PNL-MA-599

Analytical Chemistry Laboratory Department

ANALYTICAL CHEMISTRY LABORATORY (ACL) PROCEDURE COMPENDIUM

Volume 6: Physical Testing

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Approved for Use
and Application by

A. G. King
Department Manager

Battelle
Pacific Northwest Laboratories
Richland, Washington

MASTER

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(ICN)

ICN - PNL-MA-599-Vol.6-1
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A.

Document Number: See Attachment Revision Number: ____

Document Title: See Attachment

Document's Original Author: See Attachment

Effective Date of ICN: 12 / 23 / 92

Change Requested by: AG King

B. **Action:** Place the attached procedures in PNL-MA-599 manual, Volume 6. Place this ICN and attachment with the Table of Contents.

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

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

Incorporates the procedures from PNL-MA-597 manual into PNL-MA-599 manual by changing the procedure numbers. This eliminates the need for maintaining two sets of technical procedures. Procedural references in these procedures have been updated. See attachment for the procedures to be incorporated into PNL-MA-599 manual, Volume 6.

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

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

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

Approval Authority: AG King Date: 12/23/92

Other Approvals: ______ Date: __/__/__

: ______ Date: __/__/__

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New Doc#	Rev.	Author	Document Title	Old Doc#
PNL-ALO-530	0	MC Burt	Particle size distribution by laser scanning (time of transition)	2-50.3
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PNL-ALO-532	0	RF Keough	Procedure for filling sp-100 fuel capsules	7-30.5 & 7-40.5
PNL-ALO-533	0	RF Keough	Procedure for sodium filling of beatrix-II type capsules	7-30.7
PNL-ALO-534	0	RF Keough	Removal of alkali metals with ammonia	7-30.10
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PNL-ALO-537	0	RF Keough	Purification of lithium by hot gettering and filtration	7-40.41
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Volume 6: Physical Testing

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PNL-ALO-534	0	0	REMOVAL OF ALKALI METALS WITH AMMONIA	11/15/89
PNL-ALO-535	0	0	SPECIFIC GRAVITY OF HIGHLY RADIOACTIVE SOLUTIONS	08/02/88
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PNL-ALO-538	0	0	LITHIUM FILLING OF MOTA CAPSULES	07/15/91

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-501 Laboratory Procedure for Measurement of Physical and Rheological Properties of Solutions, Slurries and Sludges.

APPLICABILITY

This procedure will be used to measure the following physical properties of solutions, slurries, and sludges:

- Density or Specific Gravity
- pH of solutions
- Physical Appearance
- Settling Rate
- Shear Strength
- Shear Stress versus Shear Rate
- Vol% Centrifuged Solids
- Vol% Settled Solids
- Wt% Dissolved Solids
- Wt% Centrifuged Solids
- Wt% Total Oxides
- Wt% Total Solids
- Yield Stress

This procedure is applicable to samples that are homogenous and representative of the bulk sample with the exception of the sample used for shear strength. If not homogenous, the sample will be mixed and the procedure documented in or on the appropriate Laboratory Record Book (LRB), data record, or test instruction.

DEFINITIONS

Apparent Viscosity - Viscosity of a fluid defined as a ratio of the shear stress (at a particular shear rate) and the shear rate.

Density or Specific Gravity - Density is the mass per unit volume and specific gravity is the ratio of the density of the sample and a reference material.

Interstitial Solution - The solution contained within the original sludge sample.

Author RD Scheele RD Scheele	Date 3/9/92	Project Mgr. TE Jones TE Jones	Date 3/9/92	CAD Representative GK Gerke GK Gerke	Date 3/9/92
Technical Reviewer Tingey JM Tingey	Date	Line Mgr. GH Bryan GH Bryan	Date 3/10/92	Other	Date
Procedure No. PNL-ALO-501	Revision No. 0	Effective Date MAR 10 1992	Page 1 of 11		

Newtonian - A fluid with no yield stress and a viscosity that is independent of shear rate.

Non-Newtonian - A fluid whose viscosity varies with shear rate.

pH - pH is -log [H^+]. pH is applicable to aqueous solutions or slurries only.

Physical Appearance - The physical state (solid, liquid, sludge, slurry), color, and consistency.

Rheogram/Flow Curve - A plot of a fluid's shear response as a function of the shear rate. A plot of shear stress versus shear rate.

Sludge - Wet solids having little or no standing liquid, i.e. mud-like.

Slurry - A thin mixture of solids and solution.

Solution - A liquid phase containing dissolved material.

Solids Settling Rate - The rate at which the solids in a homogenized sample settle.

Vol% Settled Solids - The percentage of the volume of the sample that the settled solids occupy.

Vol% Centrifuged Solids - The percentage of the volume of the sample that the solids occupy after being centrifuged for a specific time and force.

Wt% Total Oxides - The percentage of the mass of the sample that remains after converting all non-volatile elements to oxides. Some volatile elements such as cesium might be lost in this process.

Wt% Centrifuged Solids - The percentage of the mass of the sample that the solids occupy after being centrifuged.

Wt% Dissolved Solids - The percentage of the mass of sample that is dissolved in the aqueous portion of the sample.

Wt% Total Solids - The percentage of the mass of the sample that remains after removing volatiles including free water by drying at 105 ± 5°C for 24 h.

Yield Stress - The minimum stress required to initiate fluid movement.

RESPONSIBLE STAFF

Analyst
Cognizant Scientist

PROCEDURE

1.0 General Requirements

The COGNIZANT SCIENTIST is responsible for preparing the test instructions to implement each step of this procedure and supplying the analyst with the test instructions. Because of the nature and diversity of samples that will be analyzed using this procedure, the cognizant scientist is responsible for assuring that the test instructions satisfy the requirements of this procedure and provide a unique sample or container identifier to insure sample traceability and control.

All measurements will be made at the temperature specified (± 5°C) in the test instructions or at ambient temperature if unspecified. Temperature will be measured using a calibrated thermocouple or RTD and digital thermometer or a mercury thermometer. If the test instructions specify a temperature for any measurement except, vol% centrifuged solids, wt% solids, wt% dissolved solids, or wt% total oxides; a constant temperature bath/circulator will be used.

The results of all measurements will be recorded in the appropriate LRB or on the test instructions or data sheet. A copy of the test instructions sheet will be entered into the LRB or the project records. If used, the LRB will be the responsibility of the COGNIZANT SCIENTIST. The ANALYST or other authorized personnel may also record information in the LRB, test instruction, or data sheet.

The calibrated instrumentation used will be recorded in the LRB, on the test instruction, or data sheet.

2.0 Procedure for Physical Appearance Measurement

This procedure will be used to observe some general physical properties for solutions, sludges, and slurries.

2.1 Equipment and Materials

None

2.2 Determination of Physical Appearance

Describe the sample in terms of its physical state (solution, slurry, or sludge), its color, its ability to hold its shape, and any other observable physical characteristics.

The ANALYST'S ability to observe these properties may be limited by work location. For example if the sample is located in the 325A shielded facility, the actual color and the observed color may be different due to the yellow leaded glass used in the shielded cell observation windows. The properties observed in this procedure are qualitative not quantitative.

3.0 Procedure for Settling Rate and Vol% Settled Solids Measurement

3.1 Equipment and Materials

- 15 or 50 mL Graduated Plastic Centrifuge Tube with Cap
- Analytical Balance, 2-place (minimum sensitivity)
- Plastic Rod or Plastic Spatula
- Centrifuge

3.2 Determination of Solids Settling Rate and Vol% Settled Solids

Label and weigh the centrifuge tube to be used. Determine the cm/mL for the centrifuge tube by measuring the distance between the 4 and 14 mL graduations for the 15 mL tube or between the 10 and 20 mL graduations for the 50 mL tube. Calculate cm/mL.

Transfer the sample to the preweighed, labeled centrifuge tube and seal. Reweigh and determine the sample mass by difference. Measure the volume of the total sample using the graduations on the centrifuge tube. Begin the settling rate measurements on a Monday, Tuesday, or Wednesday and no later than 1 h after the start of the working day. Record the start time and the times that all succeeding measurements are taken. Allow the solids in the sample to settle and measure the total sample and the solids volumes. The time between settling measurements is dependent upon the settling rate of the sample. The cognizant scientist will determine the time period between measurements to obtain appropriate settling rate data. The solids and total sample volumes should be measured at time increments no longer than every two hours during a the working day. Also, measure the total sample and solids volumes at the end of the working day and at the beginning of the next working day. Measure every two hours until no change is observed between three successive measurements or until 3 days have transpired.

Volumes will normally be measured to ± 0.2 mL when using the 15 mL centrifuge cone and to ± 1 mL when using the 50 mL centrifuge cone. The recommended sample volumes are ≥10 mL for the 15 mL tube and ≥30 mL for the 50 mL tube.

Present the settling rate as the solids height or vol% solids versus time. The solids height will be calculated by multiplying the solids volume by the height of 1 mL. Calculate Vol% Settled Solids by dividing the solids volume by the total volume and multiplying by 100%.

Some samples may stick to the side of the centrifuge tube. Centrifuge these samples briefly to drive them to the bottom of the tube to measure the sample volume. If the centrifuging causes separation of the solids and liquid, shake or blend with a plastic rod or spatula or as directed by the COGNIZANT SCIENTIST before beginning the settling procedure. Reweigh the tube and sample and calculate the new sample weight by difference.

The upper solids level may be difficult to determine because of different solids settling rates. The solids volume will be defined as the uppermost volume in which solids are present or the solids-solution interface which is the point where the sample becomes opaque.

