized water.

(8) Close the valve and turn off the pump.

(9) Record the volume of water removed on the sign-up sheet in Room 332.

(10) Measure the conductivity of the water using the Amber Science conductivity meter which should be less than 2.5 μ mho cm^{-1}.

(11) Label the container clearly indicating the conductivity of the water and the date on which it was filled.

(12) Remove all unused deionized water after two weeks.

C. Additional Checks on the System

(1) Water from the Milli-RO system.

(a) Determine the concentration of Si in the water every month according to the procedure for silicon analysis (See Analytical Procedures) and record the results in the "Si Colorimetric Analysis" Notebook. If the concentration of silicon is greater than 100 ppb consult the Laboratory Supervisor or Project Manager.

(b) Submit a sample of the water for analysis using the DC Plasma method (see Analytical Procedures) every month and record the results in the "Millipore Records" Notebook.

(2) Deionized Water from the Milli-Q System

(a) Determine the concentration of Si in the water after consultation with the Project Manager on each occasion when important experiments are begun in which very low concentration levels of Si are important according to the procedure for silicon analysis. If the concentration of silicon is greater than 10 ppb consult the Laboratory Supervisor or Project Manager.

(b) Submit a sample of DI water for analysis and DC Plasma method (see Analytical Procedures) after each replacement of the ion exchange cartridge and record the results in the "Millipore Records" Laboratory. Notebook. If discrepancies of greater than 1 ppb

are found for the concentration of silicon from the Si analysis and DC Plasma analytical methods consult the Project Manager.

6.2.2 Procedure for Preparation of Ref. Grande Ronde

Equipment and Supplies

Qty	Device	Manufacturer	Model #	Calib. Req.
	Polyethylene Containers	Nalgene		N.A.
	Volumetric Flasks	Nalgene		N.A.
1	pH Meter	Fisher	Acumet-810 or 910	I

Calibration Notes:
I: Calibration Accuracy: ± 0.05 pH units; Calibration Frequency: Daily or every 25 measurements.

Chemicals

Na_2CO_3 (Sodium carbonate) dried at 120° for two hours and stored in a desiccator

$Na_2SiO_3 \cdot 9H_2O$ Reagent grade sodium silicate

NaOH 50 wt% solution of reagent grade sodium hydroxide

KCl	Reagent grade sodium sulfate dried at 120°C for one hour and stored in a desiccator
Na_2SO_4	Reagent grade sodium sulfate dried at 80°C for one hour and stored in a desiccator
NaF	Reagent grade sodium fluoride dried at 80°C for one hour and stored in a desiccator
HCl	2.00 M Hydrochloric acid
$CaCl_2 \cdot 2H_2O$	Calcium chloride
$MgCl_2 \cdot 6H_2O$	Magnesium chloride

Procedure

(1) Prepare stock solution "A" as follows:

(a) Add 750ml of DI water to a 1 litre volumetric flask.

(b) Add the following chemicals to the above flask as per the quantities given below and stir until they are all dissolved.

Chemical	Quantity (g)
$Na_2SiO_3 \cdot 9H_2O$	14.40
Na_2CO_3	3.80
NaF	2.95

Na_2SO_4	10.2
NaOH (50 wt %)	18.8

(c) Add DI water until the total volume equals exactly 1 litre.

(2) Prepare stock solution "B" as follows:

(a) Add 750 mls of DI water to a 1 litre volumetric flask.

(b) Add the following chemicals to the flask and stir until they are all dissolved.

Chemical	Quantity (g)
KCl	0.262
$CaCl_2 \cdot 2H_2O$	0.4043
$MgCl_2 \cdot 6H_2O$	0.0107
HCl	171.6 ml of 2.00N

(c) Add DI water until the total volume equals exactly 1 litre.

(3) Take 25ml aliquots of Stock Solution A, and Stock Solution B and add to 900ml of DI water.

(4) Measure the pH of the solution.

(5) Bring the above solution to a pH of 9.75 ± 0.1 at room temperature by adding the appropriate quantities of either 0.1N HCl or 0.1N NaOH.

(6) Dilute this solution with DI water to exactly one litre.

(7) Measure the final pH of the solution and transfer a sample to the Analytical Lab for analysis.

(8) Store the remaining solution in a tightly capped polyethylene container.

6.2.3 Procedure for Preparation of EJ-13

A. <u>Removal of Soluble Salts from Crushed Rock</u>

(1) Place 50 g of crushed rock in a 1 litre Teflon bottle.

(2) Add 500 mls of DI water.

(3) Close the bottle and shake vigorously for 2 minutes.

(4) Place the closed bottle upright on a flat surface and allow to stand for at least one hour.

(5) Decant the liquid, taking a sample for anion analysis.

(6) Repeat steps (2) through (5) 3 more times.

(7) Transfer the four solution samples to the Analytical laboratory for analysis for chloride, nitrate and sulfate anions.

(8) If the last rinse solution shows less than 0.5 mg/L of each of chloride, nitrate, and sulfate it is to be concluded that the soluble salts have been removed. If the last rinse solution shows more than 0.5 mg/L, repeat steps (2) through (5) and (7)

Equipment and Supplies

Qty	Device	Manufacturer	Model	Calib. Req.
	Teflon bottles	Savillex		N.A.
1	Oven	Blue-M	Stabil-Therm OV-490A, OV-490A-3	I
1	Dark Storage bottle	Nalgene		N.A.
1	pH meter	Fisher	Acumet 810 or 910	II
1	Filter Holder, 47mm	Millipore		N.A.
1	Filter	Millipore/Nucleopore	0.1 μm	N.A.
	Crushed rock	Topopah Springs	<100 mesh	
	Tuff from Nevada Test site			
	J-13 Well water	from Nevada Test site		
	Sulfuric acid	Acs-Reagent Grade		

Calibration notes:

I: Temperature monitored daily with thermometers that are positioned as recommended by the manufacturer and meet NBS specification, Monograph 150; II: Calibration accuracy: ± 0.05 pH units, Calibration frequency: daily (see section 6.5.3).

above until a level of less than 0.5 mg/L is achieved.

B. Preparation of Equilibrated J-13 Water (EJ-13 water)

(1) To the wet crushed rock (from which the soluble salts have been removed) contained in a 1 litre teflon bottle add J-13 well water until the bottle is about 90% full and mark the level.

(2) Cap the bottle tightly and place it in an oven preheated to 90°C.

(3) Allow the bottle to remain in the oven for about 3 weeks. Shake the bottle for about 1 minute twice a day for the first week, and once a day thereafter.

(4) After three weeks remove the bottle from the oven and allow it to cool for one hour in air.

(5) Filter the solution through a 0.1 micron Millipore or Nucleopore filter using the Millipore filter holder.

(6) Measure the pH of the final solution and store it in a plastic bottle. (Beware: Do not use transparent bottles since algae may grow in the liquid if it is stored in sun light). Transfer a portion of the final solution to the Analytical lab for analysis.

Note: i) The equilibrated liquid should be stable for several months; ii) If the procedure for preparing EJ-13 water had reached step (4) above and there is no immediate use for it, leave the teflon bottle in 90°C oven and when it is needed carry-out the following procedures:

(a) Remove the bottle from the oven and allow it to cool for 1 hour in air.

(b) If less than about 5% of the water has evaporated continue with step (5) above.

(c) If more than about 5% of the water has evaporated add DI H_2O slowly to bring the liquid to the original mark.

(d) Filter through a 0.1 micron Millipore or Nucleopore filter using the Millipore filter holder.

(e) Measure the pH of the final solution and store in a suitable plastic bottle (not transparent). Transfer a portion of the final solution to the Analytical lab for analysis.

C. Preparation of Equilibrated J-13 Water with pH Adjusted to 6.9 ± 1

(1) Take the required amount of the filtered EJ-13 solution and measure its initial pH.

(2) Add dilute sulfuric acid dropwise to the solution until the pH reaches 6.9 ± 1.

(3) If the pH falls below 6.0 add EJ-13 solution to bring the pH up again.

6.3 Cleaning Procedures

6.3.1 Procedure for Cleaning Monolithic Samples

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Ultrasonic Cleaner	Bransonic	B-221	N.A.
1	Vacuum Oven	National Applicances	5831	N.A.
	Ethyl alcohol USP, absolute Reagent Quality			

(1) Place sample in a polystyrene vial.

(2) Add sufficient reagent grade ethanol to cover sample.

(3) Place in ultrasonic cleaner for 5 minutes.

(4) Transfer sample to a new vial; add fresh ethanol again.

(5) Repeat steps (2)-(4) three times.

(6) Place sample in vial in vacuum oven preheated to ~70°C and leave to dry for 20 minutes.

6.3.2 Procedure for Teflon and Steel

A. MCC procedure for cleaning new Teflon containers for IAEA tests. This procedure may be begun at step (3) for used containers.

Teflon containers: 60 ml Savillex-0102

Teflon baskets: Savillex 46SC

(1) Soak for one hour in 6 M HNO_3 + 0.2 M HF.

(2) Rinse with three container volumes of high-purity H_2O.

(3) Soak in 6 M HNO_3 for four hours at 50°C.

(4) Soak for 30 minutes in >60°C high-purity H_2O by full immersion.

(5) Soak for at least eight hours in fresh high-purity H_2O at 80°C by full immersion.

(6) Boil for 30 minutes in fresh high-purity H_2O by full immersion.

(7) Rinse with successive container volumes of high-purity H_2O until the pH of two successive rinse solutions are within 0.5 pH units of the original high-purity H_2O. A minimum of three rinses is required.

B. Procedure for cleaning Teflon containers used in pulsed flow tests. All parts are from Savillex. This procedure may be begun at step (3) for used containers.

Teflon segments Cat.#504

Teflon end cap Cat.#501

Teflon digestion ves. Cat.#560

Teflon transfer cap Cat.#501-37

(1) Soak for one hour in 6 M HNO_3 + 0.2 M HF.

(2) Rinse with three container volumes of high-purity H_2O.

(3) Boil in 6 M HNO_3 for four hours.

(4) Rinse with three container volumes of high-purity H_2O.

(5) Autoclave at 120°C for one hour in high-purity H_2O in stainless steel container.

(6) Boil for one hour in high-purity H_2O in a stainless steel beaker.

(7) Soak for a minimum of eight hours in high-purity H_2O in a polypropylene container at room temperature.

(8) Heat in a 200°C oven for five days.

(9) Boil for one hour in high-purity H_2O in a stainless steel beaker.

(10) Rinse with three container volumes of high-purity H_2O.

(11) Air dry at room temperature.

(12) Fill Teflon containers with 125 ml DI water, close lid, put rubber septum in place and leave in oven at 90°C.

(13) Measure pH of the DI water, record in 'Teflon Washing' L.N.

(14) If pH is <5.7 repeat steps 12 and 13; otherwise proceed to step 15.

(15) Air dry at room temperature.

C. Procedure for cleaning Teflon containers used in MCC-3 tests. The same Teflon parts are used as in Section B.

(1) Perform steps 1-7 of Section B.

(2) Heat in a pressure cooker of water for 10 days exchanging the water each day.

(3) Perform steps 12-15 of Section B.

D. Procedure for cleaning stainless steel containers used in pulsed flow tests. All parts are from Whitey

Stainless Steel Sample Cylinder	Cat.# 304L-HDF4-150
Stainless Steel Pipe Plug	Cat.# SS-4-P

Stainless Steel VCO Nut Cat.# SS-4-VCO-4

Stainless Steel VCO Male ConnectorCat.# SS-4-VCO-1-4

(1) Use as-received pickled or machined (rather than passivated) stainless steel vessels.

(2) Clean with analytical grade acetone for 5 minutes in an ultrasonic bath.

(3) Clean with reagent quality ethanol for 5 minutes in an ultrasonic bath.

(4) Rinse thoroughly with DI water.

(5) Let stand in a nitric acid solution overnight in a 90°C oven. The nitric acid solution is made by dissolving 1 gram of concentrated nitric acid (about 70% by weight, analytical reagent grade) in 180 ml of deionized water or by diluting 4 mls. of concentrated nitric acid to 1 litre.

(6) Rinse thoroughly with DI water.

(7) Dry overnight in an oven at 90°C.

E. Procedure for cleaning stainless steel parts used in PCT tests. Parts are as in Section D.

I. New Stainless Steel Parts

(1) Clean with analytical grade acetone for 5 minutes in an ultrasonic bath.

(2) Clean with reagent quality ethanol for 5 minutes in an ultrasonic bath.

(3) Rinse with DI water 3 times.

(4) Let stand in a 1% nitric acid solution for 1 hour in a 90°C oven.

(5) Rinse with DI water 3 times.

(6) Let stand in DI water for 1 hour.

(7) Rinse again with DI water.

(8) Fill each vessel to about 80-90% of its volume, close the vessel and let them stand for 16 hours in a 90°C oven.

(9) Remove the vessels from the oven, remove an aliquot of water from each vessel and measure its pH.

(10) If the pH falls outside the range of 5-7, repeat steps 6 through 9.

II. Used Stainless Steel Parts

(1) Remove all remaining glass from the vessels by brushing with a test-tube brush under tap water and then rinse with DI water.

(2) Let stand in a 1% nitric acid solution for 1 hour in a 90°C oven.

(3) Rinse thoroughly with DI water.

(4) Place the vessels in a stainless steel beaker filled with DI water and boil for 1 hour.

(5) Proceed as in step (8) and (9) of part I for new stainless steel parts.

(6) If the pH falls outside the range of 5-7 repeat steps (4) and (5).

6.3.3 Cleaning Ross Type pH Electrodes

MAINTENANCE

Weekly maintenance:

(1) Inspect electrode for scratches, cracks, salt crystal buildup, or membrane/junction deposits.

(2) Rinse off any salt build-up with DI water, and remove any membrane/junction deposits as directed in cleaning procedures below.

(3) Drain the reference chamber, flush it with fresh fill solution and refill the chamber.

Cleaning the electrode:

REFERENCE JUNCTION

(1) Rinse electrode with deionized water.

(2) Soak in 0.1M HCl or HNO_3 for half an hour.

(3) Remove electrode from acid solution, drain the reference chamber, flush it with fresh filling solution and refill the chamber.

(4) Rinse electrode with deionized water.

(5) Soak in storage solution for at least one hour before using.

6.4 Test Procedures

6.4.1 Pulsed Flow Tests

Equipment and Supplies

Qty	Device	Manufacturer	Model#	Calib. Req.
1	Balance	Mettler	PJ3000	I
1	Balance	Mettler	AE160	II
1	Balance	Scientech	5200	III
18	Ovens	Blue-M	Stabil-Ther, OV-490A, OV-490A-3	IV
1	pH Meter	Fisher	Accumet-810	V
1	pH Meter	Fisher	Accumet-910	V
1	Polypropylene wrench set	Savillex		N.A.
1	Grad. Cylinder	Nalgene		VI
1	Plastic Funnel	Nalgene		N.A.
	Thermometers	Various	-20 to 150°C, ± 1°C	V
	Desiccator			N.A.
	Metal box	Hoffman Eng. Co.	NEMA Type 4, in-house modif.	N.A.
	Syringes with gauge 20, 4 inch hypodermic needles			N.A.
	Syringes with gauge 20, 6 inch hypodermic needles			N.A.
	Teflon sections	Savillex	#504, #501, #50-37	N.A.
	Stainless steel sections	Whitey	#304L-HDF4150	N.A.
		Whitey	#SS-4-P	
		Whitey	#SS-4-VCO-4	
		Whitey	#SS-4-VCO-1-4	
		Cajon	#SS-4-VCO-3-4TA	
		Swagelok	#SS-400-C	
	Three-layer rubber septa	Hamilton	76-6006	N.A.
	O-ring	Whitey		N.A.

Calibration Notes: I: Calibration accuracy: ± 0.1 g, Calibration frequency monthly; II: Calibration accuracy: ± 1 mg, Calibration frequency, monthly; III: Calibration accuracy: ±

10 mg, Calibration frequency: every six months; IV: temperature monitored daily with thermometers that are positioned as recommended by the manufacturer and meet NBS Specification, Monograph 150; V: Calibration accuracy: ± 0.05 pH units, Calibration frequency: daily, (see VSL-LT-12); VI: check accuracy of volume by weighing a measured volume of DI water prior to first use; VII: meeting NBS Specification, Monograph 150.

PROCEDURES FOR PULSED FLOW TESTS

Procedure

TEFLON CONTAINERS

A. Leachant: Deionized (D.I.) water

(1) Weigh sample. Record data in the "West Valley Project" L.N.

(a) If a powdered sample is required, grind as prescribed in section 6.1.1 and select 40-60 mesh powder.

(b) If a block sample is required, prepare following section 6.1.2, clean following section 6.3.1 and record dimensions and other information pertinent to the test in the "West Valley Project" L. N.

NOTE: ***In the case of radioactive samples prepared and weighed in the α- Lab, ~5 ml of DI water are added to the powder to facilitate transfer to the non-radioactive lab.***

(2) Transfer sample into a pre-cleaned 125 ml PFA teflon pipe section (Savillex #504) with a well tightened screw on end cap on one end (Savillex #501). Clean all Teflon parts as prescribed in section 6.3.2.

(3) In a 2L SS beaker, place 1L of DI water and bring to a boil. Bubble nitrogen into water

and continue boiling for ~10 minutes.

(4) With a graduated cylinder measure 100 ml (95ml for radioactive samples) of boiled DI water and pour into Teflon pipe section with sample; mark water level. To prepare blanks, eliminate sample. While container is open, blow nitrogen in to prevent CO_2 contamination.

(5) Close the Teflon pipe section using the screw on transfer cap (Savillex #501-37) with rubber septum secured in place and tighten it using the polypropylene wrench.

(6) Remove rubber septum. Blow nitrogen into container for ~2 minutes and secure septum in place again.

(7) Place ascarite in a dish which is placed in a Petri dish in the center of the desiccator below the desiccator plate. A plastic weighing boat may be used instead of the Petri dish for test temperatures below 70°C.

(8) Transfer closed pipe sections with samples, and blanks into the desiccator or metal box.

(9) With lid partially opened. introduce nitrogen into the desiccator for about 5 minutes. When using the metal box desiccator introduce nitrogen through the inlet valve keeping the outlet valve open; close both valves when finished.

(10) Close desiccator lid.

(11) Place desiccator or metal box in an oven preheated to the required test temperature as per instructions of the Project Manager.

(12) After 24 hours remove the dessicator or metal box from the oven and remove the pipe sections from the dessicator.

(13) Check and if necessary retighten the end and transfer caps of the teflon pipe sections.

(14) Repeat steps (8) through (11).

(15) At the specified intervals, determined for each test by the Project Manager, replace 25 ml of leachate or a different volume according to project manager's instruction with an equal volume of fresh leachant, using a syringe with a gauge 20, 4 inch hypodermic needle. Perform the exchange as follows:

(a) Remove desiccator or metal box from oven.

(b) Remove pipe sections from desiccator.

(c) Inserting needle through septum, extract 25 ml or appropriate volume of leachate.

(d) Transfer 3-4 ml of the sample leachate into a plastic cup placed in a water bath at room temperature and measure pH. Record measurement in the "pH Meas. on Flow Tests" L. N.

(e) Transfer the rest of the extracted leachate into a polystyrene vial appropriately labeled for analysis.

(f) Using a syringe and needle dedicated exclusively to use with DI water, transfer 25 or appropriate volume ml of DI water, boiled as prescribed in step 3, into the pipe section. Be sure the needle does not touch the liquid inside the container. If necessary add more DI water to each individual pipe section in order to bring the solution to the level marked in Step 4.

NOTE: New syringes and needles must be used for each new test.

The same syringe and needle may be used for duplicate or triplicate samples. In this case, wash the unit 3 times with ~10 mL of boiling DI water.

(g) When sampling is finished, check ascarite and rubber septums, return closed pipe section into the desiccator or metal box, blow nitrogen in for ~5 minutes, and put lid in place.

(h) Return desiccator or metal box to oven to continue test.

(16) Transfer the samples to the Analytical Laboratory for analysis according to the instructions of the Project Manager.

(17) Store results on floppy disk (refer to section 8.1) and file hard copy in the appropriate binder. Durability data binders are labelled according to name of tests contained within.

B. Leachant: Ground water or EJ-13 Solution.

(1) Weigh sample. Record data in the 'West Valley Project' L.N.

(a) If a powdered sample is required, grind as prescribed in section 6.1.1 and select 40-60 mesh powder.

(b) If a block sample is required, prepare following section 6.1.2, clean following section 6.3.1 and record dimensions.

(2) Transfer sample into a pre-cleaned 125 ml PFA Teflon pipe section (Savillex #504) with a well tightened screw on end cap on one end (Savillex #501). Clean all Teflon parts as prescribed in section 6.3.2.

(3) Add 100 ml of leachate into Teflon pipe section with sample. To prepare blanks eliminate sample.

(4) Close Teflon pipe section using screw on transfer cap with rubber septum secured in place. Tighten the transfer cap using the polypropylene wrench.

(5) Transfer closed pipe sections with samples, and blanks into the metal box or desiccator and put lid in place.

(6) Place a metal box or desiccator without ascarite in an oven preheated to the required test temperature as per instructions of the Project Manager.

(7) Perform steps (12) through (16) of Section A, however, do not introduce nitrogen into the desiccator.

(8) Store results on floppy disk (refer to section 8.1) and file hard copy in the appropriate durability data binder.

C. Radioactive Samples (All leachants)

(1) Tightly fit the end cap on the appropriate side of the Teflon pipe section.

(2) Transfer the Teflon pipe section along with the transfer cap and rubber septum to the glove box in the laboratory where radioactive samples are stored.

(3) Weigh the required amount of glass powder in a plastic weighing boat or polystyrene vial on the scientech balance inside the glove box.

(4) Carefully transfer the glass powder into the Teflon pipe section together with 20 ml of leachant.

(5) Close the transfer cap and wipe the Teflon pipe section with a wet tissue in order to ensure that no glass powder remains on the outside of the container.

(6) Remove the Teflon container from the glove box and, while wearing disposable gloves, rinse and dry it again with DI water.

(7) Return the vessels containing the samples to the leach laboratory.

(8) Open the transfer cap and transfer 80 ml of boiling DI water under nitrogen or other leachant if leachant used is not DI water. Immediately close and tighten the transfer cap using the appropriate wrench.

(9) Continue the test from step 6 in Part A for DI water as the leachant or from step 5 in Part B for ground water or EJ-13 solution as the leachant.

STAINLESS STEEL CONTAINERS

D. Non-radioactive Samples

Note: 1) For tests with leachants other than Deionized water all procedures below are to be followed except that no nitrogen or ascarite is to be used.

2) No ground water is used in stainless steel vessels.

(1) Fit the stainless steel pipe plug on the appropriate end of the stainless steel sample cylinder, using Teflon tape (according to the manufacturer's instructions). Tighten the pipe plug using an adjustable wrench and vice.

(2) Weigh the required amount of glass powder.

(3) Transfer the glass powder into the stainless steel sample cylinder together with 100ml DI water boiled under nitrogen if DI water is the leachant or with just fresh leachant in the case of other leachants.

(4) Immediately attach the stainless steel VCO male connector to the open end of the cylinder using the teflon tape.

(5) In the case of DI water as leachant introduce nitrogen through the hole of the VCO male connector for 1 minute.

(6) Immediately place a rubber O-ring on top of the VCO male connector and then place the rubber septum and secure it with the stainless steel VCO nut containing a stainless steel O-ring on the inside.

(7) Tighten the connector properly using an adjustable wrench and vice.

(8) If required by the Project Manager's instructions screw the safety extender onto the vessel.

(9) Weigh and record the total weight of each individual stainless steel vessel.

(10) Place the stainless steel vessel horizontally or vertically in a dessicator or metal box containing a dish of ascarite, and introduce nitrogen.

(11) Place the above in a preheated oven and record the time as immersion time.

(12) After 24 hours, take out all vessels from the oven and weigh the stainless steel vessels.

(13) If the weight measured differs by less than 5% from the weight determined in Step 8 continue with the test otherwise consult the Project Manager before proceeding.

(14) At the specified intervals sample the leachate as follows:

a) Remove all stainless steel vessels and place them vertically in a stand. Allow them to cool to room temperature.

b) Weigh all stainless steel vessels and record the weighing in the Flow Test LN.

c) If a safety extender is attached to the vessel remove the cap from the vessel.

d) Using a designated syringe and needle withdraw the exact volume of solution as specified by the Project Manager.

e) Collect the above solution in a vial and label it properly (a part of this solution is to be used to measure pH and the remaining portion to be sent to Analytical Lab for analysis.

f) Replace with an exact amount of fresh leachant. *(Note: In the case of DI water as leachant, it should be replaced with boiling DI water under nitrogen.)*

g) If a safety extender is attached to the vessel replace the stainless steel cap.

h) Weigh all the containers again and compare their weights with those before sampling. If the weight is less than the weight before sampling, add some leachant; if the weight is slightly higher than before, do not remove any solution.

i) Inspect all rubber septa and check if there are any holes present due to injection. If holes are found, replace the rubber septa.

j) Return all the stainless steel vessels to the oven.

E. Radioactive Samples (All Leachants)

(1) Perform step (1) as in Part D of this procedure.

(2) Label each stainless steel vessel ensuring that all the parts are together, however, do not tighten the VCO male connector.

(3) Transfer the vessels to the Glass Preparation Laboratory, Room 39.

(4) Weigh the required amount of glass powder in a plastic weighing boat on polystyrene vial on the sartorius balance inside the glove box in Room 39.

(5) Carefully transfer the glass powder into the stainless steel vessel and lightly close the VCO male connector.

(6) Wipe the vessel with a wet tissue in order to ensure that no glass powder remains on the outside of the container.

(7) Return the vessels containing the samples to the leach laboratory.

(8) Place the vessels vertically in a stand in the fume hood.

(9) Open the VCO male connector and transfer 100 mls of fresh leachant to the vessel using a plastic funnel. (If DI water is the leachant 100 mls of DI water boiled under nitrogen should be used.)

(10) Rinse the plastic funnel after each transfer.

(11) Proceed as in Steps (4) - (13) of section D of this procedure.

6.4.2 PROCEDURE FOR PCT TESTS

Equipment and Supplies

Qty	Device	Manufacturer	Model	Calib. Req.
1	Balance	Mettler	PJ300	I
5	Oven	Blue-M	Stabil-Therm OV-490A, OV-490A-3	II
1	pH meter	Corning	245	III
1	Graduated Cylinder			IV
2	Pipettes (1.0 and 5-10 ml)	Oxford/Eppendorf		V
	Thermometers	Various	-20 to 150°C, ± 1°C	VI
	Syringes with SS needles			N.A.
	Stainless steel sections	Whitey	#304L-HDF4-150	N.A.
			#SS-4-P	
			#SS-4-VCO-4	
			#SS-4-VCO-1-4	
		Cajon	#SS-4-VCO-3-47A	
		Swagelok	#SS-400-C	
	Three-layer rubber septa	Hamilton	76006	N.A.
	Syringe filter	Gelman	4217	N.A.
	Racks for holding stainless steel containers			

Calibration notes: I: calibration accuracy: ± 100 mg, calibration frequency: monthly; II: temperature monitored daily with thermometers that are positioned as recommended by the manufacturer and meet NBS specification, Monograph 150; III: calibration accuracy: ± 0.05 pH units, calibration frequency: daily or every 25 measurements (see section 6.5.3); IV: calibrated before first use; V: calibration accuracy: ± 5%, calibration frequency: monthly; VI: meeting NBS specification, Monograph 150.

Procedure

(1) Grind the glass sample as prescribed in section 6.1 and select 100-200 mesh powder.

(2) Weigh the required amount of glass as per instructions of the Project Manager to ± 100 mg with an analytical balance.

(3) Preclean the stainless steel containers according to procedure in section 6.3.2.

(4) Weigh the empty stainless steel container with its top and record the weight in the current West Valley LN for PCT tests.

(5) Transfer a glass sample into the stainless steel container and weigh and record the weighing again. Each sample should be tested in triplicate.

(6) Add the required volume of DI water and mix well to wet the powdered glass and remove entrapped air.

(7) Close the stainless steel container using a wrench with the rubber septum secured in place.

(8) Weigh the closed, loaded container and record the weight in the current West Valley L.N. for PCT Tests.

(9) Shake each container thoroughly.

(10) Prepare two blanks as described above without introducing the powdered glass sample.

(11) Place all the containers horizontally into an oven preheated to the required test temperature as per instructions of the Project Manager.

(12) After one day remove the containers from the oven, weigh them again and return them to the oven if the loss in weight is less than 5% of the total weight of the leachant. Otherwise start the test again.

(13) At the specified intervals as determined by the Project Manager, sample leachate as follows:

(a) One day before sampling stand the containers vertically with the rubber septum at the top in a rack in the oven.

(b) On the day of sampling remove the loaded stainless steel containers from the oven. Try not to shake the containers. Weigh the container and record the weight in the current West Valley L.N. for PCT tests.

(c) Unscrew the top using a wrench.

(d) Remove about 4 ml of leachate from each container using a polypropylene syringe with a stainless steel needle which is inserted through the rubber septum. Detach the stainless steel needle from the syringe and attach the 0.45 μm syringe filter to the syringe. Filter the leachate through the filter into a clean vial.

(e) Pipette 1.0 ml of the sampled leachate to a vial prefilled with 20.0 ml DI-water and label appropriately for analysis.

(f) Pour the remaining 3 ml of the sampled leachate into a 4 ml plastic cup placed in a water bath at room temperature and measure pH. Record measurement in the current West Valley L.N. for PCT Tests.

(g) Inject 4 ml of fresh DI-water into the container using another clean polypropylene syringe with a stainless steel needle which is inserted through the rubber septum.