4.0 Procedure for Density or Specific Gravity Measurement

This procedure will be used to measure the density or specific gravity of sludges, solutions, and slurries. This procedure will refer only to the measurement of density. If the user desires specific gravity, divide the measured density by the density of the reference material.

4.1 Equipment and Materials

- Graduated Plastic Centrifuge with Cap
- Centrifuge
- Analytical Balance, 2-place (minimum sensitivity)
- Volumetric Flask (Option for Solutions)

4.2 Determination of Density

Transfer the sample to a preweighed, labeled centrifuge tube and seal. Reweigh and calculate the sample mass by difference. As an alternative to a new sample, the sample from 4.3.2 may be used. The sealed centrifuge tube will be centrifuged for 1 h at ~1000 gravities. Measure the total volume of sample using the graduations on the centrifuge tube.

Calculate the density by dividing the sample mass by the sample volume. The sample mass will normally be measured to ± 0.02 g and the sample volume will normally be measured to ± 0.2 mL for the 15 mL tube or ± 1 mL for the 50 mL tube. The recommended sample volumes are 10 and 30 mL for the 15 and 50 mL centrifuge tubes, respectively.

With sludge samples the solids will often slope because of the centrifuging, the volume of the sample will be the average of the high and low volumes observed for the sample.

An alternative method of determining a solution's density will be to transfer a sample into a preweighed, labeled volumetric flask. Determine the sample mass by difference. This alternative method is preferable to the use of a graduated centrifuge tube because of increased accuracy for the volume measurement. The volume of a volumetric flask will normally be known to ± 0.04 mL.

5.0 Procedure for Determination of Vol%, Wt% and Densities of Centrifuged Solids and Supernate

This procedure will be used for determining the vol%, wt%, and the densities of centrifuged solids and centrifuged supernates for sludges and slurries.

5.1 Equipment and Materials

- Graduated Plastic Centrifuge Tube with Cap
- Clinical Centrifuge
- Analytical Balance, 2-place (minimum sensitivity)
- graduated cylinder
- Transfer Pipet and tips

5.2 Determination of Vol%, Wt%, and Densities of Centrifuged Solids and Supernate.

Transfer sample to a preweighed, labeled centrifuge tube and reweigh. Calculate the mass of the sample by difference. The sample and tube from Part4.2 may be used as the centrifuged sample. Centrifuge the sample for 1 h at maximum speed on the centrifuge. Record gravities apply. Measure the total sample and solids volume using the centrifuge tube graduations. The recorded solids volume will be the average of the high and low solids volume measurements. The supernate volume is the total sample volume less the solids volume. Volume is normally measured to ± 0.2 or ± 1 mL for the 15 and 50 mL centrifuge tubes, respectively.

The vol% centrifuged solids is the solids volume divided by the total volume multiplied by 100%. The vol% centrifuged supernate is 100% - vol% centrifuged solids.

To determine the wt% centrifuged solids, decant or transfer with a pipet the centrifuged supernate into a labeled, preweighed graduated cylinder. Measure the mass of the centrifuge tube and solids. Calculate the centrifuged solids mass by difference. Measure the volume of the supernate in the graduated cylinder and weigh the recovered centrifuged supernate andgraduated cylinder. Calculate the mass of the centrifuged supernate by difference.

The wt% centrifuged solids is the solids' mass divided by the total sample mass multiplied by 100%. The wt% centrifuged supernate is the mass of the supernate divided by the total sample mass multiplied by 100%. The centrifuged solids density is the mass of the solids divided by the solids volume and the centrifuged supernate density is the supernate's mass divided by its volume.

6.0 Procedure for Determination of Wt% Total Solids, Wt% dissolved Solids, and Wt% Total Oxides.

This procedure will be used for determining the wt% total solids, wt% dissolved solids, and wt% total oxides in solutions, sludges, and slurries.

6.1 Equipment and Materials

- Ceramic Crucibles
- Glass Vials
- Analytical Balance, 2-place
- Desiccator Containing Dry Indicating Desiccant
- Muffle Furnace (100 to >1000°C)
- Drying Oven

6.2 Determination of Wt% Total Solids, Wt% Dissolved Solids, and Wt% Total Oxides.

Transfer sample to a preweighed, labeled crucible or vial and weigh the sample in the vial or crucible. Use crucibles for samples for which total oxides will be determined and use vials for samples for which only wt% solids are to be determined. Calculate the sample mass by difference. Allow the sample to air dry at least overnight to remove free liquid and to prevent splattering in the oven.An alternate method for removing free liquid, such as using a heat lamp, may be designated by the COGNIZANT SCIENTIST. When the free liquid has evaporated, transfer the sample and container to a 105 ± 5°C drying oven or furnace. Hold at temperature for 24 h. Remove the dried samples and containers and place in the desiccator to cool to room temperature. It should take at least 1 h to cool the sample. Reweigh the dried sample and container. Determine the residual sample weight by difference. The mass of the sample will normally be measured to ± 0.02 g.

The wt% total solids is the residual mass divided by the initial sample mass multiplied by 100%. For solutions the wt% dissolved solids is the residual mass divided by the initial sample mass multiplied by 100%. For slurries or sludges with interstitial solutions that are recoverable using centrifugation, the wt% dissolved solids is the weight fraction dissolved solids in the centrifuged supernate times the weight fraction centrifuged supernate in the sludge/slurry determined using the procedure found in Section5 times 100%.

Place the sample and crucible from the wt% total solids procedure into the furnace. Do not perform this procedure with the glass vials. Heat the furnace to >1000°C and hold for 30 min between 1000 and 1050°C. Turnoff the furnace and cool to 150°C. Transfer the crucibles using tongs to the desiccator and cool to room temperature. It should take 1 to 2 h to cool the sample. Once cool weigh the sample and crucible. Determine the residual oxide mass by difference. Consider that volatile elements may also be lost.

The wt% total oxide is the residual oxide mass divided by the initial sample mass multiplied by 100%.

7.0 Procedure for Determining pH

This procedure will be used to determine the pH of a solution or slurry.

7.1 Equipment and Materials

- pH Meter and Electrode
- pH 4, 7 and 10 Buffers
- Plastic beakers or vials

7.2 Determination of pH

Standard Laboratory procedure will be used to measure the pH of solutions or slurries. Prior to use daily calibration of the pH meter and electrode will be performed using a two or three standard method. The temperature of the standards and samples will be taken into account. The electrode calibration will be done using pH buffers that are traceable to the manufacturers lot number. The expiration date for the buffers used in the check must not have lapsed. The electrode will be prepared for use and stored in accordance with the manufacturer's directions.

Sufficient sample will be added to a beaker or vial to cover the sensing portion of the electrode. Remove the probe from the storage solution, rinse with deionized (DI) water, and blot dry with a tissue. Insert the probe into the sample. Once the reading has stabilized, record the pH value and rinse the electrode with DI water. After the pH for the last sample has been determined, rinse and blot dry the electrode, and return it to its storage fluid.

The pH meter must have an accuracy of ±0.02 pH units. Data will normally be reported to the nearest 0.1 pH unit.

8.0 Procedure for Determination of Shear Stress vs Shear Rate and Yield Stress

This procedure will be used for determining the shear stress versus shear rate, yield stress, and shear strength for solutions, sludges, and slurries.

8.1 Equipment and Materials

- Viscometer
- Certified Newtonian Viscosity Standards
- Constant Temperature Bath/Circulator

8.2 Performance Requirements

Performance checks of the viscometer will be performed monthly or within approximately 30 days of measurement using certified Newtonian viscosity standards traceable to the manufacturer's lot number. The viscometer used must have a demonstrated accuracy of ± 15% at apparent viscosity measurements less than 10 CP and ± 10% at apparent viscosity measurements greater than 10 CP.

The data will be generated following the instructions provided in the instrument's Instruction Manual. The data will be in the form of a rheogram or flow curve, which is a plot of shear stress as a function of shear rate.

8.3 Measurement of Shear Stress vs Shear Rate and Yield Stress

Select and install the Sensor. For measurements at elevated temperatures, adjust the temperature setting for the constant temperature circulator to the desired level. Install the temperature control shroud. Transfer the sample by weight into the viscometer beaker. If the MV I Rotor is used transfer 40 mL. If the MV II Rotor is used transfer 55 mL. The weight transferred equals the density times the volume. After the coolant in the shroud reaches the desired temperature, stir the sample, and install the sample and beaker in the viscometer. Allow the sample to remain in position for 5 min to bring the sample to temperature unless instructed otherwise by the <u>cognizant scientist</u>. Obtain a rheogram. Adjust the temperature controller to the next temperature. Once the temperature of the coolant in the shroud reaches the desired level, allow the sample to equilibrate for 5 min before obtaining a rheogram. Repeat as necessary to obtain rheograms at the temperatures of interest.

It is important that the time between installation of the sample and beaker in the viscometer and the acquisition of the rheogram be as short as possible to minimize the effects of any solids settling.

To calculate the apparent viscosity, measure the shear stress (from the y axis) of the sample at a selected shear rate (from the x axis) and divide the shear stress by shear rate.

The fluid yield stress is obtained from the rheogram. A rheogram for a material with a yield stress will have two portions to it. The first appears as a nearly vertical line beginning at the origin and running up the ordinate. This line forms an angle, ß, with the ordinate. This portion of the rheogram is recording the behavior of the material as it acts like a solid or gel. When sufficient force is transmitted to the material to break the gel or make it yield, the rheogram will angle sharply to the right, and from then on the behavior of the material as a fluid will be recorded. This sharp angle that is recorded as the material becomes fluid is the yield point. The height of this break measured in Pascals along the ordinate is the value of the material's yield stress.

Some samples exhibit a creeping transition from solid to liquid behavior. this creep is recorded as a rounded yield point that is more difficult to identify. In cases where creep is exhibited, the yield point is defined as the intersection of a tangent drawn along the solid portion of the rheogram with a tangent drawn along the fluid portion of the rheogram.

Yield stress data is normally reported with a degree of precision of ± 0.1 Pa.

9.0 Procedure for Determination of Shear Strength

This procedure will be used to measure the shear strength of sludge samples. Shear strength is a semi-quantitative/qualitative/relative measure of the force that is required to move the material. No calibration standards are currently available to calibrate the shear vane.

9.1 Equipment and Materials

- Viscometer
- Shear Vane

9.2 Measurement of Shear Strength

Install shear vane into the viscometer. Position sample beneath the shear vane. Raise the sample slowly using the lab jack, centering the shear vane in the sample. Submerge the vane with at least 3 mm of sample above and below the vane. Based on the appearance of the sample, the COGNIZANT SCIENTIST or ANALYST will select the stress scale and the shear rate. Obtain the rheogram. Note: Shear Strength is dependent on sample history. The sample should be disturbed as little as possible before measurement or should be allowed to age for at least 2 days before the shear strength is determined.

The size and geometry of the sample is important when measuring shear strength. Try to select a sample geometry with a diameter of at least 4 shear vane diameters and a depth such that there is at least 3 mm of sample above and below the shear vane. The shear vane should be located at least two shear vane diameters away from the container walls.

The rheogram should show a peak at the beginning, level off, and finally drop off. The shear strength is calculated by taking the peak torque at a fraction of the full-scale reading on the chart, multiplying by $\%\tau$, multiplying by the full scale τ, and dividing by the surface area of the shear vane fins. The shear strength is reported in dynes/cm^2.

10.0 Quality Assurance

Work performed using this technical procedure will meet Impact Level II requirements as described in PNL-MA-70. All data generated using this procedure will be recorded on test instructions or directly in a LRB. The completed test instructions will later be entered into the appropriate LRB.

Changes to the test instructions can be made only by Cognizant Scientist and will be documented by crossing out the original information with a single line, and recording, initialling, and dating the changes. Major changes will be made by revision of the test instruction.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-502, Laboratory Procedure for Measurement of Rheological Properties with a Cone and Plate Viscometer.

APPLICABILITY

This procedure will be used to measure shear stress as a function of shear rate. The viscosity of the sample will be determined as a function of shear rate. This procedure will be used on sludges, slurries, and liquids which are difficult to transfer to the cup and spindle sensor systems or require small sample volumes.

DEFINITIONS/ACRONYMS

Apparent Viscosity - Viscosity of a fluid defined as a ratio of the shear stress (at a particular shear rate) and the shear rate.

Interstitial Solution - The solution contained within the original sludge sample.

Newtonian - A fluid whose viscosity is independent of shear rate.

Non-Newtonian - A fluid whose viscosity varies with shear rate.

Rheogram/Flow Curve - A plot of a fluid's shear response as a function of the shear rate. A plot of shear stress versus shear rate.

Sludge - Wet solids having little or no standing liquid, i.e. mud-like.

Slurry - A mixture of solids and solution.

Solution - A liquid phase containing dissolved material.

Yield Stress - The minimum stress required to initiate fluid movement.

RESPONSIBLE STAFF

Analyst
Cognizant Scientist

Author Elma A Shade EH Shade	Date 4/3/92	Project Mgr TE Jones	Date 4/14/92	QAD Representative LJ Ethridge for TL Ehlert TL Ehlert	Date 4/3/92
Technical Reviewer JM Tingey JM Tingey	Date 4/3/92	Line Mgr GH Bryan	Date 4/3/92	Technical Reviewer GM Richardson	Date 4/3/92

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PROCEDURE

1.0 Equipment and Materials

- Cone and Plate Viscometer System
- Certified Newtonian Viscosity Standards
- Constant Temperature Bath/Circulator

2.0 Quality Control / Specific Qualification

The viscometer is a Category 2, User to Calibrated piece of Measuring and Test Equipment. The Calibration checks of the viscometer will be performed before and after each batch of samples are completed or at the beginning of each day (whichever is shorter) using certified Newtonian viscosity standards traceable to the manufacturer's lot number. The viscometer must have a demonstrated accuracy of ± 20%.

The process using this viscometer to measure rheological properties is considered self-qualifying due to the use of certified viscosity standards and is qualified through the Independent Technical Review of the Technical Procedure.

3.0 Measurement of Shear stress vs Shear Rate and Yield Stress

3.1 Alignment

The alignment of the viscometer is critical to the proper operation of the system and the attainment of accurate test results. The transverse bar must be level in the horizontal position and the sensor system must be vertical to the transverse bar. The plate must be horizontal in both the X and Y axis. These alignments should be checked when the equipment is moved or the calibration checks do not meet the required specifications. This check can be performed with a bubble level. If any component is out of alignment, the leveling feet and/or sensor system should be adjusted to obtain proper alignment.

3.2 Operating Elements and Adjustments

3.2.1 Course Adjustment:

(a) The knurled thumb screw (ring nut) on the top of the transverse bar adjusts the height of the sensor system. This changes the gap between the cone and the plate. The sensor system can be fixed in place with the knurled knob on the rear of the transverse bar.

(b) The lever located on the front panel of the unit raises and lowers the plate about 30 mm. This allows the plate to be cleaned and another sample to be added.

(c) Interchangeable cones are available. The appropriate cone should be selected for the desired results. This is dependent upon the expected viscosity of the sample.

3.2.2 Fine Adjustment:

(a) The height of the plate can be adjusted by turning the knurled knob located on the right side of the unit. Turning the knob clockwise widens the gap and counterclockwise closes the gap.

(b) The connections for the constant temperature bath/circulator are located on the left side panel of the unit. The arrows marked on the connectors indicate which connector is the inlet and outlet connector.

3.3 Operation

1. Connect the constant temperature bath/circulator with the connecting sleeves (section 3.2.1 b). Preselect the required temperature on the constant temperature bath/circulator.

2. Turn the lever (section 3.2.1 b) clockwise until it clicks into the upper position. The plate is now in the working position. Turn the lever counterclockwise (lowered position). This is an operational check of the mechanical systems.

3. Place the sensor system in the transverse bar and connect the selected cone to the shaft of the sensor system. Return the plate to its working position (clockwise) using the lever on the front of the unit (section 3.2.1 b). Rotate the ring nut (section 3.2.1 a) to lower the sensor system with the cone in place until the cone and plate are almost touching. The sensor system is then fixed by turning (clockwise) the knurled knob on the rear of the transverse bar.

4. The gap between the cone and plate is then adjusted by turning the fine adjustment knob on the right side of the panel (section 3.2 item 2a) counterclockwise until contact between the cone and plate is made. This contact is observed as a positive inflection of the shear stress

(Y-axis) on the Rotovisco RV100 plot of shear stress vs. shear rate.

5. Turn the fine adjustment knob clockwise until the shear stress as observed on the RV100 plot is back to the zero. This gap must be accurately adjusted for correct measurements.

6. Move the plate to the lower position with the lever. In this position it is possible to put the test sample onto the middle of the plate or clean the cone and plate.

7. Each time the temperature of the plate is modified or a new cone is used, this system must be readjusted. **CAUTION: The gap between the cone and plate will change with temperature. Setting the gap incorrectly will damage the sensor system. Always be aware of the temperature changes within the system and carefully check the gap when the temperature of the system is adjusted.**

8. Select the desired settings for the rheogram ($\%\tau$, %D, t_1, t_2, and t_3). Set for either an up/down or an up rheogram. The initial settings will be determined by the cognizant scientist.

9. Place the sample in the middle of the plate, slowly turn the lever so that the plate is in the working position. Press start and obtain the rheogram.

10. After the rheogram has been obtained, move the lever so that the plate is in the lower position. Clean the cone and plate with a damp rag.

11. Adjust the constant temperature bath/circulator to the next temperature. Ensure uniform temperature adjustment on the plate.

12. Once the temperature has stabilized, repeat steps 7 through 11 to obtain rheograms at the temperatures of interest.

3.4 <u>Calculations</u>

The apparent viscosity is the shear stress (Y-axis) at a selected shear rate divided by the shear rate.

The fluid yield stress is obtained from the rheogram. A rheogram for a material with a yield stress will have two portions to it. The first appears as a nearly vertical line beginning at the origin and running up the ordinate. This line forms an angle, β, with the ordinate. This portion of the rheogram is recording the behavior of the material as it acts like a solid or gel. When sufficient force is transmitted to the material to break the gel or make it yield, the rheogram will angle sharply to the right, and from then on the behavior of the material as a fluid will be recorded. This sharp angle that is recorded as the material becomes fluid is the yield point. The height of this break measured in Pascals along the ordinate is the value of the material's yield stress.

Some samples exhibit a creeping transition from solid to liquid behavior. This creep is recorded as a rounded yield point that is more difficult to identify. In cases where creep is exhibited, the yield point is defined as the intersection of a tangent drawn along the solid portion of the rheogram with a tangent drawn along the fluid portion of the rheogram.

4.0 Records

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

INTERIM CHANGE NOTICE
(ICN)

ICN - PNL-ALO-504.3 R1
Page 1 of 1

A.

Document Number: PNL-ALO-504 **Revision Number:** 1

Document Title: Percent Solids Determination of Soils/ Sludges/ Solids

Document's Original Author: RT Steele

Effective Date of ICN: 5/11/92

Change Requested by: TE Jones

B. **Action:**

Deleting ACT 89.1 and replacing with established records management practices.