(h) When sampling is finished, replace and tighten the stainless steel cap with a wrench. Weigh the container again and record the weight in the current West

Valley L.N. for PCT tests.

(i) Return the containers to the oven and position them horizontally to continue the test.

(14) Transfer the samples to the analytical laboratory for analysis according to the instructions of the Project Manager.

(15) Store results on a floppy disk (see section 8.2) and file hard copy in the appropriate durability data binder for PCT test.

6.4.3 PROCEDURE FOR IAEA (HIGH DILUTION) TESTS

Equipment and Supplies

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Balance	Mettler	AE160	I
18	Ovens	Blue-M	Stabil-Therm OV-490A	II
1	pH Meter	Fisher	Accumet-810	III
1	pH Meter	Fisher	Accumet-910	III
	Grad. cylinder	Nalgene		IV
	Thermometers	Various	-20 to 150°C, ± 1°C	V
1	Teflon vessel	Savillex	#0102	N.A.
1	Teflon basket	Savillex	#46SC	N.A.

Calibration notes: I: calibration accuracy: ± 1 mg, calibration frequency: monthly; II: temperature monitored daily with thermometers that are positioned as recommended by the manufacturer and meet NBS Specification, Monograph 150; III: calibration accuracy: ± 0.01 calibration frequency: daily; IV: check accuracy of volume measured prior to first use; V: meeting NBS Specification, Monograph 150.

PROCEDURE FOR IAEA (HIGH DILUTION) TESTS

Procedure

(1) Weigh sample. Record data in the 'West Valley Project' L.N.

(a) If a powdered sample is required, grind as prescribed in section 6.1.1 and select 40-60 mesh powder.

(b) If a block sample is required, prepare following 6.1.2, clean following section 6.3.1 and record dimensions.

(2) Transfer sample into a precleaned 60 ml PFA Teflon vessel (Savillex #0102). If block samples are being used, place a PFA Teflon basket (Savillex #46SC) inside the vessel. Clean all teflon parts as prescribed in section 6.3.2.

(3) Measure the required volume of leachant (40 ml) using a graduated cylinder and transfer into the teflon vessel.

(4) Screw on lid and tighten properly to minimize vaporization.

(5) Place closed teflon vessel in an oven preheated to the specified test temperature as per instructions of the Project Manager. Record the time of this operation as the "immersion time" in the "West Valley Project" L.N.

(6) Replace the entire volume of leachate with a similar volume (40 ml) of fresh leachant, daily to begin with, then weekly, and then monthly, or as specified for each individual test by the Project Manager. Carry out this operation as follows:

(a) Remove the container from the oven and let it cool for about 10 minutes.

(b) If a powdered sample is being used, remove the lid and decant the liquid carefully if necessary using a disposable transfer pipette.

(c) If a block sample is being used, remove the lid, take out the sample with clean plastic tweezers, empty the vessel, and return the sample to it.

(d) If requested by Project Manager, transfer ~ 4 ml of the sampled leachate into a plastic cup placed in a water bath at room temperature and measure pH using a Ross-type electrode. Record pH reading in the "pH Data for IAEA Tests" L. N.

(e) Refill the container as per steps (3) and (4) and return to the oven.

(f) Record sampling time to the nearest 10 minutes in the 'pH Data for IAEA Tests' L.N.. If this operation is carried out on many samples, record the average time at which sampling is carried out as the sampling time for all.

(7) Analyze samples using DC plasma spectroscopy and colorimetry. Refer to Analytical Procedures.

(8) Store results on floppy disk (refer to section 8.3) and file hard copy in the appropriate binder. Durability data binders are labelled according to the tests contained within.

(9) Alternatively all data from this test may be recorded in the 'Glass Composition' LN rather than the 'West Valley Project' LN and the 'pH Data for IAEA Tests' LN.

6.5 Calibrations

6.5.1 Balance

Frequency: Monthly for Mettlers and Sartorius; six monthly for all other balances except those which are for qualitative use only.

Required Accuracy: As specified in individual procedures or as per instructions of the Project Manager.

(1) Obtain a set of Class S-type standard weights.

(2) Obtain a "Balance Calibration Check Record" form and supply requested information on balance to be calibrated (e.g. manufacturer, model #, etc.).

(3) Weigh the standard weights in the balance and record the nominal weight, actual weight, and percent error under the appropriate columns.

(4) Calculate the percent error as follows:

$$\frac{\text{(Actual weight) - (Nominal weight)}}{\text{(Nominal weight)}} \times 100 = \%\ \text{Error}$$

(5) Examine results and reports deviations from required accuracy to the Project Manager.

(6) Sign and date and file form in the 'Calibration Records' binder.

6.5.2 Pipette

PIPETTE CALIBRATION CHECK PROCEDURE

Method: Gravimetric using a Mettler AE160 balance.

Frequency: Monthly except Rainin pipette which is six monthly.

Required Accuracy: As specified in individual procedures or as per instructions of the Project Manager.

(1) Obtain a "Pipette Calibration Check Record" form and supply requested information on pipette to be calibrated (e.g. manufacturer, model #, etc.).

(2) Tare out the weight of a 20 ml plastic vial on the Mettler balance.

(3) Pipet out deionized water from the pipette to be calibrated into the plastic vial. Record nominal capacity, actual capacity (weight displayed on the Mettler balance), and percent error under the appropriate columns.

(4) Repeat steps (2) and (3) five times. For variable volume pipettes perform the measurement for 2-5 volume settings.

(5) Calculate the percent error as follows:

$$\% \text{ ERROR} = \frac{(\text{Actual capacity}) - (\text{Nominal capacity})}{(\text{Nominal capacity})}$$

(6) Examine results and report deviations from required accuracy to the Project Manager.

(7) Sign and date and file form in the "Calibration Records" binder.

6.5.3 pH Meter

pH METER CALIBRATION PROCEDURE

Frequency: Daily or every 25 measurements
Required Accuracy: ± 0.05 pH units
Instruments: Fisher Accumet-810, 910 pH meters and Corning 245 pH meter.

(1) Remove the pH electrode from the routine storage solution.

(2) Wash the pH electrode and beaker with DI water.

(3) Adjust the instrument to the pH measurement mode.

(4) Adjust the temperature setting to room temperature.

(5) Choose two standard buffer solutions traceable to NBS Standards which covers the expected range of pH to be measured.

(6) With the slope dial on 100% calibrate the instrument with one of the standard buffer solutions. Allow the reading to stabilize. The pH should be corrected according to the pH-temperature table on the bottle. Record the buffer used, temperature and date in the appropriate LN.

(7) Wash the beaker and electrode with DI water and then insert the electrode in the second standard buffer solution. Adjust the slope dial such that the stabilized pH reading corresponds to the value of the pH expected from the pH-temperature table on the bottle. Again record the buffer used, temperature and date in the appropriate LN. The pH meter is now calibrated.

(8) Wash the electrode well with DI water before and between measurements of the pH of the samples.

(9) On completion of all measurements return the pH electrode to the routine storage solution and set the instrument to "Standby".

(10) If measurements fall outside the calibration range of pH meter, calibrate again with an appropriate buffer to cover the whole pH range of measurements. An accuracy of _+0.3 pH units is required for this final calibration.

6.5.4 Oven Thermometers

PROCEDURE FOR CALIBRATION OF OVEN THERMOMETERS

Equipment and Supplies

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Standard Thermometer (Traceable to NIST)			I
1	Glass Beaker			N.A.

Calibration notes: I: calibrated by manufacturer

PROCEDURE

NOTE: This procedure shall be performed once a year on all oven thermometers.

1. Heat a tall beaker of water to about 55°C.

2. Place the standard thermometer (traceable to NIST) in the water so that the mercury bulb and the scale up to 30°C are immersed in the water.

3. Place the thermometers to be calibrated in the water to a depth of 76 mm as indicated by the appropriate mark on the thermometer for 76 mm partial immersion thermometers, or to a depth corresponding to 55°C on the scale for total immersion thermometers.

4. Record the temperature of the standard thermometer and the temperatures of the test thermometers.

5. Place a second thermometer adjacent to the standard thermometer such that the bulb of the second thermometer is centered halfway between the surface of the water and the temperature indicated on the standard thermometer.

6. Record the temperature indicated by the second thermometers.

7. Calculate the stem correction for the standard thermometer from the formula

Stem correction = 0.00016 x N x (T - ST)

where N is the number of degrees centigrade of the mercury column in the standard thermometer above the surface of the water. T is the temperature is °C indicated on the standard thermometer and ST is the temperature in °C indicated on the second thermometer.

8. Calculate the corrected standard temperature by adding the stem correction to T.

9. Repeat steps 1 through 8 for temperatures of around 70°C and 90°C.

10. A calibration accuracy of ± 1°C is acceptable.

7.0 SPECIMEN AND DATA TRACEABILITY

Samples arrive in the leach laboratory from the glass preparation laboratory. Each time a glass sample is received in the leach laboratory, the following particulars are documented in the laboratory notebook:

Number of the glass
Lab notebook # and the page # documented in the glass preparation laboratory

The glass sample is loaded into the leach vessel (stainless steel vessel with a permanent number inscribed on it). This part is done in the glass preparation laboratory (for safe radioactive handling purpose).

Sampling details of the leach for each glass are recorded in the appropriate laboratory notebook and sent to analytical laboratory for analysis.

8.0 DATA PROCESSING

8.1 Pulsed Flow

PROCEDURE FOR RUNNING PULSED FLOW
DATA ANALYSIS PROGRAMS

Equipment List

Qty	Device	Manufacturer	Model	Calib. Req.
1	Computer	IBM compatible	386	N.A.
1	Monitor	Princeton	Max-12	N.A.
1	Keyboard	US Keyboard	US101	N.A.
1	Printer	Epson	FX286e	N.A.
1	Flow Software Package			N.A.

Procedure

Note: <CR> indicated the "enter" key on the keyboard.

(1) Turn the computer, monitor and printer on.

(2) Type E: <CR>

(3) Type CD\FLOW <CR>

(4) Type FLOWMAIN

(5) Type 1 to print the original data
Type 2 to calculate averaged data
Type 3 to sort the averaged data
Type 4 to calculate normalized data
Type 5 to search for sample names on the disk files
Type 6 to translate data from the present format to a format which may be read

by LOTUS 1,2,3.
Type 8 to print an index of parameters for a test.

(6) Follow the instructions on the screen in order to run the desired program.

(7) At the end of the session type 0 and on obtaining the prompt E:\Flow> type OFF <CR> and the Y<CR>.

(8) Turn off the computer, monitor and printer.

8.2 PCT

PROCEDURE FOR RUNNING PCT DATA ANALYSIS PROGRAMS

EQUIPMENT LIST

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Computer		IBM compatible 386	N.A.
1	Monitor	Princeton	MAX-12	N.A.
1	Keyboard	US Keyboard	US101	N.A.
1	Printer	Epson	FX286e	N.A.
1	MCC3 Software Package			N.A.

Procedure

Note: <CR> indicates the "enter" key on the keyboard.

(1) Turn on the computer, monitor, and printer.

(2) Type E: <CR>.

(3) Type CD\MCC3 <CR>.

(4) Type MCC3MAIN.

(5) Type 1 to print the original data.
Type 2 to calculate averaged data.
Type 3 to sort the averaged data.
Type 4 to calculate normalized data.
Type 5 to search for sample names on the disk files.
Type 6 to translate data from the present format to a format which may be read by LOTUS 1,2,3.
Type 7 to print an index of parameters for a test.
Type 8 to print experiment dates on a calendar.
Type 9 to obtain an experiment data and print a timetable for sampling.
Type C to calculate the weight percentage and molar percentage of components within a glass composition.

(6) Follow the instructions on the screen in order to run the desired program.

(7) At the end of the session type 0 and on obtaining the prompt E:\MCC3 > type OFF <CR> and then Y <CR>.

(8) Turn off the computer, monitor, and printer.

8.3 IAEA

PROCEDURE FOR RUNNING IAEA DATA
ANALYSIS PROGRAMS

Equipment List

Qty	Device	Manufacturer	Model #	Calib. Req.
1	Computer		IBM Compatible 386	N.A.
1	Monitor	Princeton	MAX-12	N.A.
1	Keyboard	US Keyboard	US101	N.A.
1	Printer	Epson	FX286e	N.A.
1	IAEA software program			N.A.

Procedure

Note: <CR> indicates the "enter" key on the keyboard.

(1) Turn on the computer, monitor, and printer.

(2) Type E: <CR>.

(3) Type CD\IAEA <CR>.

(4) Type IAEAMAIN.

(5)

Type 1	to print the original data.
Type 2	to calculate leach rates based on the original data.
Type 3	to average the leach rate data.
Type 4	to sort the means of the leach rates.
Type 5	to search for sample names on the disk files.
Type 6	to translate data from the present format to a format which may be read by LOTUS 1,2,3.
Type 7	to print an index of parameters for a test.
Type 8	to normalize the leach rate data.

(6) Follow the instructions on the screen in order to run the desired program.

(7) At the end of the session type 0 and on obtaining the prompt E:\IAEA > type OFF <CR> and then Y <CR>.

(8) Turn off the computer, monitor, and printer.

Section 9.0

ACCURACY AND RELIABILITY OF TEST RESULTS

The data used to generate the measures of precision is the result of intra- and inter-laboratory round robins. These measures are typical of the methods and applied to the glasses and standards used in the round robins, and are not all inclusive with respect to other types of glasses. The measures of precision were determined in accordance with procedures in ASTM Practice E691. These measures are designated as follows:

Repeatability: the standard deviation for within-laboratory determinations.

Reproducibility: the standard deviation for between-laboratory determinations.

PCT-Within laboratory precision: approved reference ARM-1 (a simulated borosilicate nuclear waste glass). Within-lab relative standard deviation for B was 2.3% and for Si was 1.8%.

PCT Between - Laboratory precision: approved reference glass ARM-1 (a simulated borosilicate nuclear waste glass). Between-laboratory standard deviation (including within laboratory and between laboratory %RSD) for B was 12% and for Si was 10.2% for laboratories with varying analytic capabilities (data in table C.2).

NIST reference glass SRM 623 (a borosilicate glass). Between-laboratory standard deviation (including within laboratory and between laboratory %RSD) for B was 19.8% and capabilities (data in table C.2).

Bias: the average corrected leachate concentrations for the standard glass allow assessment of long-term bias or variability of the test, e.g. how reproducible the experimental variables such as oven temperature, sieving, leachate analyses, etc. are over time. Use of a standard glass provide the basis for both within-laboratory and between data comparisons.

SECTION 10.0

RECORD KEEPING

The following records are to be maintained in the leach testing laboratory:

(1) Calibration Data:

All calibrations carried out for balances, pipettes, should be documented. The calibration data should include the weight/volume observed vis-a-vis marked data, the percentage error detected, pass/rejection, date of the calibration and the signature of the person carrying out the calibration.

(2) Leach test data for each of the leach test - pulsed flow, IAEA, PCT, should be documented.

(3) Sample preparation/cleaning records, details of sample preparation, cleaning of vessels.

(4) Leachant details:

Recipes for leachants prepared, and Millipore records should be maintained.

The above laboratory record books are subject to periodic surveillances as part of the Quality Assurance Program.

WASTE CHARACTERIZATION PROCEDURES

1) Chemical composition/DC plasma
2) ICPMS

VSL Technical Procedure

TITLE: Analysis Procedures

DOCUMENT: TPI-AL.WVN

ISSUED: 10/91 REV #: 0

Documents Incorporated:

TPI03.WVN	Rev. #0
TPI-AL.WVN	Rev. #3
TPI-CA.WVN	Rev. #3
TPI-DP.WVN	Rev. #1

Date Issued: 10/91

Prepared by: _____
Marek Brandys
Project Manager

Approved by: _____
Pedro B. Macedo
Co-Director, VSL

_____
C. Sivaprakash
Quality Assurance Officer, VSL

Document Replacement Record

Prevous Sections	Descriptions	Rev #	Replaced in this Manual by:
VSL-AL-1.WVN	Record Keeping	NEW	SECTION 10.0
VSL-AL-2.WVN	Acceptance of Samples and Release of Results	NEW	SECTION 7.0
VSL-AL-3.WVN	Stock Standard Solutions	2	SECTION 4.2
VSL-AL-4.WVN	Preparation of Samples for Analysis	NEW	SECTION 6.1.1
VSL-AL-5.WVN	General Solution Analysis	3	SECTION 6.1.2
VSL-AL-6.WVN	Solution Analysis with Atomic Absorption Spectrophotometer (Water Matrix only)	2	SECTION 6.2.1
VSL-AL-7.WVN	Solution Analysis with DC Plasma Emission Spectrophotometer (Water Matrix only)	NEW	SECTION 6.3.1
VSL-AL-8.WVN	Solution Analysis with Ion Exchance Chromatograph	NEW	SECTION 6.4.1
VSL-AL-9.WVN	Glass and Sludge Dissolution for Analyses	2	SECTION 6.1.3
VSL-AL-10.WVN	DC Plasma Emission Spectrophotometer Operating Procedure	3	SECTION 6.3.2
VSL-AL-11.WVN	Atomic Absorption Spectrophotometer Operating Procedure	2	SECTION 6.2.1
VSL-AL-12.WVN	Dionex Ion Exchange Chromatography Operating Procedure	NEW	SECTION 6.4.2
VSL-AL-13.WVN	Assurance of Reliability of Analytical Results	NEW	SECTION 9.0
VSL-AL-14.WVN	Solution Analysis with the Inductively Coupled Plasma-Mass Spectrometer	NEW	SECTION 6.5.1
VSL-AL-15.WVN	Inductively Coupled Plasma Mass Spectrometer Operating Procedure	NEW	SECTION 6.5.2

VSL-CA-1.WVN	Perkin Elmer 330 Spectrophotometer Start up and Operating Procedure	Rev #3	SECTION 6.6.2
VSL-CA-2.WVN	Silicon Analysis	Rev #4	SECTION 6.6.1
VSL-CA-3.WVN	Procedure for Spectrophotometer Accuracy Verification	Rev #4	SECTION 6.6.3
VSL-DP-1.WVN	Data Processing	NEW	SECTION 8.0
VSL-DP-2.WVN	Procedure for Running Analytical Laboratory Data Collection Programs		

ANALYTICAL LABORATORY PROCEDURES MANUAL

Table of Contents

Section	Description
1.0	Purpose
2.0	Applicability
3.0	Safety
	3.1 Hazards
	3.2 Hazard Mitigation
	3.2.1 Identification of Hazards
	3.2.2 Handling and Storage of Chemicals
	3.2.3 Emergencies
	3.3 Personnel Protection
4.0	Requirements
	4.1 Training
	4.2 Control of Standards
5.0	References
6.0	Procedures
	6.1 Sample Preparation
	6.1.1 Preparation of Samples for Analysis
	6.1.2 General Solution Analysis
	6.1.3 Glass and Sludge Dissolution for Analysis
	6.1.4 Calibration of Pipettes
	6.2 Analysis with Atomic Absorption Spectrophotometer
	6.2.1 Solution Preparation and Analysis
	6.2.2 Atomic Absorption Spectrophotometer Operating Procedure
	6.3 Analysis with DC Plasma Emission Spectrophotometer
	6.3.1 Solution Preparation and Analysis
	6.3.2 DC Plasma Emission Spectrophotometer Operating Procedure
	6.4 Analysis with Ion Exchange Chromatography
	6.4.1 Solution Preparation and Analysis
	6.4.2 Ion Exchange Chromatography Operating Procedure
	6.5 Analysis with ICPMS
	6.5.1 Solution Preparation and Analysis
	6.5.2 ICPMS Operating Procedure

6.6 Analysis with Perkin Elmer Spectrophotometer
6.6.1 Solution Preparation for Silicon Analysis
6.6.2 Spectrophotometer Operating Procedure
6.6.3 Procedure for Spectrophotometer Accuracy Verification

7.0 Control of Samples and Release of Results

8.0 Data Processing

9.0 Assurance of Reliability of Analytical Results

10.0 Record Keeping

1.0 PURPOSE

These procedures describe methods, materials, equipment and special conditions required to perform chemical analyses of liquid and/or solid samples. These procedures provide the means for obtaining verifiable, reproducible, documented data from tests and experiments.

2.0 APPLICABILITY

An indispensable part of the work carried out in our laboratories is chemical analysis. Various instruments are available for this purpose including a Perkin Elmer Model 503 atomic absorption spectrophotometer (AA), a Spectrametrics Deplasma spectrophotometer (DCP), a Dionex Model 2010I ion-chromatographer, Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and two Perkin Elmer Models 330 and 323 spectrophotometers.

Work with the AA, DCP and DIONEX devices is performed in our "Analytical Laboratory". The other two instruments mentioned above, as well as other chemical analysis tools, are used in our "General Chemistry Laboratory". Analysis on ICP-MS is performed in Mass Spectrometry Laboratory.

These procedures apply to all employees trained and authorized to perform chemical analysis of liquid and/or solid samples in the VSL Analytical Facilities. Specific activities covered by these procedures include: a) acceptance of samples for analysis; b) preparation and

handling of stock standard solutions and other reference materials; c) preparation of liquid and/or solid samples for various types of analysis; d) calibration and operation of (i) the atomic absorption spectrophotometer; (ii) the DC plasma emission spectrophotometer; (iii) the ion exchange chromatograph; (iv) the inductively coupled plasma-mass spectrometer; (v) the Perkin Elmer 330 spectrophotometer; e) release and assurance of reliability of analytical results; f) record keeping; g) data processing of analytical data.

These procedures will be implemented by personnel from the VSL.

3.0 SAFETY

3.1 HAZARDS

The definition of a hazardous chemical is given in Section 8.3 of the CUA Chemical Materials Safety Manual, adopted from the OSHA Hazard Communication Standard. The CUA Chemical Materials Safety Manual is hereafter referred to as the CCMSM. This Standard and its application to CUA facilities are described in Sections 8.1 of the CCMSM, with the exceptions noted in Section 8.28.

3.2 HAZARD MITIGATION

3.2.1 Identification of Hazards

The identification of chemical hazards should include an education program (Section 8.2 of the CCMSM). This program should include familiarization with the CCMSM as a whole.

including the toxic properties of chemicals according to Sections 8.22, 8.23, 8.24 and 8.25 of the CCMSM, other hazards of chemicals classified under Sections 8.9, 8.10, 8.11, 8.12, 8.13 and 8.14 of the CCMSM, chemical handling and storage procedures (see paragraph 3.2.2 below), and emergencies (see paragraph 3.2.3 below). The education program will also include familiarization with the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University.

Other elements of hazard identification include the proper use of labels (Section 8.4 of the CCMSM) and of Material Safety Data Sheets (Sections 8.5, 8.26 and 8.27 of the CCMSM). Workplace chemical lists should be compiled, maintained, and made available for employees in accordance with Section 8.31. In addition, a copy of the CCMSM should be kept in the laboratory and its use should be included in the education program cited above. The same should apply to the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University.

3.2.2 Handling and Storage of Chemicals

Handling of chemicals should be conducted according to Section 8.6 of the CCMSM. Storage of chemicals should follow Section 8.8 of the CCMSM. Special precautions should be taken in handling and storage of incompatible chemicals, solvents. compressed gases, and radioactive materials according to Sections 8.10, 8.12, 8.13, and 8.14 of the CCMSM. respectively. Unstable chemicals according to Section 8.9 should be excluded from the analytical facilities except in cases where the introduction of such a material is sanctioned by the

laboratory manager in writing. In such a case the manager shall specify the maximum quantity of the material and the maximum period it may be stored before being discarded. Shock-sensitive chemicals according to Section 8.11 should never be introduced into the laboratory under any circumstances. No work requiring the use of restricted areas according to Section 8.15 should be performed within the analytical laboratories, except on temporary basis and only if adequate modifications have been made to the facilities and the specific procedures have been established. This includes all operations involving radioactive materials.

Waste disposal of hazardous chemicals should follow procedures established by the CUA Environmental safety Office according to Section 8.16 of the CCMSM. No radioactive waste shall be disposed of by analytical laboratories. All processed samples and their overflow should be returned to the originator of the samples for disposal. Any solid radioactive waste generated during operations is to be collected in separate containers and transferred to CUA Radiation Safety Office (RSO).

3.2.3 Emergencies

Chemical spills should be dealt with according to Section 8.17 of the CCMSM. Fire and fire-related emergencies should be controlled according to Section 8.21 of the CCMSM. Cases of personal contamination should be treated according to Section 8.19 of the CCMSM, cases of injury and illness according to Section 8.18, and cases requiring minor first aid according to Section 8.20. All emergencies involving radioactive materials should be reported immediately to the RSO and dealt with according to the procedures outlined in the Radiation Safety Manual

distributed by the RSO.

3.3 PERSONNEL PROTECTION

Personnel protection should consist of two elements. The first is familiarization and compliance with the instructions of the CUA Chemical Materials Safety Manual (CCMSM), including identification of hazards (see paragraph 3.2.1 above), handling and storage of chemicals (see paragraph 3.2.2 above), and dealing with emergencies (see paragraph 3.2.3 above). The second element is familiarization and compliance with the CUA Chemical Hygiene Program (CCHP) when the document describing this Program is finalized and approved for distribution by the University. The overall chemical hygiene program (Section 8.34 of the CCHP), based on the OSHA Regulation on Occupational Exposure to Hazardous Chemicals in Laboratories, should be followed. In detail, exposure reduction measures (Section 8.35 of the CCHP) will include environmental monitoring (8.35.1), inspections, maintenance and housekeeping (8.35.2), use of protective apparel and equipment (8.35.3), posting of signs and labels (8.35.4), and dealing with accidents and spills (8.35.5). Ventilation of both general laboratory spaces and of special areas and local devices such as chemical fume hoods and glove boxes should follow the instructions of Section 8.36 of the CCHP. Employees should take part in the safety information and training program which exists in the University according to Section 8.37 of the CCHP. All personnel involved in handling of radioactive materials should be approved by the RSO and should participate in Radiation Safety Training Program provided by the RSO. Certain laboratory operations may require approval from the laboratory manager

prior to implementation according to Section 8.38 of the CCHP. Employees should be informed about the medical program provided by the University in cases of work with hazardous substances according to Section 8.39 of the CCHP. Responsibility for chemical hygiene rests with all employees. Specific chemical hygiene responsibilities as applied to the analytical facilities are specified in Section 8.40 of the CCHP. Analytical laboratories personnel workers should be familiar with the basic rules and procedures for working with chemicals included in Section 8.41 of the CCHP and should work in full compliance with these rules and procedures. Animal work, whether involving chemicals of high chronic toxicity according to Section 8.41.5 of the CCHP or not involving chemicals of this type, should not be carried out in the analytical facilities.

4.0 REQUIREMENTS

4.1 TRAINING

All analytical laboratory personnel are trained in the understanding and use of the technical methods that they will use by the laboratory supervisor or by a trained and experienced person designated by the laboratory supervisor. Upon completion of training for a method, a technician is qualified to use that method independent of direct supervision.

4.2 CONTROL OF STANDARDS

Stock Standard Solutions

(1) All the instrumental analysis in the Analytical Laboratory are performed on relative basis

by comparison with known standards.

(2) Sufficient stock of concentrated Standard Solutions should be kept in the Analytical Laboratory to allow at least 30 days of continuous work. (This means about 200 ml of solution containing approximately 1000 ppm of specimen.)

(3) The term "concentrated solution" means the solution contains 1000 $\pm$ 20% ppm of the analyte in question. No stock of more diluted standard solutions is allowed to be kept in the laboratory for a period exceeding 24 hours. Diluted solutions containing one or more of the following elements: Si, Fe, U, Th should be freshly prepared every 8 hours.

(4) Stock of standard solutions to be analyzed by atomic emission/absorption techniques should be purchased from major commercial sources. No use of solutions is allowed beyond expiration dates, if such dates are provided by the manufacturer or when the volume in the bottle falls below 1/8 of the total volume.

(5) Standard Solutions of anionic species for ion chromatography should be prepared according to the following procedures:

F- : Dissolve 2.210 g of NaF in water and dilute to 1.000 liter.

Cl- : Dissolve 1.648 g of NaCl in water and dilute to 1.000 liter.

Br- : Dissolve 1.288 g of NaBr (or 1.489 g of KBr) in water and dilute to 1.000 liter.

NO2-: Dissolve 1.850 g of KNO2 in water and dilute to 1.000 liter.

NO3-: Dissolve 1.631 g of KNO3 in water and dilute to 1.000 liter.

PO4-: Dissolve 4.002 g of Na3PO4-12H2O in water and dilute to 1.000 liter.

SO4-: Dissolve 1.376 g of (NH4)2SO4 in water and dilute to 1.000 liter.

The above procedures yield 1.000 liter of solutions containing 1000 ppm of corresponding species. The chemicals used in the preparations should be in the form of fresh, dry crystals of analytical grade materials. These solutions should not be stored for the periods exceeding 2 years.

All standard solutions of cations shall be analyzed relative to NIST standards on a monthly basis and a limit of ± 5% will be acceptable.

5.0 REFERENCES

Vogel, A. "Textbook of Quantitative Inorganic Analysis," 4th ed., Longman Scientific and Technical, England 1987.

Willard, H. H., Merritt, L. L. Jr., Dean, J. A. and Settle, F. A. "Instrumental Methods of Analysis," 6th Ed., D. Van Nostrand Co., New York 1981.

Boumans, P. W. J. M. (Ed.) Inductively Coupled Plasma Emission Spectroscopy," John Wiley and Sons, New York, 1987.

A. R. Date and A. L. Gray (Ed.) "Applications of Inductively Coupled Plasma - Mass Spectrometry," Champman and Hall, New York 1989.