Replace pages 1 through 2 with 1 through 2 due to new format.

C. **Effect of Change:**

Brings procedure into compliance.

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

ACT NOW Directive 89.1 no longer in existence.

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

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

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

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-504.2-R1
Page 1 of 1

A. Document Number: PNL-ALO-504 Revision Number: 1
Document Title: Percent Solids Determination for Soils
Effective Date of ICN: 12/11/91
Document's Original Author: R. T. Steele
Change Requested By: J. M. Robbins

B. Action

Pen and ink correction, change Revision Number from 0 to 1 on ICN Number PNL-ALO-504.1-R0 and ICN Number from ICN-PNL-ALO-504.1 R0 to ICN-PNL-ALO 504.1 R1

C. Effect of Change

1. Correct Revision Number on previous ICN (ICN-PNL-ALO-504-1-R0).

D. Reason for Change/Description of Change

Incorrect Revision Number.

E. Approval Signatures

(Please sign and date)

Type of Change: (Check (✓) one)

☒ Minor Change ☐ Major Change

Process Quality Department: G K Gerke Date: 12/16/91
Approval Authority: A G King Date: 12/11/91
Other Approvals: B M Gillespie Date: 12/11/91
: Date: / /

INTERIM CHANGE NOTICE
(ICN)

ICN-PNL-ALO-504.1-R0
Page 1 of 1

A. Document Number: PNL-ALO-504 Revision Number: 0

Document Title: Percent Solids Determination for Soils

Effective Date of ICN: 9/24/91

Document's Original Author: R. T. Steele

Change Requested By: J. M. Robbins

B. Action

Replace page 2 with new page 2.

C. Effect of Change

1. None in terms of quality.
2. Reduces analyst time.

D. Reason for Change/Description of Change

Gravity oven cannot be held to ± 1°C.

Change drying oven temperature from 104 ± 1°C to 105 ± 5°C. (Section 2.3)

E. Approval Signatures

(Please sign and date)

Type of Change: (Check (✓) one)

☐ Minor Change ☒ Major Change

Process Quality Department: G. Goerke Date: 9/26/91
Approval Authority: Date: 9/30/91
Other Approvals: B M Gillespie Date: 9/25/91
: Date: / /

TITLE: PNL-ALO-504, PERCENT SOLIDS DETERMINATION OF SOILS/ SLUDGES/ SOLIDS

APPLICABILITY

This procedure provides a uniform method for determining the weight percent solids fraction of soils, sludges, and other solids. The methodology is consistent with the CLP inorganic percent solids determination method.

DEFINITIONS/ACRONYMS

None

RESPONSIBLE STAFF

Cognizant Scientist
Analyst/Technician

PROCEDURE

1.0 Equipment and Materials

- Analytical Balance capable of weighing to at least 0.001g.
- Drying Oven
- Porcelain Crucibles with covers or 10 ml glass beakers (without covers for analysis in hot cells)
- Desiccator

2.0 Percent Solids Determination

Duplicate one to ten-gram samples are weighed into separate tared containers, dried for 12 to 24 hours and reweighed to determine the solids fraction of the original sample.

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

2. Weigh duplicate samples into tared containers and record the tare weights and the sample + tare weights to the nearest 0.01g on the Percent Solids Data Form (Exhibit 1).

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

Procedure No.	Revision No.	Effective Date	Page
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3. Place the weighed samples in tared containers, with cover (if any), tipped to allow for moisture escape, into a drying oven maintained at ~~103 —~~ 105 ± 5°C for 12 to 24 hours. Record date, time, and oven temperature on the Percent Solids Data Form (Exhibit 1).

4. Remove the samples from the oven and record date, time, and temperature on the Percent Solids Data Form (Exhibit 1). Cool in a desiccator.

5. Weigh and record weight to the nearest 0.01g on the Percent Solid Data Form (Exhibit 1). An unstable balance display is indicative of:

   a. a container that hasn't cooled to ambient temperature; or

   b. hydrostatic changes occurring in the sample. Repeat Step 3 for a minimum drying time of 1 hour (maximum 24 hours) and proceed with Steps 4-5 until constant weight is achieved. If the loss in weight between the start weight and final weight of the last drying cycle is $\leq$ 0.01g, then constant weight has been attained, and the final weight recorded is used as the dry weight.

3.0 Calculation

Calculate percent solids by the formula below:

$$\%\ \text{Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

4.0 Records

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

5.0 References

USEPA CLP SOW for Inorganic Analyses, SOW No. 788, 7/88, Rev. 2, 2/89. Exhibit D, page D-83.

PNL TEST PROCEDURE

TITLE: 2-50.3, REV. 0; PARTICLE SIZE DISTRIBUTION BY LASER SCANNING (TIME OF TRANSITION)

1.0 APPLICABILITY

The sample material is dispersed ultrasonically and with stirring in a liquid. The analyzer uses a focused scanning laser spot and time of transition (to move from one side of the particle to the other) to measure particle diameters. Data presentation includes number, volume and area of particles.

(a) Material	Any material insoluble in a suspension media. Almost any liquid is acceptable as suspension media.
(b) Range	Particle diameters from 0.5 to 600 μm in three steps.
(c) Reliability	Confidence limit is operator selectable. (See Operations Manual)
(d) Interferences	None

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

4.1 Discussion

There are many different techniques used to measure the particle size distributions of powders. A complete classification of methods is given in a review paper prepared by a committee on particle size analysis.[a] The six classes of methods given in that paper are: 1) relative motion between particles and a fluid, 2) image formation, 3) scattering of radiation, 4) diffraction of radiation, 5) electrical properties, and 6) sieves. This method falls into the first and third classes.

Concurrence	Date	Approved Walter C. Weimer	Date
N/A		W. C. Weimer	12/4/89
Prepared by	Date	QAD Concurrence	Date
M. C. Burt MCBurt	12/4/89	G. K. Gerke GKGerke 1/16/90	12/4/89
Procedure No.	Revision No.	Effective Date	Page of
2-50.3	0	12/4/89	1 5

The analysis is based on the time required for a fixed velocity scanning laser beam to traverse the diameter of a particle. The beam passes through a spinning 1° wedge prism rotating at a constant velocity which creates a 600 µm diameter scanning circle. The beam passes through a microscope objective creating a 1.2 µm spot focused within the sample cell. The focal plane, the laser spot and the scanning circle define the measuring zone. The rotating beam then falls on a photodiode that measures beam intensity. A particle moving through the measuring zone interrupts the beam causing an interactive pulse or shadow on the photodiode. The time required to traverse the particle is converted to particle size. Out of focus or off center interactions generate rise times that are too long in proportion to particle diameter. Using an algorithm based on overall pulse signature with normalized rise-time criteria, each interaction is accepted or rejected. Only data from accepted signals are used for analysis.

4.2 Apparatus

(a) Ultrasonic bath.

(b) 1 cm cuvettes, plastic disposable or glass.

(c) Particle Size Analyzer. Brinkmann Instruments Model PSA 2010 Westbury, NY.

(d) Stir bars 3/8 inch diameter x 5/16 high, star.

4.3 Reagents

(a) Distilled H_2O or other suitable liquid. Heavier particles require more viscous media e.g., H_2O-glycerol mixtures. Surfactants may be required for some samples.

(b) Calgon, 1% solution in water.

(c) Daxad 23, 20 mg in 200 ml 50 v/o H_2O-glycerin.

4.4 Standards

(a) Glass or latex beads traceable to NIST database. Duke standards 10.4 µm, 20.0 µm, and 50.7 µm are currently available.

4.5 Safety

(a) Observe the general laboratory safety rules.

(b) Care must be exercised when performing analysis on low level radioactive materials. Samples dispersion should be performed in a hood and the cuvette covered to prevent spilling.

(c) Analysis of Pu or other highly radioactive material requires the instrument be installed in a glove box.

4.6 Quality Control

4.6.1 Calibration

The instrument does not require calibration and no provisions are made for calibration. Accuracy of the instrument may be verified by analyzing standard materials.

4.6.2 Control

A control standard is analyzed to assure the instrument is responding consistently with time. The standard is analyzed at least once with each group of samples as follows:

(a) Prepare a suspension of the appropriate standard in a cuvette with magnet using 50 v/o glycerin.

Follow steps in 4.7.

This cuvette may be saved and reused.

4.7 Analysis

4.7.1 Instrument Set Up

(a) Turn switches to "ON" position for the:

- Analyzer
- Video Screen
- Computer
- CRT
- Printer

(b) At c:\> prompt type CIS1. This loads the controlling software program.

4.7.2 Sample Dispersion

Because of the number of operational parameters available, only a cursory procedure can be given here. Different samples may of necessity require unique suspension media and the use of surfactants to avoid agglomeration. Operators should familiarize themselves with the PSA 2010 Operations Manual for additional information.

(a) Samples are dispersed in an appropriate liquid in the cuvette. Unless a material is water soluble, water or 50 v/o H_2O-glycerin will be used most frequently. If particles cling together (agglomerate) a surfactant will be required.

Particles in motion may be seen on the video screen. Stopping the stirrer slows down particle movement to allow a better visual determination of agglomeration, concentration, etc.

Trial and error learning is required to determine the proper amount of sample; typically 10^4-10^5 particles.

4.7.3 Sample Analysis

The main menu is displayed [from 4.7.1 (b)].

(a) Press F5 to set parameters. The SET MENU is now displayed. The default values are used in F1 unless special conditions are required (see Operations Manual).