The Catholic University of America Chemical Materials Safety Manual, January 1989.

The Catholic University of Chemical Hygiene Program, in preparation.

Radiation Safety Manual of the Catholic University of America, January 1980, W. E. Keene RSO.

PART II

6.0 OPERATIONAL PROCEDURES

6.1 SAMPLE PREPARATION

6.1.1 Preparation of Samples for Analysis

(1) Only liquid samples can be analyzed.

(2) With liquid samples, proceed as per procedure in section 6.1.2 below.

(3) Solid samples have to be converted into liquid form as per procedure in section 6.1.3 below.

6.1.2 General Solution Analysis

Procedure

Depending on what elements and ions are expected to be present, solutions are analyzed using an atomic absorption spectrophotometer (AA), a D. C. plasma spectrophotometer (DCP), or a Dionex ion exchange chromatograph. Generally, the AA is used for Cs, Li, Mg and Ni analysis, the DCP for Zr, Zn, P, Si, Ti, B, Mn, Fe, Co, Ca, Al, Cu, Mo, Ce, Sr, K, Na, Nd and Cr analysis, and the Dionex to analyze anions such as F-, Cl-, NO2-, Br-, PO4---, NO3- and SO4--.

Qualitative handling of the solutions should be performed utilizing calibrated volumetric tools. These include volumetric flasks of various sizes and automatic dispensing pipettes (see Table in this section) with disposable tips (having fixed or variable volumes). To assure the

Table

Qty	Device	Manufacturer	Model #	Calib. Req.
10	Auto. Pipettes			
1	50 microliter	Eppendorf	3130	I
1	100 microliter	Eppendorf	3130	I
1	200 microliter	Eppendorf	4700	I
1	1000 microliter	Eppendorf	4700	I
1	250 microliter	Eppendorf	4700	I
1	500 microliter	Eppendorf	4700	I
1	1-4 milliliter	Oxford	Macroset	I
1	5 milliliter	Oxford	Macroset	I
1	5-10 milliliter	Oxford	Macroset	I
1	0.025-10 milliliter	Rainin	EDP-25	II
	Volumetric flasks (PMP)	Various		N.A.

I: Calibration check performed every month according to the procedure described in section 6.1.4.

II: Calibration check performed according to the procedure described in section 6.1.4 every six months.

accuracy of the volumetric tools, the following routine procedure should be applied:

- volumetric flasks : visually examine every volumetric flask prior to use. If there is any mechanical damage to the flask or any permanent, visible solid residue inside, the flask should be discarded. Carefully rinse the flask after use with DI water to avoid deposition of solids.
- dispensing pipettes : gravimetric check of the calibration is required every month as per procedure in section 6.1.4). If the calibration cannot be adjusted, the tool should be replaced. If an adjustment has been performed, the calibration of the instrument should be immediately rechecked before it is returned to general use. The calibration check reports should be filed into the folder and kept in the Analytical Laboratory.

6.1.3 Glass and Sludge Dissolution for Analysis

Note: *Deviations from the methods described below may occur and are recorded in the Analysis Procedures Laboratory Notebook*

Method #1

Glass Dissolution

(1) Weigh 0.1 g of glass.

(2) Add 3-5 ml of concentrated HF and 3-5 ml of concentrated HCl as required.

(3) Leave in sand bath for 2 to 3 hours at 70°C.

(4) If the glass is completely dissolved, add DI water to bring volume to 100 ml. and analyze

the solution as per procedure in section 6.1.2.

(5) If the glass is not completely dissolved, or if there is any precipitation, add up to 5 ml HCl or HNO_3 as required and leave in a boiling water bath for 2 to 3 hours or as needed to produce complete dissolution.

Method #2

How to Dissolve Sludge That Does Not Contain Glass

(1) Take 2 ml of sludge in a test tube.

(2) Add 3-5 ml of concentrated HCl and 3-5 ml of concentrated HNO_3 to the sludge as required and shake vigorously for 15 minutes. Transfer the supernatant to the dissolving bottle.

(3) If there is any precipitation, add equal amounts of HCl and HNO_3 to the test tube and centrifuge it.

(4) After transferring all the contents of the test tube to the dissolving bottle, add 30 ml of DI water and leave in a sand bath at 70°C for one hour.

(5) When the sludge is completely dissolved, bring the volume to the mark, (100 ml, 200 ml, etc.) and analyze the solution as per the procedure in section 6.1.2.

Method #3

How to Dissolve a Sludge Which Contains Glass

(1) Take 2 ml of sludge in a test tube.

(2) Add 3-5 ml of concentrated HCl and 3-5 ml of concentrated HNO_3 to the sludge as required and shake vigorously for about 10 to 15 minutes. Centrifuge and transfer the

supernatant to the dissolving bottle.

(3) Add ~ 10 parts HF per part of remaining precipitate to the test tube, shake and leave in a water bath at 70°C for one hour.

(4) Transfer the solution to the dissolving bottle. If there is still undissolved material, add more HF and leave the solution in the sand bath at 70°C until a clear solution is obtained.

(5) Bring the volume to the mark (100 ml, 200 ml, etc.) and analyze the solution as per procedure in section 6.1.2.

6.1.4 Calibration of Pipettes

Method: Gravimetric using a Mettler AE160 balance.

Frequency: Monthly except Rainin pipette which is six monthly.

Required Accuracy: As specified in individual procedures or as per instructions of the Project Manager.

(1) Obtain a "Pipette Calibration Check Record" form and supply requested information on pipette to be calibrated (e.g. manufacturer, model #, etc.).

(2) Tare out the weight of a 20 ml plastic vial on the Mettler balance.

(3) Pipet out deionized water from the pipette to be calibrated into the plastic vial. Record nominal capacity, actual capacity (weight displayed on the Mettler balance), and percent error under the appropriate columns.

(4) Repeat steps (2) and (3) five times. For variable volume pipettes perform the measure-

ment for 2-5 volume settings.

(5) Calculate the percent error as follows:

$$\% \text{ ERROR} = \frac{(\text{Actual capacity}) - (\text{Nominal capacity})}{(\text{Nominal capacity})} \times 100$$

(6) Examine results and report deviations from required accuracy to the Project Manager.

(7) Sign and date and file form in the 'Calibration Records' binder.

6.2 SOLUTION ANALYSIS WITH ATOMIC ABSORPTION SPECTROPHOTOMETER

6.2.1 Solution Preparation and Analysis (Water Matrix Only)

(1) About 3 ml of solution are required for each element to be analyzed separately (i.e. Cs, Li, Mg and Ni), if all four elements are to be analyzed, 10 ml are enough.

(2) Using a 100 ml flask, prepare High Std, Medium Std, and Zero Std (Blank) for each element from the stock Std's as shown in the table below:

Element	Hi Std	Med Std	Blank/Solvent
Li	2.0 ppm	1.0 ppm	DI water
Mg	0.5 ppm	0.2 ppm	DI water
Ni	5.0 ppm	2.5 ppm	DI water

Cs	2.0 ppm	1.0 ppm	KCl soln*

*The KCl solution is 100 μl/10 ml of 0.5 M KCl.

(3) If more than one element is present in the sample to be analyzed - Prepare mixed standard. Use KCl solution if the mix standard contains Cs. The same concentration of KCl must also be introduced into all samples containing Cs.

(4) Transfer the samples to be analyzed and the standard solutions to centrifuge tubes. Depending on the number of samples, several sets of standard solutions can be required. Refer to the following table:

No. of Samples	No. of Sets Required
1 - 5	2
6 - 10	3
11 - 15	4
16 - 20	5

(5) Load the automatic sampler carousel with samples and standard solutions according to the following sequence:

Position #1 : Zero Standard (Blank)

Position #2 : Medium Standard

Position #3 : High Standard

Position #4 - #8 : Samples to be Measured

Position #9 - #11: Standards as for Pos #1-#3

Position #12 - #16: Samples to be Measured

Position #17 - #19: Standards, etc.

The loading sequence should always be terminated with the set of standards.

(6) To perform the analysis and to obtain the report of the results, follow procedure in section 6.2.2 below.

(7) Repeat steps (5) and (6) for the next element.

6.2.2 Atomic Absorption Spectrophotometer Operating Procedure

Manufacturer: Perkin - Elmer

Model #: 503

Note: *Mg, Ni, and Li should be analyzed in the absorption mode while Cs should be analyzed in the emission mode. Consult M. Adel-Hadadi concerning the analysis of other elements which may sometimes be performed if the appropriate lamp is available.*

(1) Preliminary Steps (Record Start-up in the "AA Maintenance" LN)

(a) Refer to the "Standard Conditions" section of the Analytical Methods Book for data on the lamp source, fuel and oxidant, wavelength and control settings for the element being determined.

(b) Push the POWER button on.

(c) If the lamp source is installed in a universal lamp mount, make sure the Lamp Current control is set fully counterclockwise.

(d) Install the recommended lamp source.

(e) If the lamp is installed in a universal lamp mount, set the Lamp Current Meter given on the lamp label. Source controls on lamps installed in individual mounts are permanently set the first time the lamp is installed. Operation of the instrument may begin without lamp warmup for most lamps because the double beam feature automatically compensates for fluctuations in lamp output. However, the output of some hollow cathode lamps increases so greatly during warmup that it may be more convenient to wait until the lamp output has partially stabilized.

(f) Set the SLIT selector knob for the proper slit width.

(g) Select and depress the proper wavelength push button: UV or VISible RANGE. If the wavelength used is above 650 nm, also depress the FILTER button. Adjust the coarse WAVELENGTH control to obtain the proper indication on the WAVELENGTH counter.

(h) Turn the fine WAVELENGTH control very slowly to obtain the maximum needle deflection to the right on the ENERGY meter. While tuning with the WAVELENGTH control, adjust the GAIN control to set the ENERGY meter needle in the green region of the scale.

(i) Before proceeding, review these recommended safety practices:

1) Make sure the burner compartment shield is installed.

2) Keep water in the drain tube trap and submerge the end of the drain tube at least 13 cm (5 in) in the water.

3) Do not leave flame unattended.

(2) Air-Acetylene Operation

(a) Verify that a suitable burner head is installed in the burner chamber, that a click is heard when inserting the pin on the burner head hold down cable into the safety interlock at the base of the burner (otherwise the flame cannot be ignited) and that the drain tube is properly installed.

(b) Make sure the GASES control is in the SHUTDOWN position.

(c) Set the acetylene cylinder regulator output pressure at 12 psig.

(d) Set the air supply output pressure at 4.2 to 7.0 kg/sq cm (60 to 75 psig).

(e) Push the AIR oxidant selector button and press the OXIDANT FLOW CHECK button. Set the OXIDANT PRESSURE gauge for a reading of 2.1 kg/sq cm (30 psi) and adjust the AUXILIARY OXIDANT needle valve for a flow meter reading of 55.

(f) Flip the fuel selector switch to ACETYLENE. Push the FUEL FLOW CHECK button and set the FUEL PRESSURE regulator for a gauge reading of .56 kg/sq cm (8 psi) and adjust the FUEL flow needle valve for a flowmeter reading of 32. When the FUEL FLOW CHECK button is released, air will be released for several seconds to purge the burner of any remaining fuel.

(g) Flip the GASES control to ON and ignite the flame by pushing the IGNITE

button.

(h) Before shutdown, aspirate DI water for a few minutes. If organic residues have been aspirated, follow the procedure entitled "Cleaning the Burner".

(i) Turn the GASES control to SHUTDOWN to extinguish the flame.

(3) Adjusting the Flame

(a) Allow several minutes for the warmup of the burner system. If the flame is uneven, shut it off and clean the burner head slot. Also, check the burner alignment.

(b) A fuel-lean (oxidizing) mixture gives a blue, hotter flame; a fuel-rich (reducing) mixture gives a yellow, cooler flame. Adjust the Auxiliary Oxidant (usually air or nitrous oxide) control to provide the proper flame condition.

(c) Additional fine adjustments may be necessary to obtain optimum sensitivity. Remember to use a blank after each and every adjustment.

(4) Calibration

(a) Depress the ABSorbance push button and select either the REPEAT or the INT 1 SEC, 3 SEC, or 10 SEC (depending on the noise level) mode.

(b) Aspirate a blank solution and press the AUTO ZERO button. The READ indicator above the READ button will go out and the AUTO ZERO indicator will appear on the FUNCTION display. Continue aspiration until the AUTO ZERO indicator goes out READ reappears.

(c) Choose a calibration value appropriate to the standard being used, e.g. 0800 for a solution of 80 or 8 ug/ml (or any other desired unit). This value must be within the upper limit (+3999) and the expansion limit (100X) of the display.

(d) Depress the CONCentration and CALIBRATE buttons and adjust the CALIBRATE control to make the readout display the value selected in step c.

(e) Begin aspirating the standard solution and depress the AUTO CONCentration button. The READ indicator will go out and AUTO CONC will appear on the FUNCTION display. When the calibration set in Step 4 reappears on the Readout, the AUTO CONC indicator will go out and the READ indicator will reappear on the FUNCTION display. Set the decimal to the position desired with the DECIMAL position control. Check zero while aspirating a blank solution. Repeat the procedure if zero has shifted.

(5) Computer Controlled Operation

(a) Insert the diskette into the disk drive of "North Star".

(b) Turn on the computer and the terminal.

(c) "North Star" prompt should appear. Now type:

```
GO BASIC
LOAD AADATA
RUN
```

(d) At this point the automatic sampler should be on for the program to be executed.

(e) Enter input parameters as prompted.

(f) Once the computer is programmed and ready, restandardize according to paragraph 4.

(g) Type GO into the computer, insert the stainless steel aspiration tube into the sampler arm and push the RTN button on the terminal.

(h) Wait for program sequence to be completed and the report printed.

(6) Flame Emission Measurements at Fixed Wavelength

(a) Prepare the instrument for operation as described in paragraphs 1 through 3. NO lamp source is required unless the burned must be aligned. Allow about 5 minutes warmup after igniting the flame.

(b) Push in the CHOPPER button on the left front panel of the instrument and the EMISSION measurement button on the right front panel. The slit width should be set to give the resolution desired.

(c) With the WAVELENGTH counter set to the approximate analytical wavelength of interest, aspirate a blank solution and zero the readout.

(d) While aspirating the highest standard solution to be used in the calibration (i) adjust the GAIN control to set the ENERGY meter needle at midscale (ii) optimize the setting of the WAVELENGTH counter by adjusting the WAVELENGTH control for a maximum meter indication and (iii) adjust the GAIN control to bring the meter needle into the green region of the scale.

(e) Check the zero setting while aspirating a blank solution.

(f) Set the desired calibration for the standard solution on the readout using the

CALIBRATE control with the CALIBRATE button depressed. To make the reading smaller, reduce the GAIN.

(g) Press the AUTO CONCentration button while aspirating the standard solution to calibrate the readout.

(h) Because of the possibility of self-absorption effects in the flame, the linearity of the measuring range of interest should be checked by aspirating two or more standards. If nonlinearity is observed over the original range chosen, either reduce the range to one showing a linear relation, or plot a working curve from the results obtained by aspirating several standards and derive sample concentration values from the curve. (CURVE CORRECTION does not operate when emission measurements are made).

(i) Follow operation procedure in paragraph 5.

(j) Follow the instructions for instrument shutdown in paragraph 2. Depress the CHOPPER button to release it.

(7) Daily Maintenance (Record in "AA Maintenance" LN)

(a) Empty systems waste container.

(b) Adjust GAS/AIR flow.

(c) Rinse burner head.

(d) Align burner head.

(e) "Peak" system.

6.3 SOLUTION ANALYSIS WITH DC PLASMA

6.3.1 Solution Analysis with DC Plasma Emission Spectrophotometer (Water Matrix Only)

(1) At least 5 ml of the solution is required for analysis.

(2) Prepare a Hi Std solution containing all of the elements of interest. The concentrations of elements in the Hi Std should somewhat (but no more than twice) exceed the expected concentrations of elements in the solution.

(3) Use DI water as the Zero Std (Blank).

(4) Transfer the samples to be analyzed and the standard solutions to centrifuge tubes. At least two sets of standards will be required. Maximum of up to 32 samples can be analyzed per run.

(5) Load the automatic sampler carousel with the samples and the standard solutions according to the following sequence:

Position #1 : Zero Standard (always)
Position #2 : High Standard (always)
Position #3 - #12: Samples (maximum)

For higher positions the sequence can be repeated or terminated by the use of a zero standard followed by a hi standard.

Note: *There is a maximum of up to 10 samples allowed between two adjacent sets of standards. If certain series of samples consist of solutions having wide differences in concentration ranges (factor of 5 or more) and a cross-contamination is likely to occur,*

the samples can be separated by the zero standard. In that event, the zero standard has to be considered as a sample.

(6) To perform the analysis and to obtain the report of the results, follow the procedure in section 6.3.2 below.

(7) If the sample (or samples) contain elements which have to be analyzed in a single element mode, perform the multiple element mode analysis first.

6.3.2 DC Plasma Emission Spectrophotometer Operating Procedure

Manufacturer: Spectra Metrix Inc.
Model #: Spectra Span III-B

(1) Start-up procedure (to be performed daily or every 8 hours of continuous operation and recorded in the "DCP Maintenance" LN).

(a) Make sure that all of the power supply switches (PLS and PWR) and the argon switch are in the OFF position. Set RUN/READY switch to RUN.

(b) Remove the shield covering the jet assembly.

(c) If the instrument was operated recently, wait a few minutes to give the electrodes sufficient time to cool.

(d) Replace all consumable elements of the jet assembly (i.e. ceramic sleeves, graphite anodes, and the stainless steel cathode).

(e) Turn argon gas ON on the tank and the regulator.

(f) To see if all the electrodes are properly set up, switch the RUN/READY switch to READY. All three electrodes should meet, with the cathode in the center of the far anode, making it bow slightly. If it is not in this RUN position, move the cathode back and forth with the cylinder adjusting nut until the conditions above are satisfied.

(g) Turn the RUN/READY switch to RUN, and turn the gas switch off.

(h) Check if the aspiration hose and the waste hose are worn down; if they are, change both of them, not just one, as this may variably affect the rate of inflow and rate of outflow and excessive moisture develop inside the atomizing chamber.

(i) Carefully replace the shield and protective cover.

(2) To Light the Spectrajet

(a) Make sure that the RUN/READY switch is on RUN.

(b) Turn up the argon gas switch.

(c) Make sure to have the proper gas pressures:

20 psi nebulizer

50 psi sleeves

(d) Turn the RUN/READY switch to READY.

(e) Push the PLS button.

(f) Set the peristaltic pump switch on and have DI water aspirating, as well as the pump clamp engaged.

(g) Once a constant sound is heard, watching the electrodes through the shield, flip the RUN/READY switch to RUN. The flame should appear and have the characteristic inverted "Y" appearance. If only a partial flame appears, or if no flame appears, quickly turn the RUN/READY switch back to READY, wait 5 seconds, and once again flip the switch to RUN. If, again, flame is not there or is not complete, try two more times, and if no success is achieved, flip to READY, turn PLS button off, gas switch off, and readjust the electrodes. If after this the flame does not light, consult the manual.

(3) Element Programming

(a) At this point, choose the elements desired among the twenty elements on the cassette. To do this, flip the black switches corresponding to the elements in your high std up. The rest of the switches must be down.

(b) Now push in the light above the first black switch that is turned up. The LED display will now show information corresponding to that element.

(c) Set all the PMTs according to the temporary list posted.

(d) Now look at the first lit element. To check whether the correct high std value happens to be already entered from the last run, press DIS HI. The LED display will show the high std concentration for that element from the last run. If a change is desired, press C (to clear), enter the desired high std on the keyboard, and press ENT HI. Now the correct high std has been entered. Again to check,

press DIS HI.

(e) To enter the correct low std, do as above, except with DIS LO, and ENT LO.

(f) Now push in the light above the second black switch that is up, and to the above procedure for the element. After the last element is completed, the DC Plasma is programmed to the high and low standards entered.

(4) Alignment of The Flame

(a) Visually inspect the flame - should have a stable, "straight-up" appearance. If not, adjust electrodes.

(b) Listen for an unusually high whistling sound - if present, adjust the gas flow to each anode and cathode with a small screwdriver. Caution should be exercised as this changes the shape, the focus, and the temperature of the flame.

(c) Look at the reflection of the flame on the entrance slit. The "Y" should have a sharp, in-focus appearance. If not, consult the trouble shooting section of the manual.

(d) The central point of the "Y" should be just below the third slit from the bottom, just illuminating the very bottom of the slit. To move the "Y" horizontally or vertically, use the silver set of knobs on the front part of the electrode assembly.

(5) Alignment of the Cassette

(a) Depending on the cassette used have a 10 ppm Cu or Ca solution aspirating.

(b) Turn up the Cu or Ca element switch, as well as the light above it.

(c) Turn the MODE switch to 1, the DIAG switch up, the REPEAT switch to 0, the

AVG ONLY up and down, RST.

(d) Put the TIME setting high enough to read about 5000 on the LED display.

(e) Tune in the plasma position.

(f) AVG only up and down, RST.

(g) Optimize the Cu or Ca wavelength - turn the "vertical" and "horizontal" dials until the LED display is as high as it can get. Use the fine adjustment dials for this, as gentle rotation produces the best results.

(h) Once the cassette is aligned according to the Cu or Ca wavelength, switch the MODE switch to INT, TIME to 8, and REPEAT to 3.

(i) Other settings should be:

PRINT	up	BKGRD	down
DIAG	down	STD DEV	up
XMIT	up	LED	down
INT STD	down	ALL CHAN	up
CASSETTE	1	LP to DCP	
TEST CURRENT on PMT		DCP	to stand alone
AVG ONLY	down	RST	momentarily pressed

(j) Turn off the Cu or Ca element switch and turn on the light to one of the other elements in your run.

(k) AVG ONLY up and down, RST.

(l) Aspirate DI water.

(6) Standardization

(a) Divide the high and low standards to the appropriate test tubes on the carousel.

with enough left in the flasks for calibration.

(b) Aspirate high std solution.

(c) Push A/R button.

(d) Once the A/R button goes off, HI STD button automatically comes on. Once this button goes off, the high std is calibrated.

(e) Have the low std (or blank) aspirating, for at least a minute since no carry-over from the previous high std is desired.

(f) Push LO STD button.

(g) Once this button goes off, the low std is calibrated.

(h) A printout on the high standard will show how accurate the high std was. If these are not satisfactory, both stds should be made new, and the DC Plasma restandardized.

(i) Aspirate DI water.

(7) Computer Programming

(a) Insert the disk with the printed side to the right and the notch toward the outside. Close the disk drive opening.

(b) Turn on the computer unit and the terminal.

(c) "North Star" monitor should appear; if not, turn on the reset button in the back of the computer unit.

(d) Type:

```
GO BASIC
LOAD DCP.5
RUN
```

(e) At this point the automatic sampler should be on for the program to initiate.

(f) Type in the date and the whole program, paying attention to the HS INT (number of samples in each block) in the parameter section, as well as the correct values for the high stds.

(8) Running Samples

(a) Once the computer is programmed and ready to go, restandardize according to Section 6.

(b) Turn the LP and DCP switches down to COM.

(c) Type GO into the computer, insert the stainless steel aspiration tube into the sampler arm, and push the RETURN button on the terminal.

(d) The computer will now take over and run the samples according to the scheme programmed.

(e) Watch for the steel tube being lowered directly into each tube on the carousel!

(f) Once the run is completed, the carousel will be reset into its starting position. calculations and the final printout should follow.

(g) Take the steel aspiration tube out of the sampler arm and aspirate with DI water

(h) If a second set of samples needs to be run, go back to Section c, skip Sections d, e, f, and continue from Section g.

(9) Single Element Mode

(a) Replace multi-element cassette with single element cartridge.

(b) Use the first channel for all single mode elements.

(c) Refer to the "Handbook of the Spectral Lines of Elements for DC Plasma/Echelle Systems" and select the best line for the particular element of interest.

(d) Standardize the instrument with the standard solutions of that element (ref to para. 6 above)

(e) Run Samples as described in paragraph 8.

(10) Shutdown Procedure

(a) Take the aspiration tube out of DI water and aspirate air for about one minute.

(b) Press the PLS button so light is off.

(c) Flip the RUN/READY switch to READY

(d) Shut the argon gas off at the tank.

(e) Wait until the lines are bled, the regulator show '0', then flip the gas switch off or down. Then shut the argon gas off at the regulator.

(f) Turn the peristaltic pump switch off, and lower the pump clamp assembly.

(g) Set all PMT settings to '1'.

(h) Shut down the computer unit, the terminal, and the cooling water pump!

(11) Daily Maintenance (Record in "DCP Maintenance " LN)

(a) Replace all consumable elements of the jet assembly and align electrodes.

(b) "Peak" the system with Cu or Ca solution.

(12) Weekly Maintenance (Record in "DCP Maintenance" LN)

(a) Replace all plastic hoses.

(b) Rinse complete aspiration system with DI water.

(c) Rinse, clean and oil all ceramic rollers.

(d) Replace systems cooling water with fresh DI water.

(e) Clean the nebulizer using DI water and compressed air.

(f) Replace all consumable elements of the jet assembly

(g) Align electrodes

(h) "Peak" the system with Cu or Ca solution and align optics

(i) Seal all connections with teflon film tape

(j) Check channel's electronic function

6.4 ANALYSIS WITH ION EXCHANGE CHROMATOGRAPHY

6.4.1 Solution Preparation and Analysis

(1) About 2 ml of solution are required for analysis.

(2) Prepare the standard solution containing all the anions of interest, matching approximately the expected concentrations of anions in the sample to be analyzed.

(3) Refer to procedure in section 6.4.2 and perform the analysis of the standard solution first. Note if there is any change in retention time for each of the various anions by comparing the chromatogram with the most recent one. Then, perform the analysis of the sample.

(4) To obtain the results, Proceed as follows:

(a) identify the peaks of the appropriate anions by comparison with the standard output.

(b) measure the height of the peaks

(c) if no change in retention times has been observed (para. (3) above), obtain the results from the calibration curve (para. (5) below). If the retention times have changed, either compare the standard output with the sample output or construct the new calibration curve.

(5) Calibration curve is a graph showing the concentration of a particular anion species (in ppm) against the appropriate peak height (in mm) which should be performed every 6 months.

6.4.2 Dionex Chromatograph Ion Exchange Operating Procedure

Manufacturer: Dionex
Model #: 2010i

(1) Operation Instructions for System Components

(a) Analytical Pump

(i) Eluent Section

Before beginning operation, prime the eluent manifold with the desired eluents (including regenerent and water, if used). After changing or refilling an eluent reservoir, reprime the corresponding eluent valve.

Procedure:

(1) Press STOP/START to stop the pump.

(2) Attach an empty 10 ml syringe to the luer adaptor on the priming valve.

(3) Turn the small handle on the priming valve to align with the syringe.

(4) If desired, fill the eluent reservoirs and connect them to the eluent bulkhead connectors on the pump.

Note: *Prime only one valve at a time.*

(5) Select an eluent (press the switch 'ON'). Use the syringe to draw liquid from the reservoir, through the liquid lines and the eluent manifold, into the syringe. This flushes out any air or liquid trapped previously in the liquid line.

(6) Turn off the eluent valve just flushed. Remove and empty the syringe.

(7) Replace the syringe, select the next eluent, and repeat Step 5.

Note: *When making an eluent change while the pump is running, first select the new eluent, wait 1-2 seconds, then turn off the old eluent. This prevents the formation of bubbles in the eluent manifold during the change.*

(8) Repeat Steps 5 and 6 for the remaining eluents (if used).

(ii) Priming The Pump

The pump rarely loses prime when in continuous, routine use. However, if an eluent reservoir empties during operation, or if the pump has not been used for a month or more, it may be necessary to reprime the pump before resuming operation.

CAUTION

Bypass all columns before priming the pump to avoid accidental system overpressing and possible column damage.

(1) Turn the knob on the pressure transducer housing counterclockwise approximately one-half turn. This opens the pressure transducer waste valve.

(2) Select one eluent (turn on the valve).

(3) Set FLOW SELECT to 1.0 ml/min.

(4) Set LOCAL/REMOTE to LOCAL.

(5) Set the LOCAL PRESSURE LIMIT SELECT to zero (00 x 10 psi) and the HIGH PRESSURE LIMIT SELECT to 500 (5 x 100 psi).

(6) Fill the 20 ml syringe with isopropyl alcohol. Connect the syringe to the priming valve luer adaptor.

(7) Turn the small handle on the valve to align with the syringe, opening the internal valve.

(8) Press START/STOP to start the pump.

(9) Slowly push the alcohol through the pump with the syringe. Ensure that alcohol is pushed through both heads by watching the Delivery Status LEDs: each LED must light at least once while pushing the alcohol through the pump.

Note: *Avoid pushing any air trapped in the syringe through the pump. This will result in the loss of prime.*

(10) Set FLOW SELECT to 4.0 ml/min and flush the pump with eluent for 2 minutes.

(11) Turn the handle on the priming valve to the right of the open position, closing the valve.

(12) Set FLOW SELECT to the desired flow rate.

(13) Turn the knob on the pressure transducer housing clockwise to close the waste valve.

CAUTION

Overtightening may damage the pressure transducer housing or the valve seal.

(14) Place the columns in line and set the pressure limits.

(15) Wait for the READY LED to light, indicating that the pump flow-control system is operating, before beginning an analysis.

(iii) Selecting The Pressure Limits

The low and high pressure limits automatically stop the pump in the event of system malfunction (e.g., overpressuring or a leak downstream from the pump). After priming the pump, select a high pressure limit 50-100 psi above the normal system operating pressure. The pump has an automatic safety high pressure limit of 1900 psi, above which it will not operate. Select a low pressure

limit 100-200 psi below the normal system operating pressure.