(b) Press F3 to enter sample name. To save data enter sample name in form NNNNNNNN.EEE where N are characters (8 max) and E is a number (3 max). Use sample log number (89-XXXX) and record in LRB.

(c) Press ESC to return to Main Menu.

(d) Press F1 for data acquisition.

Instruction appears to remove cuvette for instrument self test. Follow instruction on screen.

(e) Data collection is automatic and will proceed to the set confidence level, usually (95%) (see Operations Manual).

Before proceeding with data collection the S.N.F. (signal normalization factor) and the S.D.U. (solution density factor) should be adjusted if necessary. The SNF should be 0.5-1.0 and the SDU 1000-2000. These are particle concentration factors. If the numbers are outside of these ranges the sample is either too dilute or too concentrated. The optimal particle concentration is easily learned through experience.

(f) When data collection is complete press any key to return to Main Menu.

(g) Press F3 for Graphics.

(h) Select type of report desired i.e., Number, Area or Volume. Distribution curves or bar graph presentations are available. Any or all data presentations may be printed.

(i) Press F4 for Tables.

Present particle data in tabular form with the same options as Graphics.

(j) Press F5 for Statistics.

Presents particle data in statistical form.

(k) Upon completion of printing of desired data presentations press ESC. The query "do you wish to save data (Y/N)?" will appear. Press desired selection.

(l) The query "terminate?" will appear, press Y or N.

Proceed to next sample.

The analyst must utilize the operators manual to familiarize themselves with all of the operational and data presentation parameters. This procedure is only a general guideline.

4.8 Calculation

None

5.0 BIBLIOGRAPHY

(a) Subcommittee on Particle Size Analysis. "Classification of Methods for Determining Particle Size, A Review," Analyst, 88, 156, March (1963).

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-506, MEASUREMENT OF THE PENETRATION RESISTANCE OF RADIOACTIVE WASTE

APPLICABILITY

Penetration resistance will be measured to determine whether a sludge exhibits a dilatant or cohesive property. At this time, the penetration resistance measurement will be a qualitative indicator of a sludge's cohesive or dilatant behavior and will not provide quantitative measurements. This measurement is Impact Level III per PNL QA Manual MA-70.

Knowledge of the cohesive or dilatant properties of a sludge are useful for 1) interpreting shear strength data, 2) applying pilot-scale sludge mobilazation equations, and 3) determining full-scale mixer pump performance for sludge retrieval. A dilatant sludge will tend to be eroded by the mixer pumps. Whereas, a cohesive sludge would be broken down into large chunks of sludge by the mixer pump. A smaller mixer pump would be required for a dilatant sludge.

The difference between the penetration resistance of a dilatant material and a cohesive material is large (a factor of 10) which makes the penetration resistance a good indicator of this sludge property. A low penetration resistance (0 - 10 psi.) indicates that a sludge is cohesive. A high penetration resistance (100 psi. or greater) suggests that a sludge is dilatant, but it must be known whether the sludge is composed of finely divided material and not some other type of material such as a solid crystal mass.

DEFINITIONS

1.0 Test Sample

The sample for the penetration resistance measurement must be a solid. The penetration resistance is a function of the moisture content of the sample. Therefore, prior to the measurement, the sample should be stored in a well sealed container. The sample should be at least 1 in. in diameter and 1.5 in. in depth. Disturbances to the sample should be minimized. The penetration resistance of a dilatant sludge will change more significantly with disturbances than for a cohesive sludge. It is important to describe the sample and size of the samples. The location of the penetration resistance measurement should also be recorded.

Author	**Date**	**Project Mgr.**	**Date**	**QAD Representative**	**Date**
	7/28/89			S L English	7-28-89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
	7/28/89		7/28/89		

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PNL-ALO-506	0	AUG 03 1989	1	3

2.0 Penetrometer

The CT-421A penetrometer supplied by Soil Test Inc. will be used for these measurements. The procedure supplied by the penetrometer manufacturer specified a penetration depth of 1.0 in. This penetrometer has a 0.25 in. diameter tip. A 1 in. diameter foot can be added to obtain very small penetration resistance measurements. If the sample size permits, the 1 in. diameter foot should be used for cohesive sludges. To obtain the measurement, the sample should be penetrated to a depth of 1 in. or to within 3/8 in. of the bottom of the sample container.

RESPONSIBLE STAFF

The staff responsible for implementing this procedure are:

- Cognizant Scientist
- Technician

PROCEDURE

1.0 Procedure for Measuring Penetration Resistance

1.1 Record the sample size (diameter, depth), shape, physical appearance, and surface smoothness on the data sheet (Exhibit 1). Select the location for the penetration resistance measurement. The penetration resistance should be measured in the center of the sample. Record the location of the measurement.

1.2 Obtain the CT-421A penetrometer. The first measurement should be obtained with the 0.25 in. diameter penetration end. Hold onto the handle end of the penetrometer and slide the red indicator ring towards the sleeve until the ring touches the sleeve.

1.3 Holding the penetrometer shaft perpendicular to the surface of the sludge, force the shaft into the sludge at a steady rate until the sludge has been penetrated to a depth of 1.0 in. as indicated by the red scribe mark on the side of the penetrometer or until the penetrometer is 3/8 in. from the bottom of the sludge container.

1.4 Slowly remove the penetrometer from the sludge. Obtain the measurement by reading the scale on the low-reading edge of the indicator ring (edge closest to the sleeve). If the surface area of the sludge is large enough, obtain at least two measurements.

1.5 If a reading of zero is obtained with the 0.25 in. diameter end and the diameter of the sample is greater than 1.0 in., place the 1 in. diameter foot on the penetrometer and repeat the measurement. The measurement may be repeated in the same location if the size of the sample does not permit selecting another location. Repeat steps 1.1 to 1.4.

1.6 The shaft of the penetrometer must be cleaned prior to each penetration test.

PNL-ALO-506, Rev. 0
Exhibit 1
Page 1 of 1

PENETRATION RESISTANCE DATA SHEET

Date: ____________

Measurement Obtained By: __________________________

Waste Type (DST #): ______________

Sample No.: ________________

Sample Description:

Diameter: ______________________ Height: ______________________

Shape: ____

Physical Appearance: ____

Surface Smoothness: ______________________

Location of Measurement: ____
____

Special Remarks: ____
____

Penetrometer No.: CT-421A

Penetration Resistance Measurements:

Number	Measurement (psi)	Diameter of End
		☐ 0.25 in. ☐ 1.00 in.
		☐ 0.25 in. ☐ 1.00 in.
		☐ 0.25 in. ☐ 1.00 in.
		☐ 0.25 in. ☐ 1.00 in.

Data Evaluation:

Data Reviewed By: ____________________ Date: ____________

Sludge Exhibits ☐ Cohesive Properties
☐ Dilatant Properties

PNL TECHNICAL PROCEDURE

TITLE: RDS-TA-1, LABORATORY PROCEDURE FOR OPERATION OF THE DIFFERENTIAL SCANNING CALORIMETER (DSC), THERMOGRAVIMETRIC ANALYZER (TG), AND HIGH TEMPERATURE DIFFERENTIAL THERMAL ANALYZER (DTA) AND DSC

APPLICABILITY

This procedure is applicable to pure compounds and mixtures of chemicals for which enthalpy changes (ΔH), temperature changes (ΔT), and weight changes (ΔWt) occur due to reaction, thermal decomposition, or phase changes. This procedure is applicable to dynamic temperature scanning measurements or isothermal measurements.

RESPONSIBLE STAFF

Staff responsible for implementing this procedure are:

- Cognizant Scientist
- Cognizant Technician

PROCEDURE

This procedure can be used to measure onset temperature, the reaction temperature range, the reaction enthalpy, and weight changes associated with a reaction using differential scanning and isothermal calorimetry (DSC and IC) and scanning and isothermal thermogravimetry (STG and ITG). Any purge gas compatible with the instrument components may be used.

1.0 Measurement of Onset Temperature, Reaction Temperature Range, and Enthalpy using the DSC

1.1 Equipment and Materials

- Differential Scanning Calorimeter
- Analytical Balance, 4-place (minimum sensitivity)
- DSC pans <u>(Do not use Aluminum Pans at > 500°C)</u>
- TADS and DSC software
- Purge gas
- Melting Point Standard(s)

Author RD Scheele	**Date** 8/9/89	**Project Mgr.**	**Date** 8/9/89	**QAD Representative** S L English	**Date** 8-10-89
Technical Reviewer L L Burger	**Date** 9Aug89	**Line Mgr.** R E Einziger	**Date** 8/10/89	**Other**	**Date**

Procedure No.	**Revision No.**	**Effective Date**	**Page**	**of**
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1.2 The COGNIZANT SCIENTIST will prepare a test instruction providing the COGNIZANT TECHNICIAN with the sample or components of the reaction mixture, the purge gas, the temperature range of the analysis, and the heating and/or cooling rate. The COGNIZANT TECHNICIAN will weigh the sample or individual components of the reaction mixture and will operate the DSC and the Thermal Analysis Data Station (TADS) following the operating procedures found in the operating manuals for the DSC and the TADS.

The Onset Temperature, which is the temperature at which lines tangent to the steepest portion of the DSC reaction peak and the baseline intersect, will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST using DSC analysis software and the PEAK command. The accuracy of the onset temperature is normally ± 5°C

The enthalpy of the reaction will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST using DSC analysis software and the PEAK command. The measured enthalpy is dependent on the interpreter's ability to determine where the reaction begins and ends. This is often difficult because of the complexity of most DSC curves and relies on the judgement of the interpreter. For a well behaved curve the normal accuracy of the enthalpy is ± 2%.