Note: *The low pressure limit may be inactivated, as during priming, by setting the LOW PRESSURE LIMIT SELECT switches to zero.*

(b) Advanced Chromatography Module

(i) Routine Operation

During an analysis, Valve A is OFF, directing eluent flow through the injection valve to the separator, the suppressor (if used), and finally, through the detector cell to waste.

Turn Valve A On during on-line regeneration of the suppressor column. This reverses the flow through the suppressor and bypasses the injection valve, the separator, the cell, and all interconnecting tubing. See the Column manual for complete suppressor regeneration instructions. (**Note:** *this procedure does not apply for fiber type suppressor which is self-regenerating.*)

Periodically empty the waste container to prevent overflow. Take appropriate precautions when handling the strong acid and/or base waste from suppressor regeneration.

(ii) Making An Injection

The Advanced Chromatography Module is equipped with a 50 μl sample loop. Load sample into the sample loop through the SAMPLE PORT by the following method:

(1) Flush Sample Loop. Attach a syringe to the SAMPLE PORT. Insert the end of the tubing from the #2 bulkhead fitting into a small container of deionized water or eluent. Set the LOAD/INJECT switch to LOAD and draw at least 10 loop volumes (e.g., 0.5 ml for a 50 ul loop) of liquid into the syringe, flushing the sample loop completely.

(2) Load sample. Wipe off the end of the tube, then insert it into the sample container. Draw at least 10 loop volumes of sample into the syringe, filling the loop completely. Subsequent repetitive injections require only 5 loop volumes of sample.

(3) Inject Sample. After the detector baseline is stable, offset it to zero, and set the LOAD/INJECT switch to INJECT.

(c) Conductivity Detector

(i) Start-up

After installing the detector, or whenever the detector power has been off, follow this start-up procedure to reset the detector microprocessor.

(1) Check that all cables are correctly connected and that the detector is plugged into the power strip.

(2) Check that the power switch on the power strip is 'ON'.

(3) Turn on the POWER switch.

(4) Set the LOCAL/REMOTE switch to LOCAL.

(5) Turn 'OFF' the AUTO-OFFSET.

(6) Turn 'OFF' THE cell, then turn it to 'ON'.

(ii) Routine Operation

Check that CELL is on. Turn off the AUTO-OFFSET during system equilibration. Select an OUTPUT RANGE which will allow the baseline to be monitored on the recorder. After the chromatographic system is equilibrated, and the baseline is stable, select the OUTPUT RANGE sensitivity required for the analysis. Set TEMPERATURE COMPENSATION to the desired value (see Section iv). Then turn AUTO-OFFSET 'ON' just before beginning an analysis. The baseline may be reset to zero at any time by momentarily turning off AUTO-OFFSET then turning it back on.

(iii) Eluents

In general, eluents used with conductivity detection should have conductivities less than 50 μS for optimum detector sensitivity. In Ion ChromatographyTM, highly conductive eluent ions are removed from the eluent stream or converted to less conductive forms by the suppressor before entering the cell.

(iv) Temperature Compensation Optimization

The TEMPERATURE COMPENSATION setting for most eluents is approximately 1.7 %/°C. Optimize the Temperature Compensation setting for each column set and eluent batch to minimize temperature-caused variations in the measured conductivity.

This is especially important when operating at high sensitivities. The optimum setting for any eluent is determined as follows:

(1) Install a 30 cm (12 in) length of 0.5 mm ID tubing between the suppressor outlet (or Port #3 on Valve A) and the cell inlet.

(2) Prepare a beaker of room-temperature water and one of boiling water. Place the tubing from Step 1 in the room-temperature water.

(3) Install the columns.

(4) Set TEMPERATURE COMPENSATION to 2.0 %/°C.

(5) Begin pumping the eluent through the system.

(6) Select an OUTPUT RANGE which keeps the baseline on scale.

(7) After the system reaches equilibrium, and the baseline is stable, set the OUTPUT RANGE to 30 μS. Turn on AUTO-OFFSET. Position the recorder pen about halfway up the paper.

(8) Record the baseline for 1 tp 2 minutes.

(9) Remove the tubing from the room-temperature water and place it in the boiling water for 1 to 2 minutes. Note the recorder baseline shift. If the baseline shifts positive, the TEMPERATURE COMPENSATION setting is too low. If it shifts negative, the setting is too high.

(10) Place the tubing in the room-temperature water and allow the baseline to restabilize for 1 to 2 minutes.

(11) Based on the results of Step 9, increase or decrease the TEMPERATURE

COMPENSATION setting by 0.5 %/°C for the first trial and by 0.1 %/°C for successive trials.

(12) Repeat Steps 9 and 10 until the recorder baseline shift is at a minimum.

(13) Disconnect the tubing and reconnect the suppressor to the cell inlet as it was originally.

(14) Close the column compartment, covering the valve compartment.

(2) Performing Analysis

(a) Initial Operation

If a new column is installed, verify that the system is operating correctly by duplicating the test chromatograms sent with the columns. This also provides an opportunity to become familiar with operating the system before beginning actual analyses.

(1) Read Paragraph 1 above. It contains detailed operating instructions for each component.

(2) From the test chromatogram sent with each separator column, determine the eluent, flow rate, and full-scale setting used to analyze the test standard.

(3) Prepare the eluent and suppressor regenerant (if required) specified on the test chromatographs and connect them to the pump eluent manifold system.

(4) Select the flow rate indicated on the test chromatogram and allow the system to equilibrate with the eluent to be used in the analysis.

Note: *Normally, at least 20 column volumes of eluent are required for complete equilibration.*

(5) Set the conductivity detector TEMP COMP to 1.7.

Note: *The value 1.7 is the nominal Temperature Coefficient of the "standard anion eluent". Use this value with any eluent for the purposes of this test. During actual analysis, use the experimentally determined eluent temperature coefficient for optimum performance.*

(6) Turn on the recorder. Set the conductivity detector OUTPUT RANGE to a value that keeps the recorder pen on scale and monitors the base line. Once the baseline is stable, select the detector output range indicated on the test chromatogram.

(7) Load the sample loop with the standard solution shipped with the columns, offset the baseline, and inject the sample.

(8) Compare the chromatogram obtained with the test chromatogram.

(9) Calculate the efficiency and line resolution of the peaks indicated on the test chromatogram. The calculated values should agree within 20-25% of those on the test chromatogram.

Note: *Slight differences are due to instrument variations and /or differences in temperature and eluent strength from test conditions.*

(b) Routine Operation

Routine operation consists of injecting samples using the procedure described in the paragraph above.

(c) Short-term Shutdown

Following completion of the daily operation, the system is normally set to stand-by state until operation is resumed.

(1) Turn off the pump, and recorder. Set the conductivity detector RANGE to '10k' μs and turn 'Off' CELL.

(2) Leave the POWER 'On'.

Note: *If the power is turned 'Off', the conductivity detector must be reset when operation is resumed.*

(d) Prolonged Shutdown

Use the following shutdown procedure if the system will not be used for two weeks or more.

(1) Prepare columns for storage.

---------- CAUTION ----------

Improper storage of columns may result in permanent degradation and loss of performance.

---

(2) Remove the columns from the system, couple the column lines together, and flush the system with deionized water for 30 minutes at 9.9 ml/min.

(3) Turn off the POWER switch.

6.5 SOLUTION ANALYSIS WITH ICP-MS

6.5.1 Solution Preparation and Analysis

(1) Obtain the run information sheet and labels for the run from the Data Processing laboratory and obtain the samples from the Leach laboratory

(2) Prepare the standards required to be used in the run according to the instructions given on the run information sheet using the automatic pipette, 20 ml scintillation vials and polymethylpentane volumetric flasks.

(3) Add about 8 mls of the WASH solution (2% HNO_3 with deionized water) and about 8 mls of the ZERO solution (1% HNO_3 prepared by dilution of 70% HNO_3 with deionized water) to the required number of scintillation vials for the run.

(4) Arrange the vials in the order given on the run information sheet and label them with the sticky labels provided.

(5) Perform the analysis according to procedure in section 6.5.2 below.

6.5.2 Inductively Coupled Plasma-Mass Spectrometer Operating Procedure

Manufacturer: VG Instruments
Model #: PQI

A. <u>Turning on of Instrument</u>

(1) Open the two valves marked "Gas Supply" and "Pressure Buildup" on the argon cylinder.

(2) Ensure that the supply of argon is sufficient for one day's work by checking that the liquid level marker in the central indicator on the cylinder is at least one quarter of the way up between the two points marked "N".

(3) Open the air by turning the black valve completely counterclockwise and then clockwise back again one quarter of a turn.

(4) Turn the intensity knob clockwise on the Tracor-Northern MCA of the instrument until the letters TN-7200 are of acceptable brightness.

(5) Ensure that the TIME switch on the Quadrupole Control panel is set to "EXT".

(6) Turn on the electric switch of the surge protection unit under the computer.

(7) Place about 100 mls of deionized water in a 120 ml urine sample cup and place the cup in the position allocated for it in the start-up and tuning rack of the autosampler.

(8) Set the start-up and tuning rack in the rightmost position of the autosampler tray.

(9) Ensure the cap has been removed from the cup.

(10) Turn on the autosampler.

(11) Load file #6 into the autosampler control keypad by hitting the "EDIT" key, the "6" key and then the "ENTER" key twice.

(12) Press the "START" key and the probe will enter the cup containing the deionized water.

(13) Load the peristaltic PVC tubes on to the head of the peristaltic pump and turn the pump on.

(14) Wait about one minute while deionized water is pumped through the instrument.

(15) Turn off the peristaltic pump.

(16) Turn on the computer and printer.

(17) At the prompt "C:\>" type "ICPMS" and strike "ENTER" key.

(18) After about 2 minutes the ICPMS options will appear on the screen and then load the instrument control program by striking the F1 key.

(19) Turn on the plasma of the instrument as follows:

WARNING: FAILURE TO EXACTLY FOLLOW THIS PROCEDURE MAY LEAD TO MELTING OF THE TORCH AND TO EXTENSIVE DAMAGE TO THE INSTRUMENT.

(a) Depress the three green buttons marked "COOL," "AUX" and "NEB" on the MS81 gas control panel.

(b) Adjust the flow rates of the gases to:

(i) 12 lit/min for the cooling gas

(ii) 2.5 lit/min for the auxiliary gas

(iii) 0.7 lit/min for the nebulizer gas

(c) Wait at least 5 minutes.

(d) Switch off the nebulizer gas.

(e) Wait until the flow indicator in the gas control panel flashes.

(f) Depress the red button marked "POWER" on the plasma radio frequency (RF)

generator.

(g) IMMEDIATELY ignite the plasma by depressing the red button marked "IGNITE" on the gas control panel.

(h) If the plasma does not form within 5 seconds depress the "IGNITE" button again.

(i) If the plasma still does not form IMMEDIATELY depress the yellow button marked "STANDBY" located on the plasma RF generator and consult with the project manager.

(j) IMMEDIATELY after the plasma is formed depress the green button marked "NEB" on the gas control panel.

(20) Turn the peristaltic pump on again in order to pass deionized water into the plasma.

(21) Hit the F4 key on the computer keyboard labelled "ICP CONTROL" followed by the F6 key labelled "TORCH POSITION".

(22) Once the torch has moved forward hit the "Esc" key.

(23) Hit the F5 key labelled "SAMPLE INTERFACE" followed by the F1 key labelled "EXPANSION PUMP".

(24) Wait until the expansion pressure reads "OK" and then hit the F3 key labelled "EXTRACTION ON/OFF".

(25) If the computer indicates that extraction lens 2 is not activated hit the F4 key labelled "EXTRACTION 1/2".

(26) Check that the expansion pressure reads "OK", then wait about one minute and then hit the F2 key labelled "SLIDE VALVE".

(27) Ensure that the pressure reading on the Edwards vacuum controller gauge is below 5 x 10^{-6} mbar.

(28) If any problem exists call the Project Manager.

(29) Hit the Esc key and then hit the F6 key labelled "QUAD STATUS" in order to switch on the quadrupole analyzer. The value 106.5 should appear on the mass indicator of the quadrapole control panel of the instrument.

(30) Hit the F7 key labelled "DETECT MODE" followed by the F1 key labelled "HT ON/OFF".

(31) Check that the rate meter on the plasmaquad preamplifier panel shows a response of less than 50 Hz when the ratemeter is set to 100 Hz FSD. If the response is greater than 50 Hz call the project manager.

(32) Hit the "Esc" key followed by the "Q" and "Y" keys in order to return to the main ICPMS driver menu.

(33) Wait half an hour for the instrument to warm up.

B. Initialization of Analysis Run

(1) Load the start up and tuning rack of the autosampler with a urine sample cup containing about 100 mls of deionized water and the vials containing the tuning solution (TSO), the marker solution (MSO) and the WASH solution placing them in the positions marked on the rack.

(2) Set the startup and tuning rack in the rightmost position of the autosampler tray.

(3) Load file #5 into the autosampler control keypad by striking the "EDIT" key, followed by the "5" key and then the "ENTER" key twice.

(4) Press the "START" key and the probe will enter the cup containing the deionized water.

(5) Set the quadrupole analyzer to 115 amu by turning the TIME switch on the Quadrupole control panel from "EXT" to "0.1" and adjusting the coarse and fine mass control dials.

(6) Press the "START" key again and the probe will enter the vial containing the tuning solution.

(7) Set the attenuation of the ratemeter in the Plasmaquad preamplifier panel to a full scale reading of 100 KHz.

(8) If the signal is greater than 20 KHz the response is acceptable otherwise call the project manager to tune the instrument.

(9) Return the TIME switch to "EXT".

(10) Press the "START" key again on the autosample control keypad and the probe will enter the WASH solution.

(11) Wait at least 3 minutes.

(12) Meanwhile load the peak jump isotope ratio program into the computer by carrying out the following:

(a) Hit the F6 key labelled "PJ ACQUIRE".

(b) Hit the F2 key labelled "IR PJ".

(13) Once the program is loaded hit the F9 key labelled "CALIB PARAM".

(14) Hit the F1 key labelled "PRINT INT" and then hit the "Y" key.

(15) Hit the F3 key labelled "PJ MARKER".

(16) Enter the name of the appropriate element menu and the message "waiting for marker sample" will appear.

(17) Press the "START" key again on the autosampler control keypad and the probe will enter the marker.

(18) Wait at least 2 minutes.

(19) Hit the F5 key labelled "ACQUIRE SAMP" in order to perform the marker run.

(20) Once the run is completed hit the F4 key labelled "MASS CAL" and then type "P" as the mass calibration type.

(21) Hit the "Esc" key.

C. Performance of Analysis Run

(1) Hit the F1 key labelled "QUEUE ACQUIRE".

(2) Enter the name(s) of the appropriate analysis file(s).

(3) Wait until the red light above the floppy disk drive A in the computer goes out and insert the first floppy diskette of the run and close the floppy diskette drive door.

(4) After the autosampler has been initialized, as indicated by an appropriate message on the computer screen, press the "START" key on the autosampler control keypad and the probe will enter the WASH solution.

(5) Wait at least 5 minutes.

(6) Press the "START" key again and the probe will enter the urine sample cup containing

deionized water.

(7) Wait at least 5 minutes.

(8) Press the "START" key again and the probe will move to the HOME position.

(9) Remove the startup and tuning rack from the autosampler.

(10) Set the five analysis racks into the autosampler.

(11) Load the racks with the first 70 samples of the analysis run as follows:

(a) Place the first sample in the forward left hand corner of the left most rack.

(b) Place the second sample behind it and continue placing samples in this way until the first column of seven sample locations is filled with vials.

(c) Repeat steps 11(a) and 11(b) for the next seven vials in the next column to the right and continue filling the racks in this way moving to the right of the autosampler until all 70 sample locations are filled with vials.

(12) Ensure that the caps have been removed from all of the sample vials.

(13) Hit any key on the computer keyboard two times.

(14) Wait about 30 seconds until the computer loads the controller of the autosampler. The message "ANALYSIS" will appear on the output display of the autosampler controller keypad and the run will begin.

(15) Wait while the analysis is performed automatically.

(16) Replace the floppy diskette with another one when the message "COULD NOT WRITE THE FILE" appears on the computer screen and hit the "RETURN" key of the computer so that the analysis run can continue.

(17) After all the samples in the first autosampler tray (maximum 70 have been analyzed, replace the samples in the racks with the next samples to be analyzed by repeating steps (11) and (12).

(18) Queue a new procedure by performing steps (1) and (2).

(19) Repeat steps (17) and (18) until all the samples in the run have been analyzed.

D. Termination of Analysis Run

(1) Remove all sample racks from the tray of the autosampler.

(2) Switch the autosampler off, wait 10 seconds and then switch it on again.

(3) Set the startup and tuning rack back into the rightmost position of the autosampler tray.

(4) Remove the vials containing the tuning solution (TSO) and marker solution (MSO) from the rack so that only those containing the WASH solution and deionized water remain.

(5) Load file #7 into the autosampler control keypad by pressing the "EDIT" key followed by the "7" key and then the "ENTER" key twice.

(6) Press the "START" key and the probe will enter the vial containing the WASH solution.

(7) Wait about 5 minutes.

(8) Press the "START" key again and the probe will enter the deionized water.

(9) Hit the "Q" key followed by the "Y" key in order to obtain the ICPMS main driver program.

(10) Hit the F1 key labelled "INSTR CONTROL" to load the instrument control program.

(11) Hit the F1 key labelled "PUMPING STATE" and then answer the question on the screen by hitting the "Y" key.

(12) Disregard the message on the screen and hit any key to continue. The instrument will be turned off except for the plasma.

(13) Hit the "Q": key followed by the "Y" key and then repeat this step again in order to obtain the C:\> prompt on the computer screen.

(14) Type PARK <CR> and turn off the computer.

(15) Press the "START" key on the autosampler control keypad and the probe will return to the HOME position.

(16) Wait about 3 minutes.

(17) Turn off the peristaltic pump.

(18) Depress the switch marked "STANDBY" on the radio frequency generator in order to extinguish the plasma.

(19) Wait about 3 minutes until the front panel of the torch box cools to around room temperature.

(20) Switch off all the gases by depressing the buttons marked "NEB", "AUX" and "COOL" on the MS781 gas panel of the instrument.

(21) Release the peristaltic PVC tubes from the pump head.

(22) Dim the Tracor-Northern MCA in the instrument by turning down the button marked "INTENSITY".

(23) Turn off the autosampler.

(24) Turn off the surge protector below the computer.

(25) Close off the air supply by turning the black valve completely clockwise.

(26) Close off the argon by closing the two valves marked "Gas Supply and "Pressure Buildup" on the argon cylinder.

(27) Collect all diskettes and printouts and transfer them to the Data Processing Laboratory.

6.6 ANALYSIS WITH PERKIN ELMER 330 SPECTROPHOTOMETER

6.6.1 Solution Preparation and Silicon Analysis

Si-1 (Molybdate, direct)

Qty	Device	Manufacturer	Model	Calib. Req.
1	Spectrophotometer	Perkin Elmer	330	I
1	Balance	Mettler	AE160	II
3	Pipettes			
	200-100 μl	Labsystems	Digital	III
	5-10 ml	Oxford	Macro Set Transf.	III
	0.1-1 ml	Clay Adams	Selectapette	III

I: Calibrated with every analysis

II: Calibration accuracy: ± 1 mg
Calibration frequency: monthly

III: Calibration accuracy: ± 5%
Calibration frequency: monthly

Spectrophotometer Parameters

Cell: 5 cm x 1 cm x 4.5 cm (quartz)

Scan range: 610nm - 780nm

Peak wavelength: 663nm

Base wavelength: 750nm

Back correction range: 580nm - 820nm

Blank: DI water + reagents

Reagents

Silicon Standards: freshly prepare a set of silicon standards by dilution of an NBS traceable commercial standard in deionized water in order to produce one set of standards which covers the range of concentrations of Si to be used.

10% Ammonium molybdate: dissolve 2.5 g of Baker reagent grade ammonium molybdate in water, add 2.8 ml of concentrated reagent grade sulfuric acid dropwise while solution is stirring, dilute to 25 ml with water.

12.5% Tartaric acid: dissolve 3.125 g of reagent grade tartaric acid in water and dilute to 25 ml with water.

ANSA-bisulfite reducing agent:

Solution A: dissolve 3.125 g of reagent grade sodium bisulfite in 17.5 mL of water.

Solution B: dissolve 0.25 g of reagent grade anhydrous sodium sulfite in 5 mL of warm water and add 0.05 g of reagent grade 1-amino, 2-naphthol and 4-sulfonic acid (Eastman #360).

Mix solution A with solution B and dilute to 25 ml with water.

*Note: ANSA-bisulfite reagent should be stored in a cool dark place and prepared fresh every 2-4 weeks. All reagents should be prepared with deionized water using

plasticware and stored in plastic bottles.

Procedure

(1) Prepare each sample by adding to a 25 ml plastic volumetric flask:

(a) recommended aliquot of sample (as per instructions of Project Manager).

(b) Deionized water to neck of flask.

(c) 0.2 ml of 10% ammonium molybdate, shake well and wait 9-10 minutes.

(2) Add 1 ml of 12.5% tartaric acid, shake and wait 2 minutes.

(3) 0.2 ml of ANSA bisulfite reducing agent, dilute to 25 ml, shake well and wait 40 minutes.

(4) Perform the colorimetric measurement on the run of standards and samples as per procedure in section 6.6.2. Include at least one set of standards per run of samples determined.

(5) If concentrations of samples fall outside range of standards dilute the samples appropriately repeat the analysis.

6.6.2 PERKIN ELMER 330 SPECTROPHOTOMETER START-UP AND OPERATING PROCEDURE

1) Remove cover.

2) Remove pen cover.

3) Install appropriate cell holder.

4) Put in sample/reference compartment 2 identical cells filled with pure solvent.

5) Close sample compartment door completely.

6) Turn on line filter.

7) Turn power on. The instrument will calibrate itself for about 13 mins.

8) When the abscissa display stops at 500 nm and the recorder pen goes to 100% transmittance, turn off power to the D2 lamp immediately. Do not turn off D2 lamp if measuring under 350 nm.

9) Wait 10-20 minutes.

10) Press "ABS".

11) Press "SCALE" (e.g. 0-0.02).

12) Press "λ_1 - λ_2 SCAN" (according to element specifications).

13) Press "BACK CORR" (according to element specifications).

14) Align recorder pen with any vertical line on chart paper.

15) Press "λ_1 - λ_2 SCAN".

16) Press "SCAN".

17) Wait for cycle to be completed.

18) Remove cell from sample compartment, wash the cell with the sample to be analyzed and place sample in cell.

19) Place sample cell in sample compartment.

20) Close compartment door.

21) Press "WAVELENGTH MAX" and press "GOTO λ".

22) Input the appropriate values of the lower and upper scales to bring the peak into scale and press "SCALE".

23) Press "λ_1 - λ_2 SCAN".

24) Press "SCAN".

25) Analyze data as per instructions of the Project Manager.

6.6.3 Procedure for Spectrophotometer Accuracy Verification

Equipment and Supplies

Qty	Device	Manufacturer	Model	Calib. Req.
1	Spectrophotometer	Perkin Elmer	330	I
1	Balance	Mettler	AE160	II
2	Pipettes 0.1-1 ml	Clay Adams	Selectapette	III
	5-10 ml	Oxford	Macro Set Transf.	III

Calibration Notes: I: Calibrated with every analysis; II: Calibration accuracy: ± 1 mg, Calibration frequency: monthly; III: Calibration accuracy: ± 5%, calibration frequency: monthly.

Spectrophotometer Parameters

Cell: 1 cm x 1 cm x 4.5 cm (quartz)

Scan range: 220 nm - 600 nm

Peak wavelengths: 257 nm, 350 nm

Base wavelengths: 235 nm, 313 nm

Back correction range: 200 nm - 620 nm

Blank: 0.001 n $HClO_4$

PROCEDURE FOR SPECTROPHOTOMETER ACCURACY VERIFICATION

Reagents

0.1 M $HClO_4$: in glacial acetic acid

1 g/l $K_2Cr_2O_7$: Dissolve 0.1 g of Potassium Dichromate of 99.9% purity or better (such as NBS Standard SRM136 or SRM935 Potassium Dichromate) in 100 ml of deionized water.

Procedure

Note: *This procedure should be performed monthly.*

(1) Prepare the following six standards in 100 ml flasks:

Standard #	0.1 M $HClO_4$ (ml)	1 g/l K_2/cr_2O_7 (ml)
1	1	0
2	1	2
3	1	4
4	1	6
5	1	8
6	1	10

(2) For each standard bring the final volume to the 100 ml mark on the flask neck with deionized water and shake thoroughly.

(3) Perform the colorimetric measurement as per procedure in section 6.6.2.

(4) Compare the measured absorbance values with those found in the NBS Special Publication Manual 260-54, Table 6 page 26 ("Standard Reference Materials" Certificaiton and Use of Acidic Potassium Dichromate Solutions as an Ultraviolet Absorbance Standard"). Log in results in the "Spectrophotometer Calibrations" L. N. and report to the Project Manager if the results fall outside a range of ± 5% of the NBS values.

7.0 Control of Samples and Release of Results

Acceptance of Samples and Release of Results

(1) Any sample entering the Analytical Laboratory Mass Spectrometry laboratory, in order to be analyzed, should be recorded in the Log-in/Log-out book. The recording is the sole responsibility of the originator of the sample. In addition, every sample should be accompanied by the standard "Request for Analysis" form, which provides adequate information about the sample.

(2) After the completion of the analysis, any results in the form of printouts, compilations, tables, graphs, etc., as well as all of the remaining specimens (unless ordered by the originator to be discarded), should be transferred to the originator. The person receiving the results should acknowledge this in the Log-in/Log-out book. Any data remaining on the magnetic media should be transferred for further processing as explained below.

(3) Steps of Data Processing:

(a) Receive DCP and AA disks from DCP and AA operators.

(b) Transfer data files onto disk with data processing programs.

(c) Run processing programs to put data into files which are in a semi-matrix form (i.e. data printed in a chart).

(d) Data such as pH and Si Colorimetry should be taken from lab notebooks and entered manually.

(e) Print data in chart format.

(f) Give printouts to originator of samples.

(g) Destroy DCP and AA files when processing is complete. Store data in chart format on data file diskettes.

8.0 DATA PROCESSING

This section includes a brief description and listings of computer programs used for data acquisition, data analysis, and data management. They are organized into two section: chemical analysis and thermal analysis.

1) Analytical Laboratory

A) Data Acquisition

The Analytical Laboratory uses two sets of programs for recording spectrophotometric data. One set is used for taking data on the Atomic Absorption/Flame Emission instrument and the second set is used to accept data from the DC Plasma Spectrophotometer. Each set consists of a three part package. These three parts can be briefly described as follows: The first part records instrument readings, the second part performs any necessary calculations, and the last part prints out the results.

The first part of the package allows the operator to describe the conditions under which the instrument is being operated. The computer has only minimal control of either of the spectrophotometers and hence requires a fairly detailed description. After the description is entered, it will be recorded in a disk file. The first section of the program will next operate a carousel which presents samples to the instrument and record the readings made by the instrument on these samples into a disk file. When all samples have been measured control will be passed to the second part of the package.

The heart of each system is the second part of the package. The purpose of this part is to use the instrument readings in the disk file to calculate a calibration curve for each sample and use this calibration to estimate a concentration for each sample. This calculation is based on fact that recalibration (or reslope) standards are mixed in with the samples on the carousel. Each sample is thus one of a small block of samples (typically three or four) surrounded by reslope standards. The instrument readings from the standards on either side of the block are used to construct the curve for that block of samples. The instrument readings on a sample and the calibration curve for that sample's block are used to calculate that sample's concentration. In the final stage of the calculation, the dilution factor for that sample is used to convert the measured sample concentration into the actual analyzed for concentration of the sample before dilution. All of these results including standard deviations are placed in a final disk file. These final disk files can be used by subsequent programs if desired. When the final data file has been written the second part will pass control over to the third part.

The third part of the program set will read the final disk file and print a report of the sample concentrations with standard deviations. It will also make some elementary checks of the results and flag some conditions known to introduce errors in the analysis. Notable among these conditions is the case where the solution analyzed has a concentration higher than the high standard for the element.

Each of these packages was developed in order to ensure that all measurements and calculations in the analysis lab were made in a defined way. The automation of the calculations is particularly valuable in that errors of transcription and methodology are minimized.

All computer programs described in I are written in North Star Basic. The following programs are currently being used:

AA - AADATA
DCP - DCP.5
DCREPRNT
DCREVRPRNT

B) Data Analysis and Data Management

Various software manipulations must be performed in order to properly store the information gathered through the data acquisition programs on permanent storage disks and obtain data outputs in the desired format. Raw data from the AA and DCP represent element concentrations and standard deviations expressed in ppm. In what follows, a step by step description of a general data processing operation applicable to leaching test is given. The processing is used with Flow Tests, MCC-type tests and others.

(1) A weekly schedule originating in the leaching laboratory and containing sampling information is sent to the Analytical Laboratory along with analysis request forms. This schedule is returned to the Data Processing Department along with a floppy disk containing raw data files from the DCP and/or AA as well as results from the DIONEX if applicable. Similar tests are run together and given a reference name which is specified in the schedule sheet.

(2) Using the Reference name, raw data files are copied onto a scratch pod disk (SPD). Names prefixed with an "A" denote files from the AA, names prefixed with a "D" denote files from the DCP. Files originating from the AA have single letter suffixes to indicate the element run, "C" for Cs, "L" for Li, "M" for Mg, and "N" for Ni. The suffix "D" and

others with the exception of C, L, M and N indicate dilution files for both the AA and DCP.