The reaction temperature range will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST by visual interpretation of the DSC curve. The beginning of the reaction is where the interpreter observes a deviation of the curve from the baseline and the end of the reaction is where the curve's slope returns to that of the baseline.

An Indium standard will be run weekly to check the temperature and enthalpy calibrations. The instrument will be recalibrated if the temperature differs from actual by > 1°C and if the enthalpy differs from actual by > 0.4 cal/g.

2.0 Measurement of Onset Temperature, Reaction Temperature Range, and Wt% Change using the TG.

2.1 Equipment and Materials

- Thermogravimetric Analyzer System
- TADS and TG Software
- DSC sample pans **(Do not use Aluminum pans at > 500°C)**
- Purge gas
- Curie Point Standard(s)

2.2 Procedure

The COGNIZANT SCIENTIST will prepare a test instruction providing the COGNIZANT TECHNICIAN with the components of the reaction mixture, the purge gas, the temperature range of the analysis, and the heating and/or cooling rate. The COGNIZANT TECHNICIAN will weigh the sample or individual components of the reaction mixture and will operate the TG and the Thermal Analysis Data Station (TADS) following the operating procedures found in the Thermogravimetric Analyzer System operating manuals.

The Onset Temperature, which is the temperature at which lines tangent to the steepest portion of the TG reaction curve and the baseline intersect, and the Wt% Change will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST using TG analysis software and the WT% command. The wt% change is dependent on the judgement of the interpreter and his ability to select the start and finish temperatures of the reaction.

An example of a particular use of Δwt% data is the determination of wt% solids. Wt% solids is the percentage of the original sample that remains after the free water has been driven off, typically by 120°C.

The onset temperature will normally have an accuracy of ± 5% and the wt% change will have an accuracy of ± 5%.

The balance calibration will be checked monthly during use or before using if the last calibration was > 1 month. The balance will be checked and/or calibrated using a 100 mg standard weight. The balance will be recalibrated if the measured mass differs by > 0.1 mg.

The temperature calibration will be performed weekly or before use if the calibration period is > 1 week. The temperature calibration will be checked or calibrated with one or more curie point magnetic transition standard(s) obtained from the equipment manufacturer. The temperature scale will be recalibrated if the measured temperature for a chosen standard differs by > 2°C. The COGNIZANT SCIENTIST will choose the calibration standard.

3.0 Measurement of Onset Temperature, Reaction Temperature Range, ΔT, and Enthalpy using the High Temperature DTA/DSC

3.1 Equipment and Materials

- High Temperature Differential Thermal Analyzer System
- Analytical Balance, 4-place (minimum sensitivity)
- DTA Crucibles
- TADS and DTA/DSC software
- Purge gas
- Melting Point Standard(s)

3.2 The COGNIZANT SCIENTIST will prepare a test instruction providing the COGNIZANT TECHNICIAN with the sample or components of the reaction mixture, the operational mode of the DSC/DTA, the purge gas, the temperature range of the analysis, and the heating and/or cooling rate. The COGNIZANT TECHNICIAN will weigh the sample or individual components of the reaction mixture and will operate the DTA and the Thermal Analysis Data Station (TADS) following the operating procedures found in the operating manuals for the DTA/DSC system and the TADS.

The Onset Temperature, which is the temperature at which lines tangent to the steepest portion of the DTA reaction peak and the baseline intersect, will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST using DTA analysis software and the PEAK command. The accuracy of the onset temperature is normally ± 10°C.

The maximum ΔT for the reaction, DTA operating mode, will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST using DTA analysis software and the PEAK command. The measured ΔT is dependent on the interpreter's ability to determine where the reaction begins and ends. This is often difficult because of the complexity of most DTA curves and relies on the judgement of the interpreter. For a well behaved curve the normal accuracy of the ΔT is ± 10%.

The enthalpy of the reaction will be determined by the COGNIZANT TECHNICIAN or the COGNIZANT SCIENTIST using DSC analysis software and the PEAK command. The measured enthalpy is dependent on the interpreter's ability to determine where the reaction begins and ends. This is often difficult because of the complexity of most DSC curves and relies on the judgement of the interpreter. For a well behaved curve the normal accuracy of the enthalpy is ± 10%.

The reaction temperature range will be determined by the ANALYST or the COGNIZANT SCIENTIST by visual interpretation of the DTA/DSC curve. The beginning of the reaction is where the interpreter observes a deviation of the curve from the baseline and the end of the reaction is where the curve's slope returns to that of the baseline.

A melting point standard will be run weekly to check the temperature and enthalpy calibrations. The instrument will be recalibrated if the temperature differs from actual by > 10°C and if the enthalpy differs from actual by > 1 cal/g.

4.0 Quality Assurance (QA)

Work performed using this technical procedure will meet the requirements described in PNL-MA-70.

TITLE: PNL-ALO-530, (Replaces 2-50.3), PARTICLE SIZE DISTRIBUTION BY LASER SCANNING (TIME OF TRANSITION)

1.0 APPLICABILITY

The sample material is dispersed ultrasonically and with stirring in a liquid. The analyzer uses a focused scanning laser spot and time of transition (to move from one side of the particle to the other) to measure particle diameters. Data presentation includes number, volume and area of particles.

(a)	Material	Any material insoluble in a suspension media. Almost any liquid is acceptable as suspension media.
(b)	Range	Particle diameters from 0.5 to 600 μm in three steps.
(c)	Reliability	Confidence limit is operator selectable. (See Operations Manual)
(d)	Interferences	None

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Analyst

4.0 PROCEDURE

4.1 Discussion

There are many different techniques used to measure the particle size distributions of powders. A complete classification of methods is given in a review paper prepared by a committee on particle size analysis.[a] The six classes of methods given in that paper are: 1) relative motion between particles and a fluid, 2) image formation, 3) scattering of radiation, 4) diffraction of

Author	Date	Project Mgr.	Date	QAD Representative	Date
MC Burt	12/4/89	N/A		GK Gerke	12/4/89
Technical Reviewer	**Date**	**Line Mgr.**	**Date**	**Other**	**Date**
N/A		WC Weimer	12/4/89	All original signatures on file	

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radiation, 5) electrical properties, and 6) sieves. This method falls into the first and third classes.

The analysis is based on the time required for a fixed velocity scanning laser beam to traverse the diameter of a particle. The beam passes through a spinning 1° wedge prism rotating at a constant velocity which creates a 600 μm diameter scanning circle. The beam passes through a microscope objective creating a 1.2 μm spot focused within the sample cell. The focal plane, the laser spot and the scanning circle define the measuring zone. The rotating beam then falls on a photodiode that measures beam intensity. A particle moving through the measuring zone interrupts the beam causing an interactive pulse or shadow on the photodiode. The time required to traverse the particle is converted to particle size. Out of focus or off center interactions generate rise times that are too long in proportion to particle diameter. Using an algorithm based on overall pulse signature with normalized rise-time criteria, each interaction is accepted or rejected. Only data from accepted signals are used for analysis.

4.2 Apparatus

(a) Ultrasonic bath.

(b) 1 cm cuvettes, plastic disposable or glass.

(c) Particle Size Analyzer. Brinkmann Instruments Model PSA 2010 Westbury, NY.

(d) Stir bars 3/8 inch diameter x 5/16 high, star.

4.3 Reagents

(a) Distilled H_2O or other suitable liquid. Heavier particles require more viscous media e.g., H_2O-glycerol mixtures. Surfactants may be required for some samples.

(b) Calgon, 1% solution in water.

(c) Daxad 23, 20 mg in 200 ml 50 v/o H_2O-glycerin.

4.4 Standards

(a) Glass or latex beads traceable to NIST database. Duke standards 10.4 μm, 20.0 μm, and 50.7 μm are currently available.

4.5 Safety

(a) Observe the general laboratory safety rules.

(b) Care must be exercised when performing analysis on low level radioactive materials. Samples dispersion should be performed in a hood and the cuvette covered to prevent spilling.

(c) Analysis of Pu or other highly radioactive material requires the instrument be installed in a glove box.

4.6 Quality Control

4.6.1 Calibration

The instrument does not require calibration and no provisions are made for calibration. Accuracy of the instrument may be verified by analyzing standard materials.

4.6.2 Control

A control standard is analyzed to assure the instrument is responding consistently with time. The standard is analyzed at least once with each group of samples as follows:

(a) Prepare a suspension of the appropriate standard in a cuvette with magnet using 50 v/o glycerin.

Follow steps in 4.7.

This cuvette may be saved and reused.

4.7 Analysis

4.7.1 Instrument Set Up

(a) Turn switches to "ON" position for the:

- Analyzer
- Video Screen
- Computer
- CRT
- Printer

(b) At c:\> prompt type CIS1. This loads the controlling software program.

4.7.2 Sample Dispersion

Because of the number of operational parameters available, only a cursory procedure can be given here. Different samples may of necessity require unique suspension media and the use of surfactants to avoid agglomeration. Operators should familiarize themselves with the PSA 2010 Operations Manual for additional information.

(a) Samples are dispersed in an appropriate liquid in the cuvette. Unless a material is water soluble, water or 50 v/o H_2O-glycerin will be used most frequently. If particles cling together (agglomerate) a surfactant will be required.

Particles in motion may be seen on the video screen. Stopping the stirrer slows down particle movement to allow a better visual determination of agglomeration, concentration, etc.

Trial and error learning is required to determine the proper amount of sample; typically 10^4-10^5 particles.

4.7.3 Sample Analysis

The main menu is displayed [from 4.7.1 (b)].

(a) Press F5 to set parameters. The SET MENU is now displayed. The default values are used in F1 unless special conditions are required (see Operations Manual).

(b) Press F3 to enter sample name. To save data enter sample name in form NNNNNNNN.EEE where N are characters (8 max) and E is a number (3 max). Use sample log number (89-XXXX) and record in LRB.

(c) Press ESC to return to Main Menu.

(d) Press F1 for data acquisition.

Instruction appears to remove cuvette for instrument self test. Follow instruction on screen.

(e) Data collection is automatic and will proceed to the set confidence level, usually (95%) (see Operations Manual).

Before proceeding with data collection the S.N.F. (signal normalization factor) and the S.D.U. (solution density factor) should be adjusted if necessary. The SNF should be 0.5-1.0 and the SDU 1000-2000. These are particle concentration factors. If the numbers are outside of these ranges the sample is either too dilute or too concentrated. The optimal particle concentration is easily learned through experience.

(f) When data collection is complete press any key to return to Main Menu.

(g) Press F3 for Graphics.

(h) Select type of report desired i.e., Number, Area or Volume. Distribution curves or bar graph presentations are available. Any or all data presentations may be printed.

(i) Press F4 for Tables.

Present particle data in tabular form with the same options as Graphics.

(j) Press F5 for Statistics.

Presents particle data in statistical form.

(k) Upon completion of printing of desired data presentations press ESC. The query "do you wish to save data (Y/N)?" will appear. Press desired selection.

(l) The query "terminate?" will appear, press Y or N.

Proceed to next sample.

The analyst must utilize the operators manual to familiarize themselves with all of the operational and data presentation parameters. This procedure is only a general guideline.

4.8 <u>Calculation</u>

None

5.0 BIBLIOGRAPHY

(a) Subcommittee on Particle Size Analysis. "Classification of Methods for Determining Particle Size, A Review," Analyst, 88, 156, March (1963).

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-531 (Replaces 7-30.3 & 7-40.3), SODIUM ROD PREPARATION FOR SODIUM BONDED FUEL

1.0 APPLICABILITY

The procedure described here is for the preparation of sodium rods for inclusion in sodium bonded FFTF fuel pins.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant scientist and technician.

4.0 PROCEDURE

4.1 Equipment and Materials

(a) Argon atmosphere glove box

(b) Sodium supply tank

(c) Balance

(d) Hydraulic extruder

(e) Plastic sodium roller

(f) Sodium transfer canister

(g) Polypropylene tubing

(h) Sodium cutter

4.2 Performance Checks

(a) Each tank of sodium shall be analyzed for oxygen and shall be less than 20 wppm. The lot analysis on the sodium supply

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RF Keough	8/10/88	N/A		LJ Ethridge	8/10/88
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N/A		WC Weimer	8/10/88	All original signatures on file	

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shall confirm that the sodium meets Class I requirements of RDT Standard M 13-1T, Sodium Purchase Specifications. It shall also meet the impurity limits specified in WHC-SP-0027, TDD 1B for MFF-2 and MMF-3 metal fuel tests. Analytical methods shall be those in RDT F 3-40.

(b) Copies of the sodium supplier's analysis and PNL's analysis of the 3 gallon lot (tank) will be provided to WHC Fuel Pin Fabrication before any sodium rods are supplied. Each day's production of rods will constitute a batch and each canister of rods will be tagged with the date of production, the batch number and the sodium lot number.

(c) The weight of every sodium rod will be recorded. Any rod not within the tolerances established by WHC Fuels Department will be modified or rejected. High, low and average weights for each batch of sodium rods and M&TE used will be recorded in a laboratory notebook. A printout of individual rod weights will be kept on file for one year.

4.3 Extrusion Cylinder Filling

(a) Establish that the sodium in the 3 gallon supply tank is approved for use by inspecting the lot identification tag on the tank.

(b) Pressurize the sodium tank to 5-10 psi with argon (Stores #21-1300-100). Confirm that the sodium valve in the glove box is fully closed.

(c) Set the controller on the sodium tank heater to 105°C and begin heating the sodium. Several hours will be required to melt the sodium.

(d) After the sodium reaches 105°C, heat the sodium transfer line to 130-150°C. Again, confirm that the valve in the glove box is closed.

(e) Place an empty extrusion cylinder under the valve outlet and fill it to about one inch from the top. If sodium doesn't flow from the valve, increase all temperatures 10-20°C.

(f) When the sodium filled cylinder has cooled, either place it in the extruder or in a plastic bag. Sodium in cylinders must be stored in the glove box at all times.

(g) Enter the date filled and cylinder number in the notebook.

4.4 Sodium Rod Forming

(a) Operating in the argon atmosphere glove box, extrude about 8 inches of sodium at a rate of 1-2 inches/second. The extruded sodium should be nearly straight to produce the optimum weight when cut.

(b) Place a plastic plate behind the hanging sodium extrusion and cut off a fixed length segment (approximately 7.5 inches) with the sodium cutter.

(c) Lay the sodium on the plastic rolling board and roll it back and forth between the two plastic plates several times to straighten and size the sodium rod.

(d) Insert the sodium rod into a plastic tube approximately 8.5 inches long, provided by WHC's Fuels Pin Fabrication group. The balance should previously be tared with the empty tube if the sample is to be weighed. The sodium rod in the plastic tube can be weighed at this time if required. Record all weights in a laboratory notebook.

(e) As soon as practical, after forming, store the sodium rods in a closed, stainless steel container under argon. Record the canister number, the date and the number of sodium rods contained in a notebook. Each canister should contain only sodium rods produced within an eight hour period.

4.5 Sodium Transfer

(a) The plastic tubes containing the sodium rods will be in a gas tight, stainless steel, sodium transfer canister within the glove box dedicated to this work. Close the canister and pressurize it with argon to 5-10 psi. Keep the canister in the argon glove box until WHC Fuels Fabrication group requests transfer.

(b) When the sodium is transferred to WHC, attach a tag indicating the batch number and the date the rods were formed. Provide a signed release card to WHC at this time.

4.6 Records

A laboratory notebook will be the recording mechanism for all data relating to sodium rod production. ~~The notebook will be used in accordance with PAP-1704~~.

4.7 Procedure Qualification

Not required. This procedure is considered self-qualifying due to its dependence on the sodium weight control.

4.8 Procedure Modification

WHC Fuel Pin Fabrication Manager will be advised prior to making any changes to this procedure.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-532, (Replaces 7-30.5 & 7-40.5) PROCEDURE FOR FILLING SP-100 FUEL CAPSULES

1.0 APPLICABILITY

Refractory metal capsules, typically 15 x 0.75 inch, are loaded with solid, purified lithium. The lithium is melted in place, under vacuum, and fuel pins are added. The fuel pin capsule assemblies are cooled and returned to the 308 building for closure by welding.

2.0 DEFINITIONS

This procedure is applicable to the assembly of capsules of TZM, niobium and other refractory metals using pins containing a uranium based fuel. Capsule length is limited to approximately 18 inches by the glovebox dimensions. Lithium quantity is presently limited to 1000 cc by existing purification facilities.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 DISCUSSION

This method was devised for loading capsules with fuel for irradiation in a reactor; however, it could also be used for placing any type of test specimen in lithium for materials testing purposes. Requirements for chemical and isotopic purity of the lithium may change, depending on the experimenter's requirements.

4.2 APPARATUS

(a) Argon atmosphere glove box, with atmosphere purified by constant circulation over molecular sieve and hot titanium.

(b) Armco iron pot

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RF Keough	8/10/88	N/A		LJ Ethridge	8/10/88
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N/A		WC Weimer	8/9/88	All original signatures on file	

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(c) Molybdenum chill plate

(d) Titanium lined capsule heater

(e) Vacuum pump

(f) Shipping cask, air tight

(g) Titanium tipped tongs

(h) Balance

4.3 REAGENTS

(a) Titanium and zirconium getter as foil or granules

(b) SAES type 707 getter granules

(c) Lithium, 99.98% lithium-7

4.4 STANDARDS

4.5 SAFETY

(a) Observe the general laboratory safety rules, the Job Safety Analysis and the Radiation Work Procedure for this work.

4.6 QUALITY CONTROL

Lithium samples will be analyzed for important trace impurities and isotopic composition. Quantity of lithium added to each capsule will be held to within the experimenter's requirements by weighing. Archive samples will be taken as requested. A QA representative's presence may be required by the experimenter during capsule loading.

4.7 PROCEDURE

4.7.1 Lithium Preparation

1. Open the sealed suppliers (ORNL) tin can of lithium in a hood. Wash off the mineral oil with toluene and quickly transfer the "oil free" lithium to an argon atmosphere glovebox. All toluene should evaporate in the vacuum transfer chamber before entering the glovebox.

2. Place the lithium in a stainless steel beaker and heat to 210 +/- 10°C. Hold at this temperature for 30 minutes, then transfer through a 50 micron filter to an Armco iron pot containing 100-200 sq. inches of getter foil or granules.

3. Heat the pot to 700-800°C for at least 6 hours. Cool to 200°C and withdraw a filtered (5 micron) sample for carbon and nitrogen analysis.

4. Repeat step 3 with additional getter if the carbon or nitrogen analyses are higher than acceptable for the intended use. Typically one purification will reduce carbon and nitrogen to less than 10 and less then 100 ppm respectively. This is regarded as the minimum acceptable purity for the current work. A second purification should, typically, half these values.

5. When both carbon and nitrogen are at acceptable levels, analyze a sample for trace metals and isotopic composition.

4.7.2 Capsule Loading

1. Heat the lithium to 220 +/- 10°C and force it through a 5 micron filter onto a polished chill plate to form balls about 0.6-0.7 inches diameter. Store these balls in a closed container in the glovebox until used. Storage should be limited to two days.