(3) The raw data transferred onto the scratch pod disk must be properly channeled into the permanent storage data disks and also used to produce printouts of results in the desired format. Two sets of programs are used for this purpose depending on whether samples from a single test or multiple test were run in the AA and/or DCP.

To process the raw data, the data disk must have files containing all the initial pertinent information about a test run. These files are created using INDEX. Another program, ENTER, is used to create files containing information on composition used to calculate normalized leach rates.

(i) The following programs are used with raw data from single test runs.

(a) FSTSELF - Transfer data from the scratch pod disk to the data disk using the index files to channel information to the proper storage spot.

(b) FILL - Allows manual input of pH concentrations, standard deviations and results from colorimetric and Dionex analysis onto the data disk. Other programs which will be described later can also be used.

(c) REPRINT - Produces a print-out containing pertinent information on the test being run, a table of concentrations, pH for the samples being tested and the elements being analyzed for.

(ii) The following programs are used with raw data from multiple test runs.

(a) BLDVP - Produces a print-out of multiple files run with the same reference

name indicating the actual sample number and the corresponding position in the carrousel (of the AA or DCP). This information is used by the operator as further inputs to the program which will, in the end, create appropriately indexed files for further processing.

(b) FST-BRV - Transfers data from the scratch pod disk to the data disk using the index files to appropriately breakup data from combined runs and channel information to the proper slot.

(c) BREAK-UP - Used with dilution files or when elements were not run for all samples specified in the index file. This program breaks up raw data files and creates _ files containing concentrations for diluted samples.

(d) DILMERG - Merges dilution files with main files. If a reading is not available for a particular element, it is stored in the main file as -999.

(e) CONC 1 - Similar to FILL. Allows manual input onto the data disk files of pH, concentrations without standard deviations, results from colorimetric analysis and results from Dionex analysis. Uses colorimetric data from U analysis to calculate uranium concentrations.

(f) REPRINT - Described in (i) - (c).

(3) Leach rates and normalized leach rates are calculated making use of index files, glass composition files and concentration files stored in the data disk. The following programs are used.

(a) LEACH - Using index files and concentration files calculates leach rates for each element and for a group of samples in a run. Stores results into a leach rate file.

(b) SUMMARY - Produce print-out of calculation performed by LEACH giving results in $\mu g/cm^2/day$.

(c) NRLPRT - Using index files, concentration files, and composition files it calculates normalized leach rates for each element and for a group of samples in a run. Produces print-out of calculations performed giving results in $\mu g/cm^2/day$. The possibility of errors either from original data or caused by processing or delays present. Therefore, all data is usually inspected for obvious mistakes. Which way these are found.

(5) Several programs have been designed to perform correction of data stored in the storage disks. Some are listed below.

(a) UTILITY - Allows changing erroneous data in leach rate files.

(b) REFILL - Allows changing concentrations and standard deviations in a concentration file for a single element and all sample in the run.

(c) S.REFILL - Allows changing concentration and standard deviation in a concentrations file for all elements of a single sample in a run.

(d) ELFACTOR - Allows making corrections in a concentrations file to account for dilution factors originally not introduced.

(2) General Chemistry Laboratory

(A) Colorimetric Analysis

Analytical methods for Colorimetric Analysis of Si, Fe and U have been in use in our

laboratories for a considerable length of time. Detailed procedures for these tests are included in Section 6.6. Colorimetric data obtained from the Perkin Elmer Model 3 spectrophotometer is translated into concentration data using a computer program called BLUEJ. This program uses absorption data of standards to calculate a calibration curve for the element being analyzed. The absorption data from the sample is used with this calibration curve to calculate concentration. The result is given in ppb. There are other data manipulation computer programs used in this laboratory. The are described below.

(a) TANAGER - This program calculates normalized leach rates, annual fractional loss rates, and the relative mole composition on the surface based on Boron Manual input of leachate concentration is required.

9.0 ASSURANCE OF RELIABILITY OF ANALYTICAL RESULTS

Assurance of Reliability of Analytical Results

(1). The entire personnel of the Analytical Laboratory is required to be familiar with and to obey strictly all the individually relevant procedures included within the "Analytical Laboratory Procedures Manual".

(2) The final decision about acceptability of the results produced by the Analytical Laboratory is always the sole and exclusive responsibility of the originator of the sample.

(3) Internal acceptability criteria of the results produced by the Analytical Laboratory are as

follows:

(a) for single point measurements: originator's decision

(b) for single-train measurements: originator's decision

(c) for replicate-train measurements: scattering of average for every train not exceeding 3 standard deviations ('3σ' test).

(4) The analysis should be repeated in each one of the following cases:

(a) if so requested by the originator

(b) if a discrepancy of more than $\pm$ 50% is found between the actual and the expected (supplied by the originator) content of a certain analyte in the sample.

(c) if the results do not meet internal acceptability criteria (para. 3 above).

(d) if any form of analytical instrumentation malfunction is discovered. In this case immediate corrective action should be undertaken and internal investigation performed in order to evaluate to what extent and for how long such a malfunction has affected (if at all) the former analyses. If the discovery of a fault in the analytical system places in doubt results obtained and reported prior to such discovery, the originator(s) of the samples in question should be immediately notified.

10.0 RECORD KEEPING

The following record books should be kept and maintained in the Analytical Laboratory:

(1) Log-in/Log-out book to record sample admittance and release of results from the laboratory.

This book should consist of the following headings:

(a) Log-in Date - the date the sample was given to the Analytical Laboratory

(b) File Name - sample designation

(c) No. of Samples

(d) Originator

(e) Run Name - given if samples of different designations are analyzed within the same batch (run)

(f) Log-out Date - the day the results were received by the originator

(g) Person Receiving the Results - an originator or a person acting on his behalf

(2) Maintenance/Troubleshooting book for DCP Spectrophotometer.

This book should contain information on daily maintenance /troubleshooting or corrective action performed.

(3) Maintenance/Troubleshooting book for AA Spectrophotometer.

This book should contain information on daily maintenance /troubleshooting or corrective action performed.

(4) Dionex IC book

MODIFIED TCLP PROCEDURE

EPA Toxicity Characteristic Leaching Procedure (TCLP) Applied to Waste Glasses at VSL

October 1990

1. Scope and Application

1.1 The unmodified EPA TCLP Method 1311 is designed to determine the immobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes.

1.2 This VSL modified version of the TCLP test is used specifically for solid waste glasses.

1.3 The waste glasses tested by this method are made at a temperature 1100°C or above in air. The amount of organics remaining in such glasses will be negligible. Therefore the procedure described here in complies with the EPA specification of EPA method 1311 when volatiles are not involved.

2. Referenced Documents

2.1 Method 1311 Toxicity Characteristic Leaching procedure, Federal Register, V.55, No. 61, 1990.

2.2 ASTM Standards

D1193 Specification for Reagent waster [1]
D1193 Standard Test Methods for pH of water [1]
D1125 Test Methods for Electrical Conductivity and Resistivity of Water [1]

4. Significance and Use

4.1 This test method provides data useful for evaluating the toxicity of a solid. A solid waste exhibits the characteristic of toxicity if, using this test method, the extract from a representative sample of the waste contains any of the contaminants listed in Table 1 at a concentration equal to or greater than the respective value given in that Table.

Title: PROCEDURE FOR TCLP TESTS

Document: VSL-8-1.ANL

Issued: 11/90

Revisions

Rev. #	Date
NEW	11/90

Prepared by: Xiangdong Feng
PCT Group Leader

Examined by: Ian Pegg
Project Manager

Approved by: Pedro B. Macedo
Co-Director, VSL

Richard Sassoon
Quality Assurance
Officer, VSL

TPI-LT.WVN

Table 1 - Maximum Concentration of Contaminants for the Toxicity Characteristic

Contaminant	Regulatory Level (mg/L)
Arsenic	5.0
Barium	100.0
Cadmium	1.0
Chromium	5.0
Lead	5.0
Mercury	0.2
Selenium	1.0
Silver	5.0

5. Apparatus

5.1 Extraction Bottles - Borosilicate glass bottles of 2.2 liter capacity (#3740-NGB, Associated Design and Manufacturing Company) or 2.2 liter polyethylene bottle (#3740-PB, Associated Design and Manufacturing Company).

5.2 Agitation Apparatus: The agitation apparatus, capable of rotating the extraction vessel in an end-over-end fashion at 30 ± 2 rpm, is of an EPA-approved design and purchased from Associated Design and Manufacturing Company (model 3740-BRE).

5.3 Filtration Devices: these devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm. The filter holder is capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation. The materials of construction of the filtration devices shall be made of glass, polytetrafluoroethylene or type 316 stainless steel.

5.3.1 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8 µm or equivalent. Filters known to EPA which meet these specifications are identified in Table 2. Prefilters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

Table 2

Company	Location	Model	Pore size
Millipore Corporation	Bedford, MA (800) 225-3384	AP40 /	0.7
Nucleopore Corporation	Pleasanton, CA (415) 483-2530	211625	0.7
Whatman Lab. Products,Inc.	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dubin, CA (800) 334-7132 (415) 826-6010		

5.4 Sieves - 9.5 mm (0.375 inch), or finer, Teflon-coated sieve.

5.5 Crushing Device - any mechanical or manual crushing device which will avoid steel contamination in the crushed specimen. A grinding device made of tungsten carbide is one such example.

5.6 Laboratory Balance - Any laboratory balance accurate to within ±0.01 grams may be used (all weight measurements are to be within ±0.1 grams).

5.7 Weight Calibration Set - NIST Class S-type weight calibration set ranging from 100 mg to 1 kg.

5.8 Pipettes - Calibrated and precleaned tips.

5.9 Sample Vials - Precleaned sample vials and caps.

5.10 pH Meter - pH meter with an accuracy of ± 0.05 pH units at 25°C.

5.11 Milli-Q Water Purification System - Water purification system for producing reagent water.

6. Calibrations

6.1 Calibrations - Initially calibrate all instruments used in this test. Perform periodic calibrations during use of the instrument to minimize possible errors due to instrumental drift.

6.2 Calibration and Standardization Schedule:

6.2.2 pH meter - Before and after series of measurements with commercial buffer solutions that bracket the solution pH being measured.

6.2.3 Pipettes - once every month.

7. Standards

7.1 The reference solution standards should be traceable to NIST, or a comparable equivalent should be used, and should have a certified shelf life.

7.2 pH Buffers - Commercial pH buffers to bracket the measured pH range of the leachant and leachate.

8. Reagent

8.1 Reagent water, made from Millipore Super-Q or equivalent system.

8.1.1 ASTM Type I water - Type I water shall have a minimal electrical resistivity of 16.67 M Ohm cm at 25°C (consult ASTM D1193).

8.1.2 The source water shall be passed through Milli-R015 System which contains 6 cartridges (Ful-Flow, Teel, Lifegard, Rogard Prefilter and Milli-Ro-20 Spiral-Wound Reverse Osmosis) and Milli-Q System that consists of five cartridges (Lifegard, Super-C, two of Ion-Exchanger, and Millipore DI-12). Pass the purified water through an in-line conductivity cell to verify its purity.

8.2 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

8.3 Nitric acid (1N), HNO_3, made from ACS reagent grade.

8.4 Sodium hydroxide (2N), NaOH, made from ACS reagent grade.

8.5 Glacial acetic acid, HOAc, ACS reagent grade.

8.6 Extraction fluid:

8.6.1 Extraction fluid #1: Add 5.7 mL glacial HOAc to 500 mL of the appropriate water (See Step 5.1), add 64.3 mL of 1 N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.

8.6.2 Extraction fluid #2: Dilute 5.7 mL glacial HOAc with ASTM Type I water to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05.

Note: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

8.7 Analytical standards prepared according to the appropriate analytical method.

9. Preliminary Evaluations

9.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle-size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500-mL beaker or Erlenmeyer flask.

9.2 Add 96.5 mL of reagent water (ASTM Type II or better) to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 10.0.

9.3 If the pH from Step 9.2 is >5.0 add 3.5 mL 1N HCl, slurry briefly, cover with a

watchglass, heat to 50°C, and hold at 50°C for 10 minutes.

9.4 Let the solution 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. Proceed to Section 10.0.

10. Procedure

10.1 Weigh out 110 gram of the solid waste, reduce the size by grinding until the material will pass through a 9.5mm (0.375 inch) standard sieve.

10.2 Transfer 100.0 gram the ground solid material into an extractor bottle.

10.3 The amount of extraction fluid to be added to the extraction vessel is 20 times the weight of solid sample used, i.e. 2000.0 grams for 100 grams of solid waste.

Slowly add this amount of the appropriate extraction fluid (see Step 9.0) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 ± 2 rpm for 18 ± 2 hours. Ambient temperature (i.e. temperature of room in which extraction takes place) shall be maintained at 22 ± 3°C during the extraction period.

Note: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

10.4 Following the 18 ± 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as follows:

10.4.1 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder. Spread the waste sample evenly over the surface of the filter.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period) stop the filtration.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration.

10.5 The filtered liquid material obtained from Step 10.4 is defined as the TCLP

extract.

10.6 Following collection of the TCLP extract, add 20.0 mL of extract to each of six labeled sample vials. Measure the pH's of two of the six vials and record the pH's. Add 1.0 mL 1N HNO_3 to each of the four remaining vials to ensure pH < 2.0 of the resulting solutions. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic contaminants. If an analysis of the undigested extract shows that the concentration of any regulated metallic contaminant exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to ±0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\textit{Final analyte concentration} = \frac{(V_1)(C_4) + (V_2)(C_4)}{V_1 + V_2}$$

where:
V_1 = The volume of the first phase (L).
C_1 = The concentration of the contaminant of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the contaminant of concern in the second phase (mg/L).

10.7 Compare the contaminant concentrations in the TCLP extract with the thresholds identified in the appropriate regulations (Table 1). Refer to 11.0 for quality assurance requirements.

11.0 Quality Assurance Requirements

11.1 Maintain all data, including quality assurance data, and keep it available for reference or inspection.

11.2 A minimum of one blank (extraction fluid #1) for every 10 extractions that have been conducted in an extraction vessel shall be employed as a check to determine if any memory effects from the extraction equipment are occurring.

11.3 A matrix spike shall be performed for each waste unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. If more than one sample of the same waste is being tested, a matrix spike needs to be performed for every twenty samples and the average percent recovery applied to the waste characterization.

11.3.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

11.3.2 Matrix spike levels should be made at the appropriate regulatory threshold limits. However, if the extract contaminant concentration is less than one half the threshold limit, the spike level may be one half the contaminant concentration but not less than the quantitation limit or a fifth of the threshold limit.

11.3.3 The purpose of the matrix spike is to monitor the adequacy of the analytical methods used on the TCLP extract and to determine whether matrix interferences exist in analyte detection. If the matrix spike recoveries are less than 50%, then the analytical methods are not performing adequately or use of the methods is inadequate. Use of internal calibration quantitation methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the contaminant concentration in the TCLP extract.

11.3.4 Use of internal quantitation methods is also required when the contaminant concentration is within 20% of the regulatory level. (See section 11.5 concerning the use of internal calibration methods.)

11.3.5 Matrix spike recoveries are calculated by the following formula:

$$\text{Percent recovery} = \frac{A-B}{C} \times 100\%$$

where A = the concentration of the spike sample.
B = the concentration of the unspiked sample, and
C = the spike level

11.4 All quality control measures described in the appropriate analytical methods shall be followed.

11.5 The use of internal calibration quantitation methods shall be employed for a contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

11.5.1 The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

11.5.2.1 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The fourth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solutions, and may need dilution adjustment to maintain the signals in the linear range of the instrumental technique. All four aliquots are analyzed.

11.5.1.2 Prepare a plot, or subject data to linear regression, of instrumental signals or external-calibration-derived concentrations as the dependent variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

11.5.1.3 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject data to linear regression of the corrected instrumental signals or external-calibration-derived concentrations as the dependent variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

11.6 Sample must undergo TCLP extraction within the following time periods (in days):

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization.

if the waste exceeds the regulatory level.

12. SAFETY

12.1 This test method must be performed in accordance with all applicable quality assurance requirements of the laboratory performing the test and using the data.

12.2 This procedure may involve hazardous materials, operations, and equipment. All personnel who are authorized to perform this procedure must consult and establish appropriate safety and healthy practices and determine the applicability of regulatory limitations prior to use.

12.3 All appropriate precautions for operation of pressurized equipment must be taken. The thermal expansion of water must be taken into account when filling the leach containers.

13. APPLICABILITY

This procedure applies to all employees trained and authorized to perform this test in the VSL.

3930

C

273-A

APPENDIX C

SOPs FOR THE MAWS BENCH-SCALE STUDY

(DURATEK TO PROVIDE)

3930

D

274-A

APPENDIX D

HEALTH AND SAFETY PLAN

Health and Safety Plan for the Remedial Design Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization

Environmental Remedial Action Project
Fernald Environmental Management Project
Fernald, Ohio

WEMCO Subcontract No. 2-21487
November 1992
Revision No. 0

Operable Unit 1, Project Order 33

PARSONS

Fairfield Executive Center
6120 South Gilmore Road
Fairfield, Ohio 45014

Health and Safety Plan for the Remedial Design Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization

APPROVED FOR ISSUE

Prepared By:

Shawn R. French 11/16/92

Health and Safety Coordinator, PARSONS — Date

Approved By:

Scott J. Mallette 11/16/92

Project Manager, Operable Unit 1, PARSONS — Date

Reviewed By:

Project Engineer, WEMCO — Date

Approved By:

Manager, Engineering, WEMCO — Date

Manager - Industrial, Radiological Safety and Training, WEMCO — Date

Health and Safety Plan for the Remedial Design Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization

CONTENTS

SECTION

1.0 Tasks to be Performed 1-1

1.1 Collect and Place Contaminated Soil in Drums and Move Drums to Plant 9 Storage Area 1-1

1.2 Transfer Contaminated Soil from the Drums to the Soil Washing Unit 1-2

1.3 Operate the Soil Washing Unit 1-2

1.4 Transfer Cleaned Soil and Concentrated Contaminated Soil to Containers for Storage 1-2

1.5 Operate the Water Treatment System 1-2

1.6 Collect and Place Contaminated Sludge in Drums/Tank Trailer from Waste Pit 5 and Move Drums/Tank Trailer to Plant 9 Storage Area 1-2

1.7 Transfer Contaminated Sludge from the Drums/Tank Trailer to the Vitrification Unit 1-3

1.8 Addition of Chemical Additives to Vitrification Feed Materials 1-3

1.9 Operate the Vitrification Unit 1-3

1.10 Transfer Empty Sludge Contaminated Drums/Tank Trailer Back to Plant 9 Storage Area 1-3

1.11 Transfer Stabilized Glass Waste Marbles to Containers for Storage 1-3

2.0 Site History 2-1

3.0 Task-Specific Hazard Assessments 3-1

3.1 Physical Hazards 3-1

3.2 Radiological Hazards 3-4

3.3 Chemical Hazards 3-4

4.0 Monitoring 4-1

4.1 Goals 4-1

4.2 Monitoring Equipment and Frequency of Monitoring 4-1

4.3 Field Action Limits Guidelines 4-4

5.0 Personal Protective Equipment 5-1

CONTENTS (Continued)

6.0 Work Site Safety Requirements 6-1
- 6.1 Equipment Safety 6-1
- 6.2 Work Area Safety 6-1

7.0 Site Control 7-1
- 7.1 Access 7-1
- 7.2 Bioassay Samples 7-3
- 7.3 Medical Monitoring 7-3
- 7.4 Training Requirements 7-3
- 7.5 Safety Meetings 7-4

8.0 Exposure Symptoms 8-1

9.0 Site Entry Procedures 9-1

10.0 Decontamination 10-1

11.0 Wastes 11-1

12.0 Contingency Plans 12-1
- 12.1 Incidents or Injuries Involving Possible Intake of Radiological or Chemical Substances by Employees 12-1
- 12.2 Pre-Emergency Planning 12-1
- 12.3 Lines of Authority 12-1
- 12.4 Evacuation 12-2
- 12.5 Emergency Equipment 12-2
- 12.6 Emergency Notification 12-4
- 12.7 Fire, Explosion, or Medical Emergency 12-4
- 12.8 Spill Control Contingency Plan 12-4
- 12.9 Additional Information 12-4

13.0 Confined Space Entry 13-1

14.0 Approval and Compliance Statement 14-1
- 14.1 Provisions 14-1
- 14.2 Amendments to Plan 14-1

CONTENTS (Continued)

15.0 References 15-1

ATTACHMENTS

A Incident Investigation Report
B Guidance for Heat Stress Monitoring and Prevention
C Guidance for Cold Stress Monitoring and Prevention
D FMPC Work Permit/Confined Space Entry Permit

LIST OF ILLUSTRATIONS

FIGURES

2-1 FEMP Site Map

12-1 FEMP Rally Points
12-2 Location of FEMP Medical Department Facility

14-1 Health and Safety Plan Acknowledgement Form

TABLES

3-1 Hazards Associated with the Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization
3-2 Radiological Hazards Table
3-3 Chemical Hazards Table

4-1 Field Action Limit Guidelines

5-1 PPE Associated with the Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization

7-1 Posting Requirements

LIST OF ACRONYMS AND ABBREVIATIONS

AEDO	Assistant Emergency Duty Officer
ALARA	As Low As Reasonably Achievable
APR	Air Purifying Respirator
CFR	Code of Federal Regulations
cpm	counts per minute
DAC	Derived Air Concentration
dBA	A-Weighted Decibels
DOE	United States Department of Energy
EMS	Emergency Message System
FEMP	Fernald Environmental Management Project
gpm	gallons per minute
HEPA	High-Efficiency Particulate Air
IH	Industrial Hygiene
IRS&T	Industrial, Radiological, Safety, and Training
MAWS	Minimum Additive Waste Stabilization
MSDS	Material Safety Data Sheets
OSHA	Occupational Safety and Health Administration
OU	Operable Unit
PID/FID	Photoionization Detector/Flameionization Detector
PPE	Personal Protective Equipment
ppm	parts per million
RCRA	Resource Conservation and Recovery Act
SAR	Supplied Air Respirator
TLD	Thermoluminescent Dosimeter
U	Uranium
WEMCO	Westinghouse Environmental Management Company of Ohio

SECTION 1

TASKS TO BE PERFORMED

This task-specific Health and Safety Plan was prepared as a supplement to the formal sitewide Health and Safety Plan for the Fernald Environmental Management Project (FEMP) site. Personnel from Westinghouse Environmental Management Company of Ohio (WEMCO) and GTS Duratek will use this Health and Safety Plan while conducting the bench-scale treatability study operational tasks as described herein. The contents of this task-specific Health and Safety Plan are consistent with Title 29 Code of Federal Regulations (CFR) 1910.120, *Hazardous Waste Operations and Emergency Response* and the *FEMP Site Health and Safety Plan* (June 1990).

The activities covered by this Health and Safety Plan are part of the Minimum Additive Waste Stabilization (MAWS) Program being conducted at the FEMP site. The bench-scale treatability study, which represents an initial MAWS Program activity, is part of a system which demonstrates the integration of soil washing, ion exchange, and vitrification processes in order to stabilize multiple waste streams while minimizing additives, process generated waste, and stabilized waste volume.

The bench-scale treatability study is divided into two phases. Phase I on-site activities consist of the following: (a) treatment of soils by a TRUclean soil wash system, (b) operation of a water treatment system for treatment of the soil wash water, and (c) operation of a Duramelter™ vitrification system. Phase II on-site activities consist of a demonstration of the fully-integrated system. Only Phase I (a), (b), and (c) activities are covered by this task-specific Health and Safety Plan. RUST Engineering has prepared a Health and Safety Plan to cover activities related to the Plant 9 modifications, installation of the soil wash system, water treatment system, and the Duramelter™. A subsequent Health and Safety Plan will be prepared to cover Phase II activities.

Subsections 1.1 through 1.11 contain a checklist of standard actions that may or may not occur during each of the major tasks associated with Phase I (a), (b), and (c) bench-scale treatability study activities.

1.1 Collect and Place Contaminated Soil in Drums and Move Drums to Plant 9 Storage Area

X	Disturb Surface Soil	X	Involve Radioactivity
X	Disturb Subsurface Soil	___	Disturb Containerized Material
X	Use Heavy Equipment		

1.2 Transfer Contaminated Soil from the Drums to the Soil Washing Unit

___	Disturb Surface Soil	X	Involve Radioactivity
___	Disturb Subsurface Soil	X	Disturb Containerized Material
X	Use Heavy Equipment		

1.3 Operate the Soil Washing Unit

___	Disturb Surface Soil	X	Involve Radioactivity
___	Disturb Subsurface Soil	___	Disturb Containerized Material
___	Use Heavy Equipment		

1.4 Transfer Cleaned Soil and Concentrated Contaminated Soil to Containers for Storage

___	Disturb Surface Soil	X	Involve Radioactivity
___	Disturb Subsurface Soil	___	Disturb Containerized Material
X	Use Heavy Equipment		

1.5 Operate the Water Treatment System

___	Disturb Surface Soil	X	Involve Radioactivity
___	Disturb Subsurface Soil	___	Disturb Containerized Material
___	Use Heavy Equipment		

1.6 Collect and Place Contaminated Sludge in Drums/Tank Trailer from Waste Pit 5 and Move Drums/Tank Trailer to Plant 9 Storage Area

___	Disturb Surface Soil	X	Involve Radioactivity
___	Disturb Subsurface Soil	___	Disturb Containerized Material
X	Use Heavy Equipment	X	Use Dredge

1.7 Transfer Contaminated Sludge from the Drums/Tank Trailer to the Vitrification Unit

___ Disturb Surface Soil
___ Disturb Subsurface Soil
_X_ Use Heavy Equipment
_X_ Involve Radioactivity
_X_ Disturb Containerized Material

1.8 Addition of Chemical Additives to Vitrification Feed Materials

___ Disturb Surface Soil
___ Disturb Subsurface Soil
_X_ Use Heavy Equipment
_X_ Involve Radioactivity
_X_ Disturb Containerized Material

1.9 Operate the Vitrification Unit

___ Disturb Surface Soil
___ Disturb Subsurface Soil
___ Use Heavy Equipment
_X_ Involve Radioactivity
___ Disturb Containerized Material

1.10 Transfer Empty Sludge Contaminated Drums/Tank Trailer Back to Plant 9 Storage Area

___ Disturb Surface Soil
___ Disturb Subsurface Soil
_X_ Use Heavy Equipment
_X_ Involve Radioactivity
___ Disturb Containerized Material

1.11 Transfer Stabilized Glass Waste Marbles to Containers for Storage

___ Disturb Surface Soil
___ Disturb Subsurface Soil
_X_ Use Heavy Equipment
_X_ Involve Radioactivity
___ Disturb Containerized Material

SECTION 2

SITE HISTORY

The FEMP site has over 350,000 m^3 of pit wastes, over 2,000,000 m^3 of potentially contaminated soils on site, and associated water that needs to be remediated. Vitrification is an attractive remediation alternative for some site soils because organic contaminants are completely oxidized to carbon dioxide and water while radionuclides, heavy metals, and other inorganic contaminants are dissolved into the glass matrix which has a very low leach rate. However, the sludges in the waste pits do not make good glass because they do not contain sufficient silica-bearing compounds. The soils make a good glass but their melting point is too high for economical operation. Based on preliminary results from laboratory studies, the pit wastes behave as a flux that lowers the soil melting point and together the pit wastes and soils make a good glass.

The MAWS Program is designed to take advantage of the fact that the pit wastes and soils make a good glass and related synergism to develop an efficient, minimum cost remediation process for soils, sludges, and other wastes found at the FEMP site. Specifically, MAWS will integrate soil washing (to separate contaminated soils from clean soils), vitrification of mixed waste streams, and ion-exchange to remediate water from the soil washing process and the vitrification off-gas scrubber. Spent ion-exchange media will either be regenerated or combined with the other waste streams and vitrified.

The bench-scale treatability study for the MAWS Program will be performed by Operable Unit (OU) 1 which is responsible for the six waste pits, the Clearwell, the Burn Pit, and the associated soils. The sludges which will be fed to the MAWS bench-scale demonstration will come from wastes existing within OU-1. For this bench-scale study, feed soils will be taken from locations other than hazardous waste management units (i.e., only soils which are not contaminated with Resource Conservation and Recovery Act [RCRA] hazardous waste will be used).

The process equipment for the MAWS bench-scale demonstration will be installed in the southeast open bay of Plant 9 at the FEMP site and are identified in Figure 2-1. The three major subsystems of the demonstration treatment process will be:

1) Vitrification system
2) Soil wash system
3) Ion-exchange water treatment system

The vitrification system capacity will nominally be 300 kg/per day of equivalent dry feed/glass product, but expected process optimization may result in a major increase in throughput. The soil wash system will be capable of handling 0.25 cubic yards of soil per hour. The ion-exchange water treatment system

will be sized to treat 100 gallons per minute (gpm) (70 gpm nominal) of contaminated water. Support facilities will include incoming and in-process material storage area, a staging area for feed makeup materials, a melter feed mixing station, and an off-gas treatment system.

The bench-scale process demonstration of the MAWS Program will take place entirely within the boundaries of the FEMP site and will demonstrate the integrated technologies to achieve a net volume reduction of wastes for OU-1. This demonstration will provide data to confirm OU-1 treatment alternative selection and to support technical feasibility prior to the Record of Decision which is scheduled for December 1994.

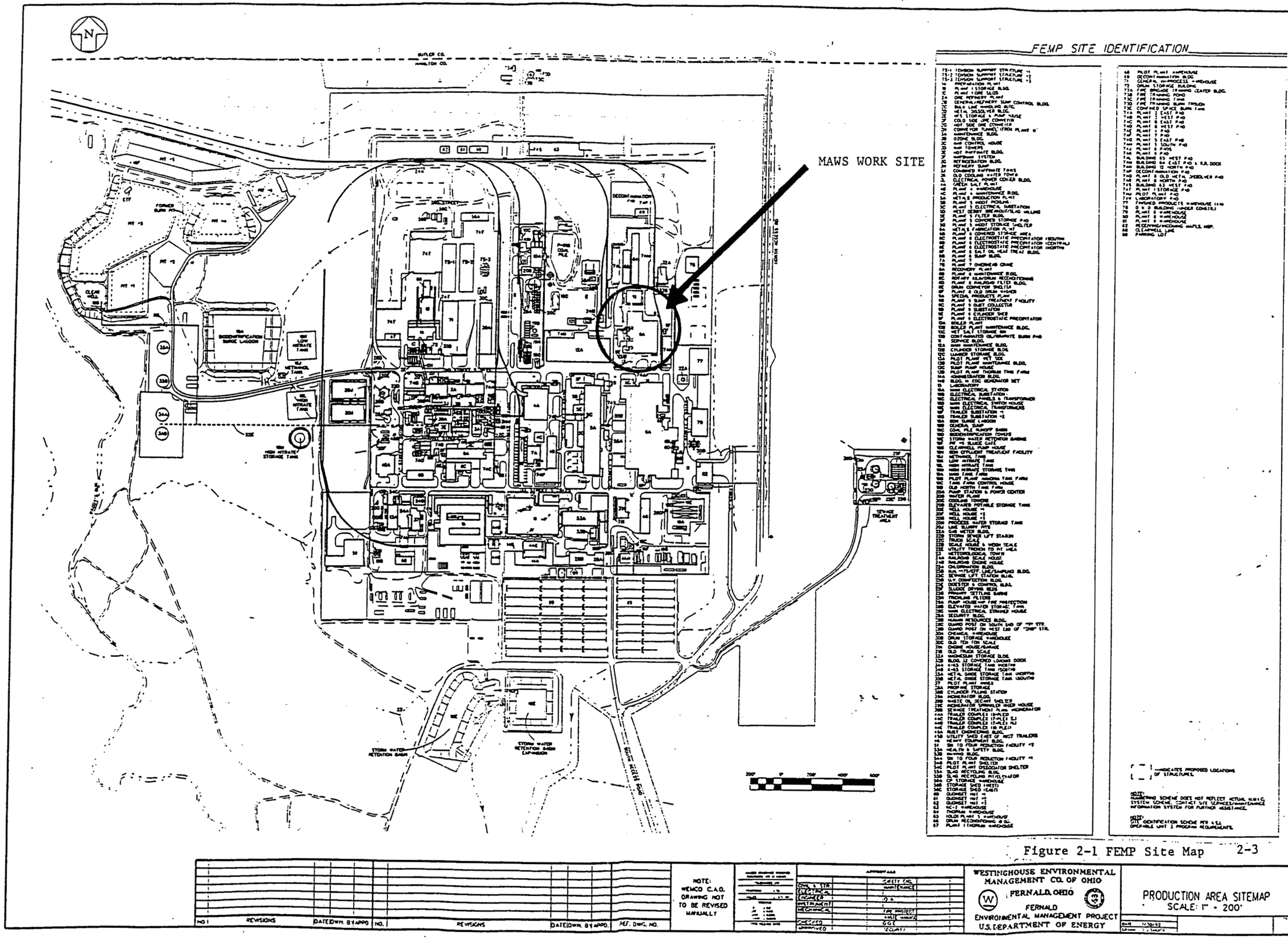


Figure 2-1 FEMP Site Map

SECTION 3

TASK-SPECIFIC HAZARD ASSESSMENTS

An assessment of the tasks to be conducted during the bench-scale treatability study indicates that physical, radiological, and chemical hazards will or may be present during operational activities. Table 3-1 lists the anticipated hazards associated with each of the eleven major work tasks identified in Subsections 1.1 through 1.11.

3.1 Physical Hazards

During all work tasks, personnel will be exposed to a variety of slip, trip, and fall hazards. These hazards include uneven ground surfaces, stairs, and elevated surfaces in the trailers which contain the soil washing, water treatment, and vitrification units.

During soil excavation and container filling operations, heavy equipment (e.g., a front-end loader or backhoe) will be used. The use of this equipment and associated service vehicles represents potential hazards to the equipment operator as well as to the personnel adjacent to the work site. Site workers could be struck directly or indirectly as a result of equipment use or breakdown. Forklifts will be used to move drums and containers of contaminated and clean soil. Site workers could be struck during the operation of these vehicles.

During transfer of soil and sludge to the soil wash unit and vitrifier, workers could be struck by moving or falling drums. Also, during operation of the soil wash unit and vitrifier, the operator and support personnel may be exposed to elevated noise levels.

During the soil washing, ion exchange, and vitrification processes, workers could be exposed to pinch points and falling objects associated with the process equipment. Also, during the vitrification process, workers could be exposed to skin contact burns from the vitrification unit shell, piping, and all other associated equipment where heat transfer takes place.

Table 3-1 - Hazards Associated with the Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization

Work Tasks	Physical Hazards	Radiological Hazards	Chemical Hazards
1.1 Collect and place contaminated soil in drums and move drums to Plant 9 Storage Area	Slip, trip, fall; moving heavy equipment and service vehicles	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 3
1.2 Transfer contaminated soil from the drums to the soil washing unit	Slip, trip, fall; moving heavy equipment; falling drums	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 3
1.3 Operate the soil washing unit	Slip, trip, fall, noise, pinch points, and falling objects	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 3
1.4 Transfer cleaned soil and concentrated contaminated soil to containers and move to Plant 9 Storage Area	Slip, trip, fall; moving heavy equipment	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 3
1.5 Operate the water treatment system	Slip, trip, fall, noise, pinch points, and falling objects	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates and liquid	
1.6 Collect and place contaminated sludge in drums/tank trailer from Waste Pit 5 and move drums/tank trailer to Plant 9 Storage Area	Slip, trip, fall; moving heavy equipment and service vehicles	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 1

290

Table 3-1 (Continued)

Work Tasks	Physical Hazards	Radiological Hazards	Chemical Hazards
1.7 Transfer contaminated sludge from the drums/tank trailer to vitrification unit	Slip, trip, fall; moving heavy equipment and falling drums	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 1
1.8 Addition of chemical additives to vitrification feed materials	Slip, trip, fall; moving heavy equipment and service vehicles	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 1 Note 2
1.9 Operate the vitrification unit	Slip, trip, fall, noise, pinch points, falling objects, and skin contact burns	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 1
1.10 Transfer empty sludge contaminated drums/tank trailer back to Plant 9 Storage Area	Slip, trip, fall; moving heavy equipment and service vehicles	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	Note 1
1.11 Transfer stabilized glass waste marbles to containers and move to designated storage area	Slip, trip, fall; moving heavy equipment and service vehicles	Low levels of penetrating gamma radiation. Potential inhalation/ingestion of radioactive particulates	

Notes:

1) Based on the Waste Pit 5 Characterization Investigation Study (Weston 1987) previous sampling of Waste Pit 5 contents indicated the presence of several organic and inorganic contaminants (i.e., barium, acetone, arsenic, cadmium, chromium, methylene chloride, and PCBs).

2) Based on the GTS Duratek Input for MAWS Work Plan (September 1992), potential chemical additives to vitrification feed materials are sodium monoxide, boron oxide, and calcium oxide.

3) Once soil locations have been identified, potential chemical hazards will be evaluated.

3.2 Radiological Hazards

The feed soils for the soil wash unit will not contain RCRA hazardous waste. Table 3-2 lists the primary hazard and exposure limits for the anticipated radionuclides to which workers may be exposed. Workers may ingest or inhale radioactive particulates from soil excavation/soil washing operations or be splashed with radioactive liquid/filter media following water treatment operations.

Based on the Waste Pit 5 Characterization Investigation Study (Weston 1987), several radionuclides (cesium, neptunium, plutonium, radium, ruthenium, strontium, technetium, thorium, and uranium) were identified in the sludge material. The sludge material from Waste Pit 5 and the contaminated fraction exiting the soil washing system will be used as feed materials for the vitrification system. Based on the radiological contaminants and exposure limits listed in Table 3-2, Thorium-232 will be the limiting radionuclide concentration used for personnel monitoring during sludge handling operations.

3.3 Chemical Hazards

During the 1987 Weston study of the waste pits at the FEMP, a variety of organic and inorganic chemical constituents were identified in the contents of Waste Pit 5. Inorganic chemicals in the pit contents were generally observed at concentrations comparable to soils found throughout the eastern United States, but arsenic and barium were observed at elevated concentrations. These chemicals may pose an inhalation/ingestion hazard to personnel involved in the collection and placement of contaminated sludge in drums/transferring contaminated sludge to vitrification unit or being splashed with liquid containing chemical contaminants during these operations.

While it is recognized that these chemicals have been placed in the pit, it is not believed that the Permissible Exposure Limit(s) (PELs) will be exceeded during the field work activities. The concentration levels are low based on the 1987 Weston study of Waste Pit 5 contents, except for the arsenic and barium constituents.

During the vitrification process, chemicals may need to be added to the feed materials. Potential additives are sodium monoxide, boron oxide, and calcium oxide. These chemicals may pose an inhalation/ingestion hazard to personnel involved in the adding/mixing operations. During the adding/mixing process, the oxide powder dust should be kept As Low As Reasonably Achievable (ALARA). Workers shall follow the manufacturer's material safety data sheets (MSDS) recommendations for material handling. MSDSs shall be provided by GTS Duratek upon receipt of chemicals and attached as an addendum to the Health and Safety Plan. Laboratory studies will determine which, if any, of these chemicals are needed for the on-site vitrification process. Each time a new chemical product is brought on site for the project, a MSDS must accompany it and WEMCO IRS&T must be notified.

The chemical additives for the vitrification process will be stored in Plant 9 in a chemical storage cabinet away from reactive sources. The chemicals will be transported from the cabinet to a loading hopper designed to feed the additives into the vitrifier, which will also be located in Plant 9. The chemicals will be added manually to the hopper system.

Table 3-2 - Radiological Hazards Table

Potential Contaminant	Primary Hazard	Exposure Limit[1/]
Cesium-137	Ingestion/Inhalation	$7x10^{-8}$ μCi/ml[2/]
Neptunium-237	Ingestion/Inhalation	$2x10^{-12}$ μCi/ml[2/]
Plutonium-238	Ingestion/Inhalation	$3x10^{-12}$ μCi/ml[2/]
Plutonium-239	Ingestion/Inhalation	$2x10^{-12}$ μCi/ml[2/]
Plutonium-240	Ingestion/Inhalation	$2x10^{-12}$ μCi/ml[2/]
Radium-226	Ingestion/Inhalation	$3x10^{-10}$ μCi/ml[2/]
Ruthenium-106	Ingestion/Inhalation	$2x10^{-8}$ μCi/ml[2/]
Strontium-90	Ingestion/Inhalation	$2x10^{-9}$ μCi/ml[2/]
Technetium-99	Ingestion/Inhalation	$2x10^{-6}$ μCi/ml[2/]
Thorium-228	Ingestion/Inhalation	$4x10^{-12}$ μCi/ml[2/]
Thorium-230	Ingestion/Inhalation	$3x10^{-12}$ μCi/ml[2/]
Thorium-232	Ingestion/Inhalation	$1x10^{-12}$ μCi/ml[2/]
Uranium-234	Ingestion/Inhalation	$2x10^{-11}$ μCi/ml[2/]
Uranium-235	Ingestion/Inhalation	$2x10^{-11}$ μCi/ml[2/]
Uranium-238	Ingestion/Inhalation	$2x10^{-11}$ μCi/ml[2/]

NOTES:

1/ The exposure limit values are given for individual radionuclides. For known mixtures of radionuclides, the sum of the ratio of the observed concentration of a particular radionuclide and its corresponding limit for all radionuclides in the mixture must not exceed 1.0.

2/ Derived Air Concentration (DAC).

SOURCE:

United States Department of Energy (DOE) Order 5480.11, "Radiation Protection for Occupational Workers," DOE, July 20, 1989.

294

Table 3-3 lists the primary hazard and exposure limits for the chemicals of concern for the contaminated sludge handling and vitrification process operations.

Table 3-3 - Chemical Hazards Table

Potential Contaminant	Primary Hazard(s)	Exposure Limit[1/]
Acetone	Inhalation/Ingestion	750 ppm
Aroclor-1248 (PCB)	Skin Absorption	0.001mg/m^3
Aroclor-1254 (PCB)	Skin Absorption	0.5 mg/m^3 (Skin)
Arsenic (inorganic)	Ingestion	0.010 mg/m^3
Barium (soluble)	Ingestion	0.5 mg/m^3
Cadmium (Dust)	Ingestion	0.005 mg/m^3
Chromium (II) and (III) Compounds	Ingestion/Contact	0.5 mg/m^3
Methylene Chloride*	Inhalation/Ingestion	500 ppm
Boron Oxide	Inhalation/Ingestion	10 mg/m^3
Calcium Oxide	Inhalation/Ingestion	2 mg/m^3
Sodium Monoxide	Inhalation/Ingestion	Note[2/]

Notes:

1/ The Exposure Limit Values are given for individual chemicals. The Exposure Limit is based on a time-weighted average concentration for a normal 8-hour work day and a 40-hour work week, to which nearly all workers may be repeatedly exposed, day after day, without adverse effect.

2/ No exposure limit(s) are published by Occupational Safety and Health Service agencies. Follow manufacturer's MSDS recommendations.

* Detection of this constituent may have been attributable to laboratory contamination.

Sources: National Institute for Occupational Safety and Health Pocket Guide to Chemical Hazards, United States Department of Health and Human Services, June 1990.

SECTION 4

MONITORING

4.1 Goals

Prior to initiating soil excavation and drum filling activities, air monitoring will be conducted by WEMCO Radiological Safety and Industrial Hygiene personnel, as required at the time of work permit(s) issuance, to ensure that exposure limits are not exceeded. Radioactive contamination monitoring will be performed to minimize the spread of contamination when soil media or sludge material is disturbed or cleaned.

4.2 Monitoring Equipment and Frequency of Monitoring

4.2.1 Airborne Radioactive Particulates

A representative air sample in the immediate breathing zone or general area of a worker actively involved in excavation, soil/sludge container filling, soil washing, water treatment, and vitrification operations will be collected to determine the concentration of long-lived airborne radioactive particulates to which workers are exposed. The sample will be collected using portable, battery-powered air pumps with 37 mm diameter membrane filters. The air sample filter will be checked for gross radioactivity to verify the adequacy of respiratory protection. A daily air sample which indicates that personnel may have been exposed to greater than 40 DAC-hours in one week without respiratory protection will trigger dose assessment by WEMCO Radiological Safety, Dosimetry Subsection.

4.2.2 Radioactive Surface Contamination

When personnel are excavating soil and filling soil/sludge containers, surveys of removable radioactive surface contamination will be performed by WEMCO Radiological Safety personnel in the work area. Direct reading instruments and/or field swipe surveys will be used on excavation equipment and containers. Alpha, beta, and gamma detectors will be used by a WEMCO Radiation Technician to monitor excavated soil/sludge. External surfaces of the soil wash, water treatment, and vitrification units will also be monitored for removable radioactive contamination.

4.2.3 Radiation Surveys

Prior radiation surveys will be used by WEMCO Radiological Safety personnel to establish general area radiation levels. Radiation surveys will be conducted periodically during operational activities by WEMCO Radiological Safety personnel. Portable radiation monitoring devices will be calibrated and maintained in accordance with WEMCO Standard Operating Procedures.

4.2.4 Potential Chemical Hazards

Exposure to significant chemical vapor concentrations is not expected during the collection and placement of contaminated sludge into drums from Waste Pit 5/transfer contaminated sludge from drums to vitrification unit. However, WEMCO Industrial Hygiene (IH) personnel will use a Photoionization Detector (PID)/Flameionization Detector (FID) to monitor the air near the breathing zone of the workers involved in the contaminated sludge handling operations. The frequency that the PID/FID meter measurements will be made are based on current readings and on the recommendation of the IH technician.

WEMCO IH personnel will conduct personal air sampling in the immediate breathing zone area of workers actively involved in the collection and placement of contaminated sludge into drums from Waste Pit 5/transfer contaminated sludge from drums to vitrification unit to determine the workers' exposure to methylene chloride, arsenic, and barium. In addition direct reading instruments, such as Dräger tubes shall be used to detect the presence of methylene chloride.

4.2.5 Thermoluminescent Dosimetry

Thermoluminescent dosimeters (TLDs) will be worn by all field personnel during all field aspects of the bench-scale treatability study.

4.2.6 Physical Hazards

Noise levels associated with the soil excavation, container filling activities, soil washing, water treatment, and vitrification operations will be monitored by a WEMCO IH representative. Worker hearing protection will be required if noise levels exceed 85 A-Weighted Decibels (dBA) over any length of time. WEMCO IH personnel will determine the need for worker hearing protection.

Heat/cold stress can be a major hazard, especially for those workers wearing protective clothing. Depending on the ambient temperature and the work being performed, heat/cold stress monitoring of personnel may be required and will be directed by the GTS Duratek Field Supervisor. Attachments B

297

and C provide guidance for heat/cold stress monitoring and prevention. Heat/cold stress monitoring of personnel will be performed by WEMCO IH personnel.

4.3 Field Action Limits Guidelines

Table 4-1 presents the field action limit guidelines for radiological and chemical contaminants that may be encountered in the work environment during field activities.

Table 4-1 - Field Action Limit Guidelines

INSTRUMENT	INTERVAL	LIMIT	ACTION
Alpha Probe[1/]	Pre-Job and Intermittent[2/]	500 counts per minute (cpm)[3/]	APR[4/]
		>25,000 cpm	Withdraw
Beta/Gamma Probe[1/]	Pre-Job and Intermittent[2/]	5,000 cpm[3/]	APR[4/]
		>250,000 cpm	Withdraw
PID/FID Meter	Intermittent[2/]	Detection to 10 ppm[5/]	APR[4/]
		10-25 ppm	SAR[6/]
		>25 ppm	Withdraw

Notes:

1/ "Frisking" for alpha contamination and beta/gamma contamination using hand held alpha scintillator and Geiger Mueller detectors respectively.

2/ "Intermittent" is as deemed necessary by the WEMCO Radiological Safety and/or IH Technician, or at a minimum of once a day.

3/ Above background.

4/ Full-face air purifying respirator with High Efficiency Particulate Air (HEPA) or organic vapor, acid gas, fume cartridges (Health Physics Review). Disposable protective clothing, such as Tyvek/Saranex coveralls and a step-off decontamination, will also be required at any time Air Purifying Respirator (APR) are used.

5/ 1 ppm above background.

6/ Supplied air respirator.

SECTION 5

PERSONAL PROTECTIVE EQUIPMENT

The following Personal Protective Equipment (PPE) is required to be worn by personnel who perform the work tasks described in Subsections 1.1 through 1.11:

Table 5-1 - PPE Associated with the Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization

WORK TASKS	POTENTIAL/EXPECTED HAZARD	PERSONAL PROTECTIVE EQUIPMENT
1.1 Collect and place contaminated soil in drums and move drums to Plant 9 Storage Area.	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Hand injury	Leather-palm gloves
	Back injury	Back support belt
	Body contamination	Disposable Tyvek over controlled area coveralls
	Inhalation of airborne particulates during excavation and drum filling operations	Full-face air purifying respirator with HEPA filter cartridges
1.2 Transfer contaminated soil from drums to the soil washing unit	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Hand injury	Leather-palm gloves
	Back injury	Back support belt
	Body contamination	Disposable tyvek over controlled area coveralls
	Inhalation of airborne particulates during soil transfer operations	Full-face air purifying respirator with HEPA filter cartridges

Table 5-1 (Continued)

WORK TASKS	POTENTIAL/EXPECTED HAZARD	PERSONAL PROTECTIVE EQUIPMENT
1.3 Operate the soil washing unit	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Body contamination	Controlled area coveralls
	Hearing loss	Ear plugs/muffs, if noise levels exceed 85 dBA over any time period
1.4 Transfer cleaned soil and concentrated contaminated soil to containers for storage	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Hand injury	Leather-palm gloves
	Body contamination	Disposable tyvek over controlled area coveralls
	Inhalation of airborne particulates during soil transfer operations	Full-face air purifying respirator with HEPA filter cartridges
1.5 Operate the water treatment system	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Body contamination	Controlled area coveralls
	Hearing loss	Ear plugs/muffs, if noise levels exceed 85 dBA over any time period

Table 5-1 (Continued)

WORK TASKS	POTENTIAL/EXPECTED HAZARD	PERSONAL PROTECTIVE EQUIPMENT
1.6 Collect and place contaminated sludge in drums/tank trailer from Waste Pit 5 and move drums/tank trailer to Plant 9 Storage Area	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Hand injury	Chemical protective gloves (IH Review)
	Back injury	Back support belt
	Body contamination	Disposable Tyvek over controlled area coveralls
	Inhalation of airborne particulates	Full-face air purifying respirator with radioactive material HEPA filter and organic vapor/acid gas combination cartridges
1.7 Transfer contaminated sludge from the drums/tank trailer to vitrification unit	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Hand injury	Chemical protective gloves (IH Review)
	Back injury	Back support belt
	Body contamination	Disposable Tyvek over controlled area coveralls
	Inhalation of airborne particulates	Full-face air purifying respirator with radioactive material HEPA filter and organic vapor/acid gas combination cartridges

Table 5-1 (Continued)

WORK TASKS		POTENTIAL/EXPECTED HAZARD	PERSONAL PROTECTIVE EQUIPMENT
1.8	Addition of chemical additives to vitrification feed materials	Eye injury	Safety goggles, if full-face respirator is not worn.
		Head injury	Hard hat
		Foot injury	Steel-toed boots/shoe covers
		Hand injury	Chemical protective gloves (IH Review)
		Body contamination	Disposable Tyvek over controlled area coveralls
		Inhalation of airborne particulates	Full-face air purifying respirator with radioactive material HEPA filter and organic vapor/acid gas combination cartridges
1.9	Operate the vitrification unit	Eye injury	Safety glasses
		Head injury	Hard hat
		Foot injury	Steel-toed boots/shoe covers
		Body contamination	Controlled area coveralls
		Hearing loss	Ear plugs/muffs, if noise levels exceed 85 dBA over any time period
1.10	Transfer empty sludge contaminated drums/tank trailer back to Plant 9 Storage Area	Eye injury	Safety glasses
		Head injury	Hard hat
		Foot injury	Steel-toed boots/shoe covers
		Hand injury	Chemical protective gloves (IH Review)
		Back injury	Back support belt
		Body contamination	Disposable Tyvek over controlled area coveralls

Table 5-1 (Continued)

WORK TASKS	POTENTIAL/EXPECTED HAZARD	PERSONAL PROTECTIVE EQUIPMENT
1.11 Transfer stabilized glass waste marbles to containers for storage	Eye injury	Safety glasses
	Head injury	Hard hat
	Foot injury	Steel-toed boots/shoe covers
	Hand injury	Leather-palm gloves
	Body contamination	Disposable Tyvek over controlled area coveralls

Additional PPE may be specified by WEMCO Industrial, Radiological, Safety and Training (IRS&T) personnel.

SECTION 6

WORK SITE SAFETY REQUIREMENTS

6.1 Equipment Safety

Excavation and drum/container moving equipment will be inspected prior to each day's use in order to ensure that all safety features (e.g., kill switch and backup alarm) are operational. A record/log of the equipment safety inspections shall be documented and made available upon request by WEMCO and PARSONS representatives. Only authorized and qualified personnel will be allowed to operate this equipment.

Safety features of the soil wash, water treatment, and vitrification units (e.g., guards and alarms) will be inspected prior to system startup to ensure that they are operational. These features will also be inspected periodically during system operation. All hazardous parts of the units (e.g., electric, moving parts) will be clearly marked.

6.2 Work Area Safety

A rope and/or caution tape barrier with posted safety requirements will be maintained around the excavation area, sludge drum filling area, soil washing, water treatment, and vitrification units work areas. One or more safety watch personnel may be stationed in the work area to ensure that no unauthorized personnel accidentally enter the work site when drums of soil/sludge are being filled and emptied into the soil wash unit and/or vitrifier system.

During the daily work activities, a GTS Duratek Field Supervisor or Job Foreman shall be at the Waste Pit 5 and/or MAWS work location at all times while work is in progress. The Field Supervisor or Job Foreman shall have an emergency communication radio at the job site at all times. Communications to WEMCO's emergency response personnel shall be by radio.

Site personnel working around moving equipment (i.e., back-hoe, forklifts, and trucks) shall wear clothing easily noticeable by the equipment operator (i.e., orange day-glow vest) to minimize the potential of being struck. Pinch points on all equipment which constitutes a hazard to the site personnel during operations shall be guarded.

During the MAWS bench-scale treatability study operations in Plant 9, RUST Engineering will also be conducting Plant 9 construction modifications. RUST, GTS Duratek, and WEMCO personnel will communicate on a daily basis to coordinate work activities to ensure all health and safety concerns are

communicated and addressed. All conflicts in work activities will be resolved by the WEMCO Project Engineer responsible for the project.

SECTION 7

SITE CONTROL

7.1 Access

The field tasks associated with this bench-scale treatability study will occur entirely inside a controlled area (Plant 9) of the FEMP site. Controlled areas of the FEMP site are maintained in accordance with the *Radiological Controls Requirements Manual* (RM-0009) which requires the following:

1) The wearing of dosimetry

2) Radiation safety training

3) Limitations on entry for personnel with open wounds or recent medical tests with radionuclides

4) Radiological area postings

5) Protective clothing

6) Limitations on food, beverages, and tobacco

7) General rules for work

8) Contamination control

9) Monitoring and showering requirements upon exiting from the Controlled Area and Radiological Areas

A Radiation Work Permit with the specifications of this task-specific health and safety plan will be required for work in the area.

Per the requirements of 29 CFR Part 1910.120, an exclusion zone (defined by a barricade rope) will be established around the immediate excavation and soil/sludge container filling area and the soil wash, water treatment, and vitrification units. The exclusion zone is an area of high potential hazard due to physical, chemical, and/or radiological dangers. Access to the exclusion zone will be restricted to trained and qualified personnel who must enter to perform their job duties. Radiological Safety will establish controls consisting of step-off pads at the controlled area exit point. This contamination reduction zone will be

used for monitoring at the step-off pad and for removal of disposable PPE. Only limited equipment decontamination will be allowed at the work site.

7.1.1 Radiological Postings

Radiological areas will be posted in accordance with *Radiological Controls Requirements Manual* (RM-0009). Table 7-1 provides a brief summary of posting requirements applicable to radionuclides likely to be encountered during removal action activities.

Table 7-1 - Posting Requirements

Controlled Area Posting	Contamination Level
Regulated Area	
(U-235 and U-238)	>1,000 dpm α/100 cm^2 removable >5,000 dpm α/100 cm^2 fixed plus removable
(Ra-226, Th-228, Th-230, Th-232, and Sr-90)	>200 dpm α/100 cm^2 removable >1,000 dpm α/100 cm^2 fixed plus removable
(Beta - Gamma Emitters)	>1,000 dpm β-γ/100 cm^2 removable >5,000 dpm β-γ/100 cm^2 fixed plus removable
Contamination Area	
(U-235 and U-238)	>10,000 dpm α/100 cm^2 removable >50,000 dpm α/100 cm^2 fixed plus removable
(Ra-226, Ra-228, Th-228, Th-230, Th-232, and Sr-90)	>2,000 dpm α/100 cm^2 removable >10,000 dpm α/100 cm^2 fixed plus removable
(Beta - Gamma Emitters)	>10,000 dpm β-γ/100 cm^2 removable >50,000 dpm β-γ/100 cm^2 fixed plus removable
Airborne Radioactivity Area	Potential for 0.8 DAC hours per shift.
Respirator Area	>8.0 DAC hours in a single shift <u>or</u> >2 DAC hours per shift averaged over 1 calendar quarter; and > 50,000 dpm α/100 cm^2 removable or 100,000 β-γ/100 cm^2 removable.
Radiation Area	$\geq$ 5 mrem/hr and < 100 mrem/hr

Source: *Radiological Controls Requirements Manual* (RM-0009), May 13, 1992.

7.2 Bioassay Samples

Personnel involved in this project are required to participate in a routine periodic urine assay program. Any circumstance which could have resulted in an intake of any radioactive materials by inhalation, ingestion, or absorption shall immediately be reported to a supervisor. The supervisor shall immediately report the circumstance of possible radioactive materials intake to the WEMCO Radiological Safety Section for evaluation. The involved employees shall report to the Urine Sampling Station at the end of their shift to complete an Incident Investigation Report (Form FMPC-ES&H-1458) and submit an incident urine sample. The involved employees shall also report to the Urine Sampling Station at the start of their next shift to submit a follow-up urine sample.

If air sample analyses indicate that airborne radioactivity levels were sufficient to deliver more than 8 DAC-hours to an individual, in-vivo monitoring and/or other bioassay measurements will be performed on that individual as deemed appropriate by the WEMCO Dosimetry Subsection. Air samples, which indicate that personnel may have been exposed to greater than 40 DAC-hours in one week, will trigger dose assessment by the WEMCO Dosimetry Subsection. Employees are responsible for complying with additional requirements as specified by the WEMCO Radiological Safety Section.

7.3 Medical Monitoring

In accordance with 29 CFR 1910.120 requirements, all bench-scale treatability study field personnel are required to participate in a medical monitoring program which consists of the following items:

1) A baseline medical examination
2) Annual medical examination
3) Required medical examinations after potential exposures
4) WEMCO respirator clearance for users

Each individual shall be subject to a medical surveillance approval by the WEMCO Director, Medical Services. The approval statement shall certify that each individual is medically qualified to perform the work and is physically fit to wear PPE.

7.4 Training Requirements

All personnel assigned to the tasks will, as a minimum, meet the following requirements:

1) Documented review of the health and safety plan for this work, including site-specific hazards and procedures

2) WEMCO radiation safety training

3) WEMCO annual respiratory training and quantitative fit test or equivalent approved by WEMCO IH

4) Site nuclear criticality training

5) Portable fire extinguisher, General Safety, You and Occupational Safety and Health Administration (OSHA), and Energy Control Procedures Awareness training

6) Forty-hour OSHA training (per 29 CFR 1910.120)

7) Eight-hour annual refresher training, as necessary

8) Eight-hour supervisory training (for supervisors)

9) 24-hour supervised field experience for general site workers or 8-hour supervised field experience for occasional site workers

The completion of this training shall be documented by the site training personnel.

7.5 Safety Meetings

A safety meeting, which must be documented, shall be conducted prior to the start of each day's work. This safety meeting will cover the following applicable subjects:

1) Work operations
2) PPE
3) All monitoring data
4) Hazard communications
5) Monitoring tests and results
6) Decontamination
7) Task organization
8) Physical stress
9) Emergency procedures
10) Communications
11) General safety
12) Housekeeping
13) Problems encountered
14) Problems anticipated

SECTION 8

EXPOSURE SYMPTOMS

Exposure to low levels of radiation does not produce acute exposure symptoms. Such exposures may cause delayed effects such as cancer. Since any radiation exposure may involve some degree of risk, exposures are to be kept ALARA. Personal radiation exposures will be monitored by TLDs worn by all personnel conducting field work tasks.

SECTION 9

SITE ENTRY PROCEDURES

Prior to the initiation of the bench-scale treatability study field activities and/or the beginning of daily work activities, the WEMCO Project Engineer or GTS Duratek Field Supervisor will ensure that the following activities have been conducted:

1) Obtain the necessary work permits (e.g., radiation, excavation, and penetration) for field operations.

2) Conduct safety inspection of all excavation and support equipment and soil wash, water treatment, and vitrification units.

3) Establish radio contact, location, and start and stop times with FEMP Control Center.

4) Conduct pre-work plan and safety meeting prior to each day's work activities; exclusion zone, contamination reduction zone, and break areas will be identified.

5) Discuss alternate communication signals (if applicable).

6) Perform respirator check-out and inspection prior to use.

7) Inspect and calibrate all devices to be used for monitoring.

8) Assign all personnel who will be working in the exclusion zone (per 29 CFR 1910.120 requirements) to a buddy system.

9) Test eyewash station and maintain clean, approved liquid in it.

10) Verify location and operation of all emergency equipment. Emergency equipment items are listed in Subsection 12.5.

Entrance to the exclusion zone will be controlled by the WEMCO Project Engineer or GTS Duratek Field Supervisor. Also, a checklist shall be used and signed daily by the GTS Duratek Field Supervisor to verify that all pre-work requirements have been met prior to work activities beginning.

SECTION 10

DECONTAMINATION

An exclusion zone will be established around the soil excavation and sludge drum filling work areas in order to control the potential spread of contamination from soil excavation and container filling activities. As stated in Subsection 7.1, a contamination reduction zone will be established at each work area for removal of any disposable personal protective clothing and cleaning of contaminated equipment. Personnel will enter and exit the posted work area through a step-off pad. At the exit point, personnel will remove any disposable protective clothing and monitor themselves and any outgoing equipment for contamination. All personnel and outgoing equipment will be monitored for contamination in accordance with WEMCO Standard Operating Procedure SP-P-35-029, Rev. 0 (6/28/91), "Unrestricted Release of Materials." Action limits (above background) on equipment of 20 dpm/100 cm^2 alpha (removable), 300 dpm/100 cm^2 alpha (total: fixed plus removable), and 1,000 dpm/100 cm^2 beta/gamma (total: fixed plus removable) will initiate decontamination activities for unrestricted use.

Any detectable alpha contamination and greater than 100 cpm beta-gamma (above background) contamination on any personnel will be reported to WEMCO Radiological Safety, who will assist in decontamination in accordance with WEMCO Standard Operating Procedure SP-P-35-017, Rev. 0 (3/30/89), "Procedure for Personnel Decontamination." Any equipment that cannot initially be decontaminated will be contained and transported to the FEMP Site Decontamination Facility. If the equipment cannot be decontaminated to acceptable levels it will be disposed as radioactive waste in accordance with approved site policies and procedures.

SECTION 11

WASTES

Waste expected to be generated during work activities includes disposable personal protective clothing, decontamination solution and material, containers the soil wash chemicals and vitrification additives came in, filter residue, spent filter media, duds from the vitrification process, spent electrodes, and refractory bricks. Oversized sludge material from Waste Pit 5 which cannot be used will be returned to the pit. Potentially contaminated waste material will be collected, segregated, and placed in drums or other containers. Disposable protective clothing will be placed in plastic bags and disposed as compactible, potentially contaminated waste. Liquid waste from decontamination efforts will be collected, stored, and disposed in accordance with applicable WEMCO procedures.

Waste drums or containers will meet the requirements of 49 CFR Parts 171-178, 40 CFR Parts 264-265 and 300. Hazard warning labels will be applied immediately to all waste containing drums as specified by WEMCO management/supervisors and OU-3 Compliance.

SECTION 12

CONTINGENCY PLANS

All contingency plans shall be consistent with the *FEMP Emergency Plan* (PL-3015).

12.1 Incidents or Injuries Involving Possible Intake of Radiological or Chemical Substances by Employees

Any circumstance which could have resulted in an intake of a radioactive material or other hazardous substances by inhalation, ingestion, or absorption shall be reported to the GTS Duratek Field Supervisor. The supervisor shall immediately report the possible radioactive material or hazardous substance intake to the Radiological Safety Section for evaluation. The involved employee(s) shall report to the Medical Services Section to submit biological samples and complete and Incident Investigation Report. Typically, samples are required at the end of the shift and at the start of the subsequent shift. If the exposure involves uranium, a urine sample is required. Appendix A contains a copy of an Incident Investigation Report.

12.2 Pre-Emergency Planning

During the training and pre-work safety meetings, employees involved in this task will be trained and reminded of the provisions of the plant emergency procedure, alarm signals and communications, evacuation routes, emergency reporting, and the importance of maintaining continual communication with FEMP Emergency Preparedness personnel via two-way radio or cellular phone.

12.3 Lines of Authority

The WEMCO Field Supervisor, or his/her designated representative, has the primary responsibility for the prevention of and the initial response to emergency conditions, in addition to directing emergency response actions at the work site until relieved by the WEMCO Assistant Emergency Duty Officer (AEDO), or the Emergency Response Team. In the event an emergency does occur, the individual involved in or observing the condition shall immediately notify the following personnel in order of availability: the WEMCO Project Engineer/GTS Duratek Field Supervisor; the communications center; the AEDO; the WEMCO Health and Safety Officer; the Project Engineer/OU Manager.

The AEDO is responsible for ensuring that corrective actions have been implemented, appropriate personnel notified, and reports completed as required. Personnel shall report unsafe conditions observed at the work site to the WEMCO Project Engineer/GTS Duratek Field Supervisor or to the WEMCO

Health and Safety Officer, who will stop work activity in the affected area until the hazardous condition(s) can be remedied.

12.4 Evacuation

In the event an evacuation of the work area is required, the WEMCO Project Engineer/GTS Duratek Field Supervisor will be responsible for notifying all personnel involved. All personnel will proceed to the rally point as designated by the WEMCO Project Engineer/Field Supervisor. The FEMP-designated rally points for the standard plant operations are shown on Figure 12-1. The designated rally point for the work area (Plant 9) is Rally Point 3. When the WEMCO Project Engineer is informed that an all-clear condition has been achieved, personnel will be released from the rally point.

In the event of an emergency which necessitates an evacuation of the Exclusion Area, the 3-3, 3-3 alarm signal shall be sounded over the plant alarm system; a voice message will follow over the Emergency Message System (EMS) instructing employees to go to their designated rally point. Personnel shall immediately proceed to the rally point. Personnel will follow instructions given by the rally point coordinator and participate in the accountability process. When an all-clear condition has been achieved, personnel will be released from the rally point. It is conceivable that the plant alarm signal, or EMS, will not be audible in the work area. For this reason, communications with the FEMP communications control center via two-way radio or cellular phone will be maintained at all times by the WEMCO Project Engineer.

12.5 Emergency Equipment

The following safety equipment will be available for use by removal action workers:

1) Fire extinguisher
2) Portable eyewash station
3) Absorbent
4) Spill drums
5) Two-way radio or telephone
6) Respirators
7) Clean-up materials
8) Local evacuation alarm

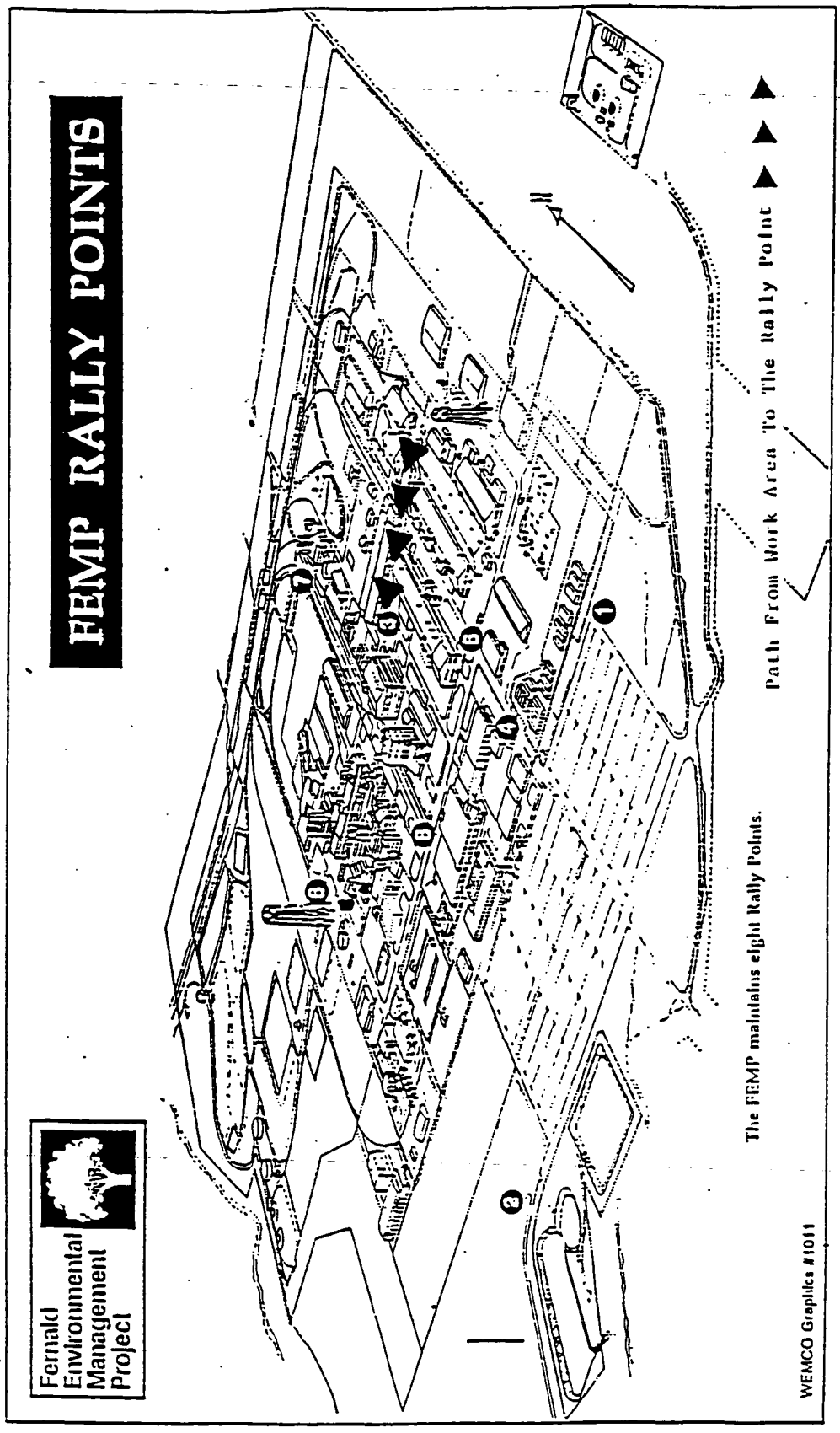


Figure 12-1 - FEMP Rally Points

12.6 Emergency Notification

All emergencies, including spills or leaks, shall be reported immediately. Emergencies can be reported by telephone dialing Extension 6511 or by contacting the communications center via two-way radio. Emergencies can also be reported by pulling a fire alarm pull box (if one is located in the work area[s]) if telephone or radio is not immediately available. Any additional information pertaining to an emergency shall be reported to the responding personnel to assist in defining appropriate response to the emergency.

12.7 Fire, Explosion, or Medical Emergency

In the event of a fire, explosion, or medical emergency, the communication center shall be notified immediately by two-way radio, by manual fire alarm, or by calling Extension 6511. The communication center operator will activate the emergency response team and dispatch them to the emergency location. If a fire is in the incipient stage and perceived controllable without endangering oneself, personnel may use available fire extinguishers. If it is not in the incipient stage, personnel in the immediate area shall evacuate to a safe position and await instructions.

If medical attention is required, and the nature of the injury or illness is minor, the affected personnel shall be taken to the FEMP Medical Department Facility (Building 53) located as shown on Figure 12-2. A map which illustrates the path from the work area to the FEMP Medical Department Facility will be posted in the work area. The FEMP ambulance will be called to transport individuals who have suffered major injury or illness.

12.8 Spill Control Contingency Plan

Spills, regardless of their size or the classification of the liquid, shall be reported immediately. Emergencies can be reported by telephone by dialing Extension 6511 or by contacting the communications center via two-way radio. The Emergency Response Team and AEDO will respond to the spill according to the FEMP Spill Control Contingency Plan.

12.9 Additional Information

12.9.1 Hospitals

The FEMP Medical Department Facility (Building 53) is the primary choice for treatment of on-site injuries. The FEMP ambulance will transport the injured workers to the nearest hospital, if necessary. FEMP maintains an emergency response capability that includes an ambulance and Emergency Medical Technicians.

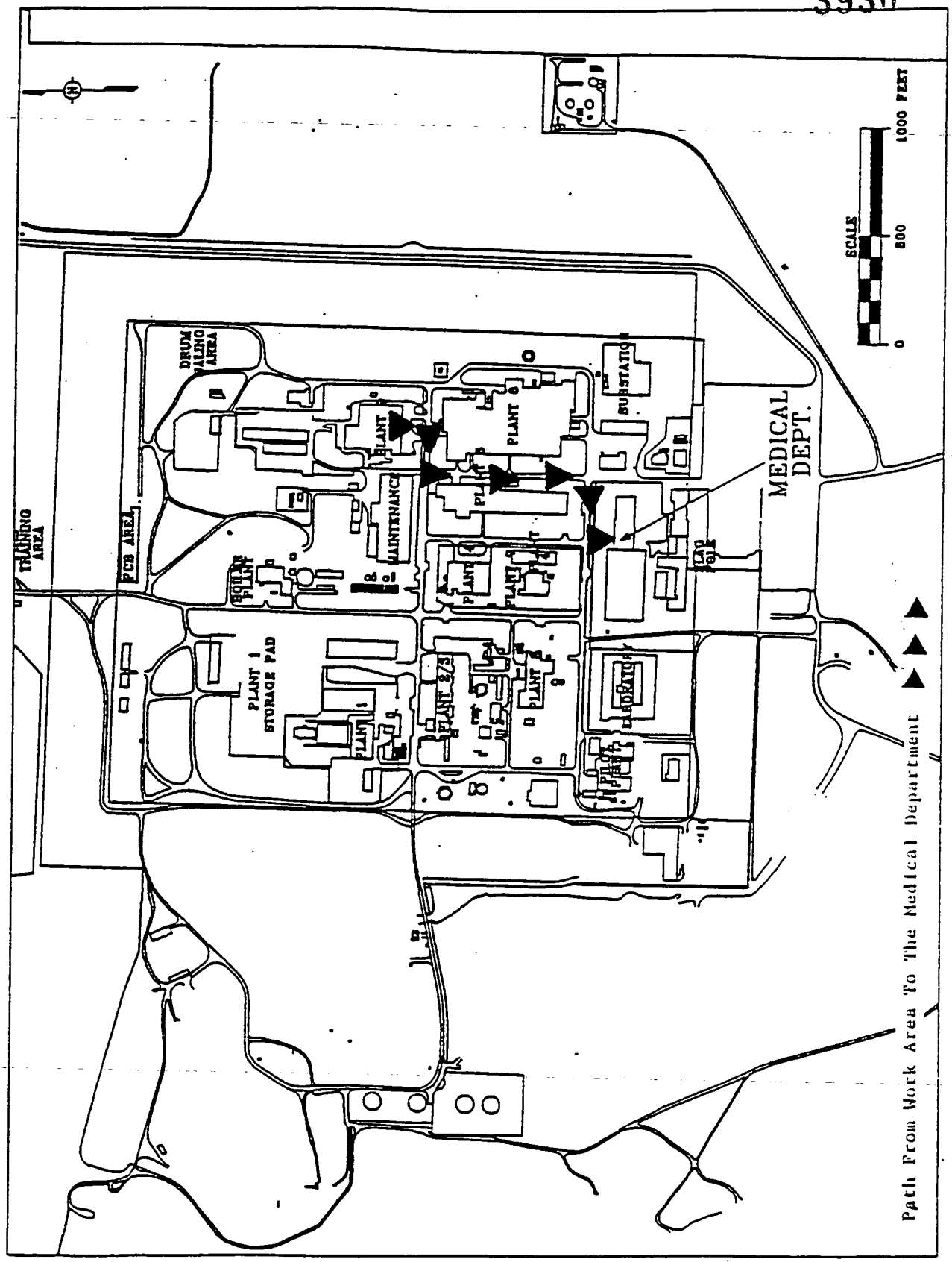


Figure 12-2 - Location of FEMP Medical Department Facility

12.9.2 Emergency Telephone Numbers

			Radio Frequency
EMERGENCY RESPONSE	x6511	Control	
Industrial Hygiene	x6207	357	F2
Radiation Safety	x6889	355	F2
Fire and Safety	x6235	303	F2
Assistant Emergency Duty Officer	x6431 or x6295	202	F2
Ambulance	x6511		
Hospital	x6511		
Fire	x6511		

SECTION 13

CONFINED SPACE ENTRY

A Confined Space Entry permit may be required for the activities associated with the bench-scale treatability study for the MAWS. Entry into vitrification unit would constitute a confined space entry. This could occur for maintenance of the refractory brick, cleaning of the internal chamber, or removal of duds.

If a confined space entry permit is needed the GTS Duratek Field Supervisor shall notify the WEMCO Facility Owner and IH personnel in addition to initiating and completing a FMPC Work Permit and request for a Confined Space Entry Permit for any entry into a confined space. The Facility Owner will ensure that the confined space requiring entry if properly prepared, labeled, and in a safe condition before authorized personnel enter. The IH representative shall conduct air quality testing inside the confined space in order to specify precautions or proper PPE requirements, ensures that the FMPC Work Permit has been filled out and signed by the Facility Owner and the GTS Duratek Supervisor when a confined space entry permit is requested, and issues the confined space entry permits.

All site personnel involved in a confined space entry shall be familiar with the hazards associated with confined space entries and have attended the necessary training. The completion of this training shall be documented by the site training personnel. No site personnel shall be allowed to enter a confined space until all permits are properly completed, signed, atmospheric testing conducted, and permission has been given by all responsible parties.

All confined space entries shall be in accordance with WEMCO Industrial Hygiene and Safety Manual Procedure IH&S-IH-05, Revision 0 (February 13, 1989), "Control of Entering and/or Working in a Confined Space" and WEMCO Procedure FMPC-516, Revision 2 (April 23, 1991), "Control of Permits for Accomplishing Hazardous Work." Attachment D contains a copy of a FMPC Work Permit/Confined Space Entry Permit.

SECTION 14

APPROVAL AND COMPLIANCE STATEMENT

14.1 Provisions

This task-specific Health and Safety Plan was produced for the FEMP and addresses health and safety aspects of all work related to the bench-scale treatability study for the Minimum Additive Waste Stabilization. Personnel who perform the tasks listed in Subsections 1.1 through 1.11 must read, understand, and agree to abide by the procedures and requirements set forth in both this Health and Safety Plan and any subsequent amendments. Site workers are required to sign the attached approval and compliance Health and Safety Plan Acknowledgement Form, Figure 14-1.

14.2 Amendments to Plan

This Health and Safety Plan is based on information available at the time of preparation. Unexpected conditions may arise which require reassessment of safety procedures. Unplanned activities and/or changes in the hazard status shall require a review of, and may result in changes to, this plan. Changes in the anticipated hazard status or unplanned activities are to be recorded as an amendment to this plan. Amendments must be approved by the plan author, Engineering Department Manager, and WEMCO IRS&T must be notified in writing of plan amendments.

Compliance with the provisions of this Health and Safety Plan may be audited through announced or unannounced site visits. All provisions of this Health and Safety Plan are to be implemented. Reasons for field actions/changes, when they are necessary, should be fully documented.

HEALTH AND SAFETY PLAN ACKNOWLEDGEMENT FORM

I have been informed and understand and will abide by the procedures set forth in the Health and Safety Plan and Amendments for the OU-1 Bench-Scale Treatability Study for the Minimum Additive Waste Stabilization at the FEMP site.

Printed Name	Signature	Representing	Date

Figure 14-1 - Health and Safety Plan Acknowledgement Form

SECTION 15

REFERENCES

(CFR 1991) Code of Federal Regulations, July 1, 1991. 29 CFR, Part 1910.120.

(CFR 1991) ——, July 1, 1991. 49 CFR, Parts 171-178.

(CFR 1991) ——, July 1, 1991. 40 CFR, Parts 264-265 and 300.

(DOE 1989) United States Department of Energy, July 20, 1989. DOE Order 5480.11, *"Radiation Protection for Occupational Workers."*

(DOE 1991) ——, November 27, 1991. *FEMP Emergency Plan (PL-3105).* Fernald, Ohio: Fernald Environmental Management Project.

(GTS Duratek 1992) GTS Duratek, September 1992. *Input for MAWS Work Plan.*

(WEMCO 1989) Westinghouse Environmental Management Company of Ohio, February 13, 1989. *Control of Entering and/or Working in a Confined Space (IH&S-IH-05), Revision 0.* Fernald, Ohio: FEMP.

(WEMCO 1989) ——, March 30, 1989. *Procedure for Personnel Decontamination (SP-P-35 -017), Revision 0.* Fernald, Ohio: FEMP.

(WEMCO 1990) ——, June 1990. *FEMP Site Health and Safety Plan.*

(WEMCO 1991) ——, April 23, 1991. *Control of Permits for Accomplishing Hazardous Work (FMPC-516), Revision 2.* Fernald, Ohio: FEMP.

(WEMCO 1991) ——, June 28, 1992. *Unrestricted Release of Materials (SP-P-35-029), Revision 0.* Fernald, Ohio: FEMP.

(WEMCO 1992) ——, May 13, 1992. *Radiological Controls Requirements Manual (RM-0009), Fernald Environmental Management Project.*

(Weston 1987) Weston, Roy F., Inc., 1987. *Characterization Investigation Study.* West Chester, Pennsylvania: Weston (FMPC/SUB-008, Vol 2).

ATTACHMENT A

INCIDENT INVESTIGATION REPORT

FMPC

ENVIRONMENT, SAFETY AND HEALTH DEPARTMENT

INCIDENT INVESTIGATION REPORT

This Section to be Completed by Employee

NAME:	BADGE:	JOB CLASSIFICATION:
PLANT/AREA:	JOB WORKED:	SHIFT WORKED:
INITIAL SAMPLE BOTTLE NUMBER:	SUPERVISOR'S NAME:	
LOCATION OF INCIDENT:	DATE OF INCIDENT:	TIME OF INCIDENT:

MATERIALS INVOLVED IN INCIDENT:

DESCRIPTION OF INCIDENT:

HOW LONG EMPLOYEE INVOLVED IN INCIDENT:

DISTANCE AND DIRECTION FROM INCIDENT:

HOW POTENTIALLY EXPOSED: ☐ Inhalation ☐ Swallowing ☐ Skin Absorption

RESPIRATOR USED: ☐ Yes ☐ No

IF USED, HOW LONG?

IF USED, INDICATE TYPE:
☐ Half-Mask Air-Purifying ☐ Half-Mask Airline ☐ Self-Contained Breathing Apparatus (SCBA)
☐ Full-Face Air-Purifying ☐ Hooded Airline ☐ SCBA Inside Acid Suit
☐ Emergency Life Support Apparatus (ELSA)

CARTRIDGE COLOR IF AIR-PURIFYING RESPIRATOR USED:
☐ Purple ☐ Purple + Yellow ☐ Yellow ☐ Green ☐ Black

OTHER PROTECTIVE EQUIPMENT:
☐ Leather-Palm Gloves ☐ Rubber Gloves ☐ Chemical Goggles ☐ Rubber Suits/Aprons

HAVE YOU TAKEN ANY MEDICATIONS IN THE LAST 24 HOURS? IF YES, LIST DRUGS:
☐ Yes ☐ No

MEDICAL COMPLAINTS POSSIBLY RELATED TO INCIDENT:

Employee's Signature: _____ Date: _____

This Section to be Completed by Bio Assay

SAMPLE NUMBER	SAMPLE DATE	SAMPLE TIME (Military)	SAMPLE TYPE	URANIUM (mgU/L)	FLUORIDE (ugF/mL)	Sp. Gr.	OTHER? _____	CASTS	PROTEIN (mg/dL)

COMMENTS:

FMPC-ES&H-1458 (REV. 5/8/86)

Investigated by _____ Date _____

ATTACHMENT B

GUIDANCE FOR HEAT STRESS MONITORING AND PREVENTION

Heat Stress and Other Physiological Factors

Wearing PPE puts a hazardous waste worker at considerable risk of developing heat stress. This can result in health effects ranging from transient heat fatigue to serious illness or death. Heat stress is caused by a number of interacting factors, including environmental conditions, clothing, workload, and the individual characteristics of the worker. Because heat stress is probably one of the most common (and potentially serious) illnesses at hazardous waste sites, regular monitoring and other preventive precautions are vital.

Individuals vary in their susceptibility to heat stress. Factors that may predispose someone to heat stress include:

- Lack of physical fitness.
- Lack of acclimatization.
- Age.
- Dehydration.
- Obesity.
- Alcohol and drug use.
- Infection.
- Sunburn.
- Diarrhea.
- Chronic disease.

Reduced work tolerance and the increased risk of excessive heat stress is directly influenced by the amount and type of PPE worn. PPE adds weight and bulk, severely reduces the body's access to normal heat exchange mechanisms (evaporation, convection, and radiation), and increases energy expenditure. Therefore, when selecting PPE, each item's benefit should be carefully evaluated in relation to its potential for increasing the risk of heat stress. Once PPE is selected, the safe duration of work/rest periods should be determined based on the:

- Anticipated work rate.
- Ambient temperature and other environmental factors.
- Type of protective ensemble.
- Individual worker characteristics and fitness.

Source:
NIOSH/OSHA/USCG/EPA Occupational Safety And Health Guidance Manual for Hazardous Waste Site Activities, October 1985.

Monitoring

Because the incidence of heat stress depends on a variety of factors, all workers, even those not wearing protective equipment, should be monitored.

- For workers wearing permeable clothing (e.g., standard cotton or synthetic work clothes), follow recommendations for monitoring requirements and suggested work/rest schedules in the current American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values for Heat Stress [11]. If the actual clothing worn differs from the ACGIH standard ensemble in insulation value and/or wind and vapor permeability, change the monitoring requirements and work/rest schedules accordingly [12].

- For workers wearing semipermeable or impermeable[1] encapsulating ensembles, the ACGIH standard cannot be used. For these situations, workers should be monitored when the temperature in the work area is above 70°F (21°C) [6].

To monitor the worker, measure:

- Heart rate. Count the radial pulse during a 30-second period as early as possible in the rest period.

  If the heart rate exceeds 110 beats per minute at the beginning of the rest period, shorten the next work cycle by one-third and keep the rest period the same.

  If the heart rate still exceeds 110 beats per minute at the next rest period, shorten the following work cycle by one-third [12].

- Oral temperature. Use a clinical thermometer (3 minutes under the tongue) or similar device to measure the oral temperature at the end of the work period (before drinking).

  If oral temperature exceeds 99.6°F (37.6°C), shorten the next work cycle by one-third without changing the rest period.

  If oral temperature still exceeds 99.6°F (37.6°C) at the beginning of the next rest period, shorten the following work cycle by one-third [12].

  Do *not* permit a worker to wear a semipermeable or impermeable garment when his/her oral temperature exceeds 100.6°F (38.1°C)[12].

- Body water loss, if possible. Measure weight on a scale accurate to ±0.25 lb at the beginning and end of each work day to see if enough fluids are being taken to prevent dehydration. Weights should be taken while the employee wears similar clothing or, ideally, is nude. *The body water loss should not exceed 1.5 percent total body weight loss in a work day* [12].

Initially, the frequency of physiological monitoring depends on the air temperature adjusted for solar radiation and the level of physical work (see Table 8-10). The length of the work cycle will be governed by the frequency of the required physiological monitoring.

Prevention

Proper training and preventive measures will help avert serious illness and loss of work productivity. Preventing heat stress is particularly important because once someone suffers from heat stroke or heat exhaustion, that person may be predisposed to additional heat injuries. To avoid heat stress, management should take the following steps:

- Adjust work schedules:

  Modify work/rest schedules according to monitoring requirements.

  Mandate work slowdowns as needed.

  Rotate personnel: alternate job functions to minimize overstress or overexertion at one task.

  Add additional personnel to work teams.

  Perform work during cooler hours of the day if possible or at night if adequate lighting can be provided.

- Provide shelter (air-conditioned, if possible) or shaded areas to protect personnel during rest periods.

- Maintain workers' body fluids at normal levels. This is necessary to ensure that the cardiovascular system functions adequately. Daily fluid intake must approximately equal the amount of water lost in sweat, i.e., 8 fluid ounces (0.23 liters) of water must be ingested for approximately every 8 ounces (0.23 kg) of weight lost. The normal thirst mechanism is not sensitive enough to ensure that enough water will be drunk to replace lost sweat [14]. When heavy sweating occurs, encourage the worker to drink more. The following strategies may be useful:

  Maintain water temperature at 50° to 60°F (10° to 15.6°C).

  Provide small disposable cups that hold about 4 ounces (0.1 liter).

  Have workers drink 16 ounces (0.5 liters) of fluid (preferably water or dilute drinks) before beginning work.

  Urge workers to drink a cup or two every 15 to 20 minutes, or at each monitoring break. A total of 1 to 1.6 gallons (4 to 6 liters) of fluid per day are recommended, but more may be necessary to maintain body weight.

  Weigh workers before and after work to determine if fluid replacement is adequate.

- Encourage workers to maintain an optimal level of physical fitness:

  Where indicated, acclimatize workers to site work conditions: temperature, protective clothing, and workload (see *Level of Acclimatization* at the end of this chapter).

  Urge workers to maintain normal weight levels.

- Provide cooling devices to aid natural body heat exchange during prolonged work or severe heat exposure. Cooling devices include:

  Field showers or hose-down areas to reduce body temperature and/or to cool off protective clothing.

  Cooling jackets, vests, or suits (see Table 8-5 for details).

- Train workers to recognize and treat heat stress. As part of training, identify the signs and symptoms of heat stress (see Table 8-11).

Other Factors

PPE decreases worker performance as compared to an unequipped individual. The magnitude of this effect varies considerably, depending on both the individual and the PPE ensemble used. This section discusses the demonstrated physiological responses to PPE, the individual human characteristics that play a factor in these

[1]Although no protective ensemble is "completely" impermeable, for practical purposes an outfit may be considered impermeable when calculating heat stress risk.

Table 8-10. Suggested Frequency of Physiological Monitoring for Fit and Acclimatized Workers[a]

ADJUSTED TEMPERATURE[b]	NORMAL WORK ENSEMBLE[c]	IMPERMEABLE ENSEMBLE
90°F (32.2°C) or above	After each 45 minutes of work	After each 15 minutes of work
87.5° - 90°F (30.8° - 32.2°C)	After each 60 minutes of work	After each 30 minutes of work
82.5° - 87.5°F (28.1° - 30.8°C)	After each 90 minutes of work	After each 60 minutes of work
77.5° - 82.5°F (25.3° - 28.1°C)	After each 120 minutes of work	After each 90 minutes of work
72.5° - 77.5°F (22.5° - 25.3°C)	After each 150 minutes of work	After each 120 minutes of work

Source: Reference [13].

[a]For work levels of 250 kilocalories/hour.

[b]Calculate the adjusted air temperature (ta adj) by using this equation: ta adj °F = ta °F + (13 × % sunshine). Measure air temperature (ta) with a standard mercury-in-glass thermometer, with the bulb shielded from radiant heat. Estimate percent sunshine by judging what percent time the sun is not covered by clouds that are thick enough to produce a shadow. (100 percent sunshine = no cloud cover and a sharp, distinct shadow; 0 percent sunshine = no shadows.)

[c]A normal work ensemble consists of cotton coveralls or other cotton clothing with long sleeves and pants.

Table 8-11. Signs and Symptoms of Heat Stress[a]

- Heat rash may result from continuous exposure to heat or humid air.
- Heat cramps are caused by heavy sweating with inadequate electrolyte replacement. Signs and symptoms include:
  - muscle spasms
  - pain in the hands, feet, and abdomen
- Heat exhaustion occurs from increased stress on various body organs including inadequate blood circulation due to cardiovascular insufficiency or dehydration. Signs and symptoms include:
  - pale, cool, moist skin
  - heavy sweating
  - dizziness
  - nausea
  - fainting
- Heat stroke is the most serious form of heat stress. Temperature regulation fails and the body temperature rises to critical levels. Immediate action must be taken to cool the body before serious injury and death occur. Competent medical help must be obtained. Signs and symptoms are:
  - red, hot, usually dry skin
  - lack of or reduced perspiration
  - nausea
  - dizziness and confusion
  - strong, rapid pulse
  - coma

[a]Source: Reference [8].

responses, and some of the precautionary and training measures that need to be taken to avoid PPE-induced injury.

The physiological factors may affect worker ability to function using PPE include:

- Physical condition.
- Level of acclimatization.
- Age.
- Gender.
- Weight.

Physical Condition

Physical fitness is a major factor influencing a person's ability to perform work under heat stress. The more fit someone is, the more work they can safely perform. At a given level of work, a fit person, relative to an unfit person, will have [5,8,15,16]:

- Less physiological strain.
- A lower heart rate.
- A lower body temperature, which indicates less retained body heat (a rise in internal temperature precipitates heat injury).
- A more efficient sweating mechanism.
- Slightly lower oxygen consumption.
- Slightly lower carbon dioxide production.

Level of Acclimatization

The degree to which a worker's body has physiologically adjusted or acclimatized to working under hot conditions affects his or her ability to do work. Acclimatized individuals generally have lower heart rates and body temperatures than unacclimatized individuals [17], and sweat sooner and more profusely. This enables them to maintain lower skin and body temperatures at a given level of environmental heat and work loads than unacclimatized workers [18]. Sweat composition also becomes more dilute with acclimatization, which reduces salt loss [8].

Acclimatization can occur after just a few days of exposure to a hot environment [15,16]. NIOSH recommends a progressive 6-day acclimatization period for the unacclimatized worker before allowing him/her to do full work on a hot job [16]. Under this regimen, the first day of work on site is begun using only 50 percent of the anticipated workload and exposure time, and 10 percent is added each day through day 6 [16]. With fit or trained individuals, the acclimatization period may be shortened 2 or 3 days. However, workers can lose acclimitization in a matter of days, and work regimens should be adjusted to account for this.

When enclosed in an impermeable suit, fit acclimatized individuals sweat more profusely than unfit or unacclimatized individuals and may therefore actually face a greater danger of heat exhaustion due to rapid dehydration. This can be prevented by consuming adequate quantities of water. See previous section on *Prevention* for additional information.

Age

Generally, maximum work capacity declines with increasing age, but this is not always the case. Active, well-conditioned seniors often have performance capabilities equal to or greater than young sedentary individuals. However, there is some evidence, indicated by lower sweat rates and higher body core temperatures, that older individuals are less effective in compensating for a given level of environmental heat and work loads [19]. At moderate thermal loads, however, the physiological responses of "young" and "old" are similar and performance is not affected [19].

Age should not be the sole criterion for judging whether or not an individual should be subjected to moderate heat stress. Fitness level is a more important factor.

Gender

The literature indicates that females tolerate heat stress at least as well as their male counterparts [20]. Generally, a female's work capacity averages 10 to 30 percent less than that of a male [8]. The primary reasons for this are the greater oxygen-carrying capacity and the stronger heart in the male [15]. However, a similar situation exists as with aging: not all males have greater work capacities than all females.

Weight

The ability of a body to dissipate heat depends on the ratio of its surface area to its mass (surface area/weight). Heat loss (dissipation) is a function of surface area and heat production is dependent on mass. Therefore, heat balance is described by the ratio of the two.

Since overweight individuals (those with a low ratio) produce more heat per unit of surface area than thin individuals (those with a high ratio), overweight individuals should be given special consideration in heat stress situations. However, when wearing impermeable clothing, the weight of an individual is not a critical factor in determining the ability to dissipate excess heat.

ATTACHMENT C

GUIDANCE FOR COLD STRESS MONITORING AND PREVENTION

COLD STRESS

The cold stress TLVs are intended to protect workers from the severest effects of cold stress (hypothermia) and cold injury and to describe exposures to cold working conditions under which it is believed that nearly all workers can be repeatedly exposed without adverse health effects. The TLV objective is to prevent the deep body temperature from falling below 36°C (96.8°F) and to prevent cold injury to body extremities (deep body temperature is the core temperature of the body determined by conventional methods for rectal temperature measurements). For a single, occasional exposure to a cold environment, a drop in core temperature to no lower that 35°C (95°F) should be permitted. In addition to provisions for total body protection, the TLV objective is to protect all parts of the body with emphasis on hands, feet, and head from cold injury.

Introduction

Fatal exposures to cold among workers have almost always resulted from accidental exposures involving failure to escape from low environmental air temperatures or from immersion in low temperature water. The single most important aspect of life-threatening hypothermia is the fall in the deep core temperature of the body. The clinical presentations of victims of hypothermia are shown in Table 1. Workers should be protected from exposure to cold so that the deep core temperature does not fall below 36°C (96.8°F); lower body temperatures will very likely result in reduced mental alertness, reduction in rational decision making, or loss of consciousness with the threat of fatal consequences.

Pain in the extremities may be the first early warning of danger to cold stress. During exposure to cold, maximum severe shivering develops when the body temperature has fallen to 35°C (95°F). This must be taken as a sign of danger to the workers and exposure to cold should be immediately terminated for any workers when severe shivering becomes evident. Useful physical or mental work is limited when severe shivering occurs.

Since prolonged exposure to cold air, or to immersion in cold water, at temperatures well above freezing can lead to dangerous hypothermia, whole body protection must be provided.

1. Adequate insulating dry clothing to maintain core temperatures above 36°C (96.8°F) must be provided to workers if work is performed in air temperatures below 4°C (40°F). Wind chill cooling rate and the cooling power of air are critical factors. [Wind chill cooling rate is defined as heat loss from a body expressed in watts per meter squared which is a function of the air temperature and wind velocity upon the exposed body.] The higher the wind speed and the lower the temperature in the work area, the greater the insulation value of the protective clothing required. An equivalent chill temperature chart relating the actual dry bulb air temperature and the wind ve-

TABLE 1. Progressive Clinical Presentations of Hypothermia*

Core Temperature °C	Core Temperature °F	Clinical Signs
37.6	99.6	"Normal" rectal temperature
37	98.6	"Normal" oral temperature
36	96.8	Metabolic rate increases in an attempt to compensate for heat loss
35	95.0	Maximum shivering
34	93.2	Victim conscious and responsive, with normal blood pressure
33	91.4	Severe hypothermia below this temperature
32	89.6	Consciousness clouded; blood pressure becomes difficult to obtain; pupils dilated but react to light; shivering ceases
31	87.8	
30	86.0	Progressive loss of consciousness; muscular rigidity increases; pulse and blood pressure difficult to obtain; respiratory rate decreases
29	84.2	
28	82.4	Ventricular fibrillation possible with myocardial irritability
27	80.6	Voluntary motion ceases; pupils nonreactive to light; deep tendon and superficial reflexes absent
26	78.8	Victim seldom conscious
25	77.0	Ventricular fibrillation may occur spontaneously
24	75.2	Pulmonary edema
22	71.6	Maximum risk of ventricular fibrillation
21	69.8	
20	68.0	Cardiac standstill
18	64.4	Lowest accidental hypothermia victim to recover
17	62.6	Isoelectric electroencephalogram
9	48.2	Lowest artificially cooled hypothermia patient to recover

* Presentations approximately related to core temperature. Reprinted from the January 1982 issue of *American Family Physician*, published by the American Academy of Family Physicians.

Source: American Conference of Governmental Industrial Hygienists, "1990-1991 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices," 1990. Reproduced with permission.

locity is presented in Table 2. The equivalent chill temperature should be used when estimating the combined cooling effect of wind and low air temperatures on exposed skin or when determining clothing insulation requirements to maintain the deep body core temperature.

2. Unless there are unusual or extenuating circumstances, cold injury to other than hands, feet, and head is not likely to occur without the development of the initial signs of hypothermia. Older workers or workers with circulatory problems require special precautionary protection against cold injury. The use of extra insulating clothing and/or a reduction in the duration of the exposure period are among the special precautions which should be considered. The precautionary actions to be taken will depend upon the physical condition of the worker and should be determined with the advice of a physician with knowledge of the cold stress factors and the medical condition of the worker.

Evaluation and Control

For exposed skin, continuous exposure should not be permitted when the air speed and temperature results in an equivalent chill temperature of −32°C (25.6°F). Superficial or deep local tissue freezing will occur only at temperatures below −1°C (30.2°F) regardless of wind speed.

At air temperatures of 2°C (35.6°F) or less, it is imperative that workers who become immersed in water or whose clothing becomes wet be immediately provided a change of clothing and be treated for hypothermia.

Recommended limits for properly clothed workers for periods of work at temperatures below freezing are shown in Table 3.

Special protection of the hands is required to maintain manual dexterity for the prevention of accidents:

1. If fine work is to be performed with bare hands for more than 10–20 minutes in an environment below 16°C (60.8°F), special provisions should be established for keeping the workers' hands warm. For this purpose, warm air jets, radiant heaters (fuel burner or electric radiator), or contact warm plates may be utilized. Metal handles of tools and control bars should be covered by thermal insulating material at temperatures below −1°C (30.2°F).
2. If the air temperature falls below 16°C (60.8°F) for sedentary, 4°C (39.2°F) for light, −7°C (19.4°F) for moderate work and fine manual dexterity is not required, then gloves should be used by the workers.

To prevent contact frostbite, the workers should wear anti-contact gloves.

1. When cold surfaces below −7°C (19.4°F) are within reach, a warning should be given to each worker by the supervisor to prevent inadvertent contact by bare skin.

TABLE 2. Cooling Power of Wind on Exposed Flesh Expressed as Equivalent Temperature (under calm conditions)*

Estimated Wind Speed (in mph)	Actual Temperature Reading (°F)											
	50	40	30	20	10	0	−10	−20	−30	−40	−50	−60
	Equivalent Chill Temperature (°F)											
calm	50	40	30	20	10	0	−10	−20	−30	−40	−50	−60
5	48	37	27	16	6	−5	−15	−26	−36	−47	−57	−68
10	40	28	16	4	−9	−21	−33	−46	−58	−70	−83	−95
15	36	22	9	−5	−18	−32	−45	−58	−72	−85	−99	−112
20	32	18	4	−10	−25	−39	−53	−67	−82	−96	−110	−121
25	30	16	0	−15	−29	−44	−59	−74	−88	−104	−118	−133
30	28	13	−2	−18	−33	−48	−63	−79	−94	−109	−125	−140
35	27	11	−4	−20	−35	−51	−67	−82	−98	−113	−129	−145
40	26	10	−6	−21	−37	−53	−69	−85	−100	−116	−132	−148
(Wind speeds greater than 40 mph have little additional effect.)	*LITTLE DANGER* In < hr with dry skin. Maximum danger of false sense of security.					*INCREASING DANGER* Danger from freezing of exposed flesh within one minute.				*GREAT DANGER* Flesh may freeze within 30 seconds.		
	Trenchfoot and immersion foot may occur at any point on this chart.											

* Developed by U.S. Army Research Institute of Environmental Medicine, Natick, MA.

TABLE 3. Threshold Limit Values Work/Warm-up Schedule for Four-Hour Shift*

Air Temperature — Sunny Sky		No Noticeable Wind		5 mph Wind		10 mph Wind		15 mph Wind		20 mph Wind	
°C (approx.)	°F (approx.)	Max. Work Period	No. of Breaks	Max. Work Period	No. of Breaks	Max. Work Period	No. of Breaks	Max. Work Period	No. of Breaks	Max. Work Period	No. of Breaks
-26° to -28°	-15° to -19°	(Norm. Breaks)	1	(Norm. Breaks)	1	75 min	2	55 min	3	40 min	4
-29° to -31°	-20° to -24°	(Norm. Breaks)	1	75min	2	55 min	3	40 min	4	30 min	5
-32° to -34°	-25° to -29°	75 min	2	55 min	3	40 min	4	30 min	5	Non-emergency work should cease	
-35° to -37°	-30° to -34°	55 min	3	40 min	4	30 min	5	Non-emergency work should cease			
-38° to -39°	-35° to -39°	40 min	4	30 min	5	Non-emergency work should cease					
-40° to -42°	-40° to -44°	30 min	5	Non-emergency work should cease							
-43° & below	-45° & below	Non-emergency work should cease									

Notes for Table 3:

1. Schedule applies to moderate to heavy work activity with warm-up breaks of ten (10) minutes in a warm location. For Light-to-Moderate Work (limited physical movement): apply the schedule one step lower. For example, at -35°C (-30°F) with no noticeable wind (Step 4), a worker at a job with little physical movement should have a maximum work period of 40 minutes with 4 breaks in a 4-hour period (Step 5).
2. The following is suggested as a guide for estimating wind velocity if accurate information is not available:
   5 mph: light flag moves; 10 mph: light flag fully extended; 15 mph: raises newspaper sheet; 20 mph: blowing and drifting snow.
3. If only the wind chill cooling rate is available, a rough rule of thumb for applying it rather than the temperature and wind velocity factors given above would be: 1) special warm-up breaks should be initiated at a wind chill cooling rate of about 1750 W/m²; 2) all non-emergency work should have ceased at or before a wind chill of 2250 W/m². In general the warm-up schedule provided above slightly under-compensates for the wind at the warmer temperatures, assuming acclimatization and clothing appropriate for winter work. On the other hand, the chart slightly over-compensates for the actual temperatures in the colder ranges, since windy conditions rarely prevail at extremely low temperatures.
4. TLVs apply only for workers in dry clothing.

* Adapted from Occupational Health & Safety Division, Saskatchewan Department of Labour.

2. If the air temperature is -17.5°C (0°F) or less, the hands should be protected by mittens. Machine controls and tools for use in cold conditions should be designed so that they can be handled without removing the mittens.

Provisions for additional total body protection are required if work is performed in an environment at or below 4°C (39.2°F). The workers should wear cold protective clothing appropriate for the level of cold and physical activity:

1. If the air velocity at the job site is increased by wind, draft, or artificial ventilating equipment, the cooling effect of the wind should be reduced by shielding the work area or by wearing an easily removable windbreak garment.
2. If only light work is involved and if the clothing on the worker may become wet on the job site, the outer layer of the clothing in use may be of a type impermeable to water. With more severe work under such conditions, the outer layer should be water repellent, and the outerwear should be changed as it becomes wetted. The outer garments should include provisions for easy ventilation in order to prevent wetting of inner layers by sweat. If work is done at normal temperatures or in a hot environment before entering the cold area, the employee should make sure that clothing is not wet as a consequence of sweating. If clothing is wet, the employee should change into dry clothes before entering the cold area. The workers should change socks and any removable felt insoles at regular daily intervals or use vapor barrier boots. The optimal frequency of change should be determined empirically and will vary individually and according to the type of shoe worn and how much the individual's feet sweat.
3. If exposed areas of the body cannot be protected sufficiently to prevent sensation of excessive cold or frostbite, protective items should be supplied in auxiliary heated versions.
4. If the available clothing does not give adequate protection to prevent hypothermia or frostbite, work should be modified or suspended until adequate clothing is made available or until weather conditions improve.
5. Workers handling evaporative liquid (gasoline, alcohol or cleaning fluids) at air temperatures below 4°C (39.2°F) should take special precautions to avoid soaking of clothing or gloves with the liquids because of the added danger of cold injury due to evaporative cooling. Special note should be taken of the particularly acute effects of splashes of "cryogenic fluids" or those liquids with a boiling point that is just above ambient temperature.

Work-Warming Regimen

If work is performed continuously in the cold at an equivalent chill temperature (ECT) or below -7°C (19.4°F), heated warming shelters (tents, cabins, rest rooms, etc.) should be made available nearby. The workers should be encouraged to use these

shelters at regular intervals, the frequency depending on the severity of the environmental exposure. The onset of heavy shivering, frostnip, the feeling of excessive fatigue, drowsiness, irritability, or euphoria are indications for immediate return to the shelter. When entering the heated shelter, the outer layer of clothing should be removed and the remainder of the clothing loosened to permit sweat evaporation or a change of dry work clothing provided. A change of dry work clothing should be provided as necessary to prevent workers from returning to work with wet clothing. Dehydration, or the loss of body fluids, occurs insidiously in the cold environment and may increase the susceptibility of the worker to cold injury due to a significant change in blood flow to the extremities. Warm sweet drinks and soups should be provided at the work site to provide caloric intake and fluid volume. The intake of coffee should be limited because of the diuretic and circulatory effects.

For work practices at or below -12°C (10.4°F) ECT, the following should apply:

1. The worker should be under constant protective observation (buddy system or supervision).
2. The work rate should not be so high as to cause heavy sweating that will result in wet clothing; if heavy work must be done, rest periods must be taken in heated shelters and opportunity for changing into dry clothing should be provided.
3. New employees should not be required to work fulltime in the cold during the first days of employment until they become accustomed to the working conditions and required protective clothing.
4. The weight and bulkiness of clothing should be included in estimating the required work performance and weights to be lifted by the worker.
5. The work should be arranged in such a way that sitting still or standing still for long periods is minimized. Unprotected metal chair seats should not be used. The worker should be protected from drafts to the greatest extent possible.
6. The workers should be instructed in safety and health procedures. The training program should include as a minimum instruction in:
   a. Proper rewarming procedures and appropriate first aid treatment.
   b. Proper clothing practices.
   c. Proper eating and drinking habits.
   d. Recognition of impending frostbite.
   e. Recognition of signs and symptoms of impending hypothermia or excessive cooling of the body even when shivering does not occur.
   f. Safe work practices.

Special Workplace Recommendations

Special design requirements for refrigerator rooms include the following:

1. In refrigerator rooms, the air velocity should be minimized as much as possible and should not exceed 1 meter/sec (200 fpm) at the job site. This can be achieved by properly designed air distribution systems.
2. Special wind protective clothing should be provided based upon existing air velocities to which workers are exposed.

Special caution should be exercised when working with toxic substances and when workers are exposed to vibration. Cold exposure may require reduced exposure limits.

Eye protection for workers employed out-of-doors in a snow and/or ice-covered terrain should be supplied. Special safety goggles to protect against ultraviolet light and glare (which can produce temporary conjunctivitis and/or temporary loss of vision) and blowing ice crystals should be required when there is an expanse of snow coverage causing a potential eye exposure hazard.

Workplace monitoring is required as follows:

1. Suitable thermometry should be arranged at any workplace where the environmental temperature is below 16°C (60.8°F) so that overall compliance with the requirements of the TLV can be maintained.
2. Whenever the air temperature at a workplace falls below −1°C (30.2°F), the dry bulb temperature should be measured and recorded at least every 4 hours.
3. In indoor workplaces, the wind speed should also be recorded at least every 4 hours whenever the rate of air movement exceeds 2 meters per second (5 mph).
4. In outdoor work situations, the wind speed should be measured and recorded together with the air temperature whenever the air temperature is below −1°C (30.2°F).
5. The equivalent chill temperature should be obtained from Table 2 in all cases where air movement measurements are required; it should be recorded with the other data whenever the equivalent chill temperature is below −7°C (19.4°F).

Employees should be excluded from work in cold at −1°C (30.2°F) or below if they are suffering from diseases or taking medication which interferes with normal body temperature regulation or reduces tolerance to work in cold environments. Workers who are routinely exposed to temperatures below −24°C (11.2°F) with wind speeds less than five miles per hour, or air temperatures below −18°C (0°F) with wind speeds above five miles per hour, should be medically certified as suitable for such exposures.

Trauma sustained in freezing or subzero conditions requires special attention because an injured worker is predisposed to cold injury. Special provisions should be made to prevent hypothermia and freezing of damaged tissues in addition to providing for first aid treatment.

ATTACHMENT D

FMPC WORK PERMIT/CONFINED SPACE ENTRY PERMIT

3930

FMPC WORK PERMIT

This work permit is to be completed in accordance with FMPC-516.

Work Permit Number: 14

SECTION A - BACKGROUND INFORMATION *(To be completed by supervisor-in-charge)*

A. MAINTENANCE REQUEST NO.	B. STARTING DATE & TIME. DATE: TIME:	C. EXPIRATION DATE & TIME DATE: TIME:

D. EXACT LOCATION:

E. EQUIPMENT

F. EXACT DESCRIPTION OF WORK TO BE CONDUCTED

G. EMPLOYEE(S) ASSIGNED TO JOB — BADGE NO

H. SUPERVISOR(S)/WMCO PROJECT ENGINEER

SECTION B - TYPES OF PERMITS REQUIRED *(Checked by supervisor-in-charge)*

- ☐ ASBESTOS (Copy to be attched)
- ☐ RADIATION (Copy to be attached)
- ☐ CHEMICAL/HAZARDOUS MATERIAL
- ☐ CONFINED SPACE ENTRY
- ☐ OPEN FLAME/WELDING

SECTION C - GENERAL PRECAUTIONS

ITEM	YES	NO
1. Equipment cleaned and purged		
2. Nuclear Safety checks completed		
3. Lock & Tag Procedures required and followed		
4. Water in space has been collected and sampled		
5. Complete isolation of process lines to space has been completed		
6. All mechanical equipment to the space have been tagged, disconnected and/or blocked		
7. Electrical isolation complete for Lock & Tag Procedure		
8. All lines within space have been cleaned and purged		

Equipment is safe and ready for work (FACILITY OWNER'S SIGNATURE):

BADGE NO.:	DATE:	TIME:

SECTION D - PERSONAL PROTECTIVE EQUIPMENT REQUIRED

EQUIPMENT	YES	NO	SPECIFY
Face Shield			
Hearing Protection			
Eye Protection			
Acid Splash Suit			
Gloves			
Respiratory Protection *(consult with IH rep.)*			
Flame Retardent Clothing			
Disposable Hood, Coveralls and Shoe Covers worn over Company-issued Clothing			

OTHER PROTECTION REQUIREMENTS:

SUPERVISOR-IN-CHARGE SIGNATURE:	BADGE NO.:	DATE:

SECTION E - CHEMICAL/HAZARDOUS MATERIAL PERMIT

TYPE OF MATERIAL:	NAME OF MATERIAL(S):

PRECAUTION TAKEN	YES	NO	DNA
1. Equipment and/or lines have been drained, flushed, purged, or neutralized			
2. Valves have been closed and locked (when feasible) and danger tagged			
3. Area isolated			
4. Safety shower is operable close to worksite			
5. Special clothing or other protective equipment required			

6. Special precautions:

FACILITY OWNER'S SIGNATURE:	BADGE NO.:	DATE:

NO.	DISTRIBUTION OF COPIES
1	POST AT JOB
2	SUPERVISOR-IN-CHARGE
3	IH&S *(RECORD COPY)*

SECTION F - CONFINED SPACE ENTRY PERMIT *(Valid for no more than 12 hours)*

ATMOSPHERIC GAS TESTING RESULTS

OXYGEN CONTENT		COMBUSTIBLE GAS		TOXICITY	
TIME	READINGS	TIME	READINGS	TIME	READINGS

PRECAUTIONS TAKEN/NEEDED	YES	NO	DNA
1. Forced ventilation required			
2. Work requires staging or ladder			
3. Ground Fault Interupting protection required			
4. Adequate/proper illumination required			
5. Standby notified what action to take			
6. Safety line and harness required			
7. Nonsparking tools required			
8. Periodic gas testing required			

STANDBY-WORKER COMMUNICATION:

SPECIAL INSTRUCTIONS:

TYPE OF CONFINED SPACE: ☐ CLASS A ☐ CLASS B ☐ CLASS C

IH&S REPRESENTATIVE SIGNATURE:	BADGE NO.:
PERMIT ISSUED DATE:	TIME:

SECTION G - OPEN FLAME/WELDING PERMIT

PRECAUTIONS VERIFIED *(within 35 feet of work)*	YES	NO	DNA
1. Combustibles, magnesium and uranium have been removed, covered or shielded.			
2. Flammable liquids have been removed or isolated.			
3. Wall and floor openings are covered or protected.			
4. A flame retardent tarp has been suspended underneath work.			
5. A combustible gas check has been made.			
6. (work on walls/ceilings) All combustibles have been removed from opposite sides.			
7. A Fire Watch will be required and will remain posted during breaks and for 30 minutes after work is completed.			
8. Fire Watch is supplied with an extinguisher and know-how to activate the nearest fire alarm.			
9. Fire & Safety Inspector shall be present during the burning operation.			
10. Fire & Safety Inspector shall be present to monitor when the system is initially opened.			

COMBUSTIBLE GAS TESTING RESULTS:

EQUIPMENT/AREA CHECKED:

SPECIAL INSTRUCTIONS/PRECAUTIONS:

FIRE & SAFETY INSPECTOR SIGNATURE:	BADGE NO.:
PERMIT ISSUED DATE:	TIME:

SECTION H - WORK AUTHORIZATION REVIEWED AND FOUND ACCEPTABLE FOR USE

SUPERVISOR-IN-CHARGE SIGNATURE:	BADGE NO.:	DATE:

FMPC-OS&H-2939 (8/12/88)