2. Weigh a suitable amount of lithium balls and drop into a TZM capsule. Heat to melt (200 - 250°C) while under vacuum of 0.01 Torr. Typically 20-30 g will be required.

   Note: In general, capsules and test pins should only contact other refractory metals, glass, cloth and polyethylene. Experimenter's may have more or less restrictive requirements.

3. Release the vacuum and lower the proper fuel pin into the capsule. Be certain the pin isn't upside down. The tri-corn on the pin may pull argon into the lithium; raising and lowering the pin in the lithium may help dislodge argon bubbles.

4. Confirm by measurement that the fuel pin is fully seated in the capsule.

5. Allow the lithium to freeze with the capsules in a nearly vertical position. Place the cooled capsules in the shipping cask. Pressurize the cask to 2-5 psig with argon.

6. Transfer the shipping cask, in a suitable container, to the 308 Building for welding.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-533, (Replaces 7-30.7), PROCEDURE FOR SODIUM FILLING OF BEATRIX-II TYPE CAPSULES

1.0 APPLICABILITY

This procedure is for the filling of BEATRIX-II type capsules with a known amount of metallic sodium. It could be used for any capsule to be filled with sodium by pressure.

2.0 DEFINITIONS

None

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Safety

Observe the general laboratory safety rules and the applicable Job Safety Analyses.

4.2 Quality Control

The experimenter may impose tolerances, impurity limits or other restrictions, depending on the test needs.

4.3 Equipment and Materials

(a) Argon atmosphere glove box

(b) Pyrex volumetric sodium supply

(c) Test capsule

(d) Heaters

Author RF Keough	Date 1/11/89	Project Mgr. N/A	Date	QAD Representative LJ Ethridge	Date 1/11/89
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(e) Sodium

4.4 Apparatus Setup and Fill Procedures

Step 1) Assemble the apparatus as shown in Figure 1. Heat tapes should be used to insure that all components in contact with sodium are above 100°C.

Step 2) Apply power to all heaters. The capsule may be heated up to 400°C for better wetting but the glass components should not be heated above 150°C.

Step 3) Set the argon pressure regulator at 5 psi.

Step 4) With all components at temperature, open the argon supply valve to pressurize the sodium.

Step 5) Note the sodium level in the pyrex supply vessel then open the sodium valve and allow the capsule to fill.

Step 6) When the proper volume of sodium (density = 0.92) has been drained into the capsule, close the sodium valve. Record the quantity of sodium used in the LRB.

Step 7) Cool all components and disassemble the apparatus.

Step 8) Package the capsule in a gas tight bag and tin can for transfer to the welding lab. As an alternative, a special, gas tight cap may be connected to the capsule for the transfer.

4.5 Records

A laboratory record book (LRB) will be the recording mechanism for all data relating to this technical procedure. ~~The LRB will be used in accordance with PAP-70-1704~~.

4.6 Procedure Qualification

Not required. This procedure is considered self qualifying due to its dependence on the sodium weight control.

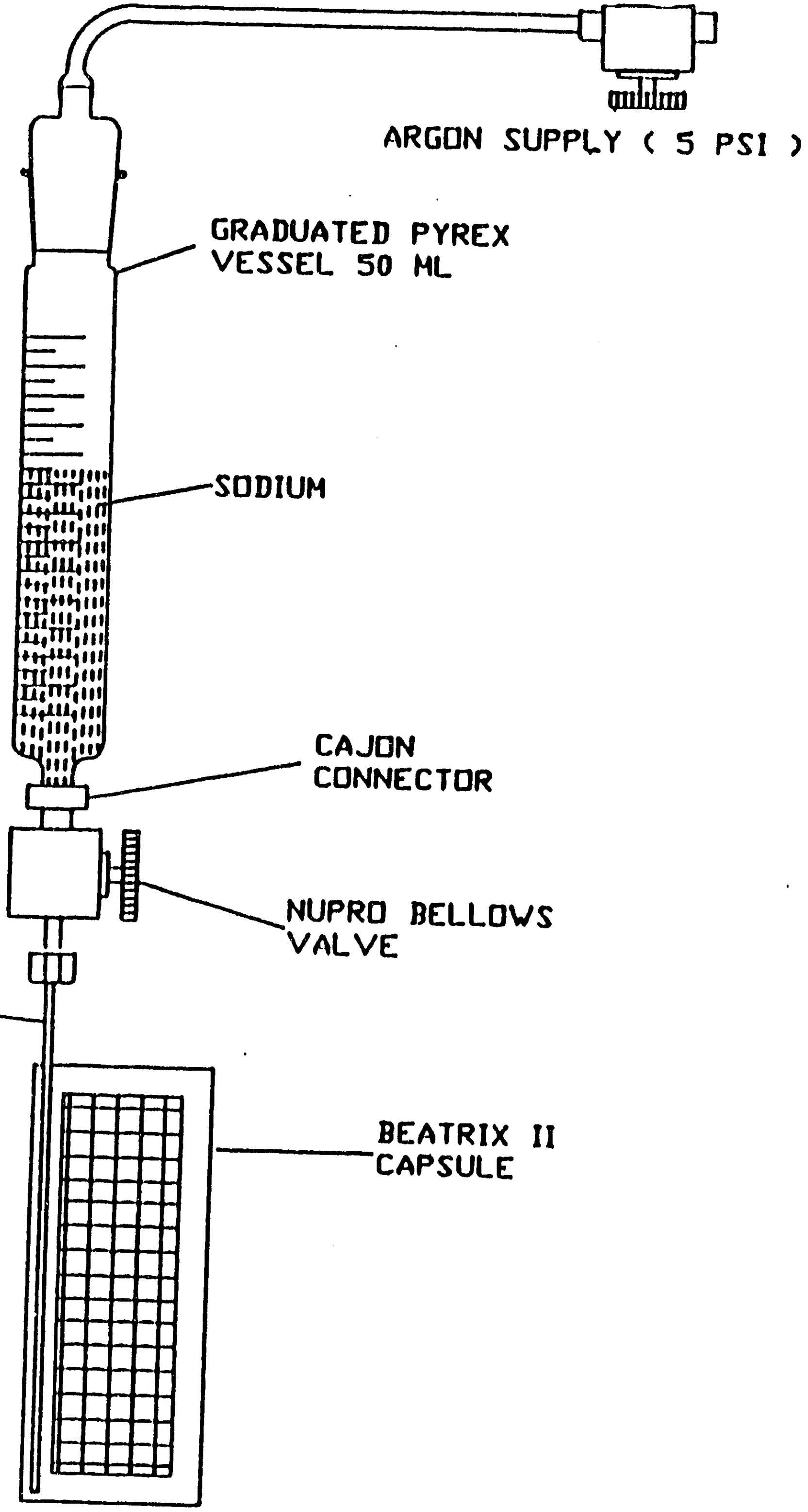

Figure 1. Capsule Filling Apparatus

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-534, (Replaces 7-30.10), REMOVAL OF ALKALI METALS WITH AMMONIA

1.0 APPLICABILITY

This procedure provides instructions for the removal of alkali metals (sodium, potassium, lithium, and their alloys) from components using cryogenic ammonia as a solvent.

2.0 DEFINITIONS

None.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Technician

4.0 PROCEDURE

4.1 Equipment and Materials

- Ammonia, compressed and liquified; refrigeration or anhydrous grade.
- Dry ice.
- Methyl or ethyl alcohol, reagent grade.
- Stainless steel tubing.
- Glass or stainless steel beakers and trays.
- Glove bag or portable glove box.

4.2 Procedure

Note 1: Ammonia gas is toxic and irritating and must be kept in a hood at all times. Liquified ammonia has the additional hazard of potentially freezing skin. Wear waterproof gloves when handling liquid ammonia.

Author Date RF Keough 11/15/89	Project Mgr. Date N/A	QAD Representative Date GK Gerke 11/16/89
Technical Reviewer Date N/A	Line Mgr. Date WC Weimer 11/15/89	Other Date All original signatures on file

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Note 2: If the components being cleaned are not hydrogen sensitive (e.g., refractory metals) the glove bag can be eliminated and the removal carried out in air.

4.2.1 Place the components to be cleaned, beakers, trays and tongs on the glove bag or box, in a hood. (see Note #2).

4.2.2 Purge air from the glove bag or box with ammonia gas.

4.2.3 Open the container holding the component to be cleaned and place it in a beaker or tray. To retain small components a basket of stainless steel screen is helpful.

4.2.4 Generate cryogenic (liquid) ammonia by passing ammonia gas in a stainless steel line through a bath of dry ice and alcohol. Route the cryogenic ammonia line directly into the glove bag and onto the component being cleaned. Wash the alkali metal off the components as with any other solvent.

4.2.5 Continue washing until fresh ammonia is no longer turned deep blue; an indication that the process is complete.

4.2.6 Remove the components from the glove bag and immediately rinse with alcohol, distilled water and again with alcohol. Dry the components in air or in a vacuum oven as required.

4.5 Records

Normally no records are required.

4.6 Procedure Qualification.

No qualification is required. The completion of alkali metal removal is clearly indicated by the lack of blue coloration to the cryogenic ammonia.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-535, (Replaces 7-40.29), SPECIFIC GRAVITY OF HIGHLY RADIOACTIVE SOLUTIONS

1.0 APPLICABILITY

This procedure applies to the measurement of the specific gravity of highly radioactive solutions in a hotcell.

2.0 DEFINITIONS

Highly radioactive solutions are solutions too radioactive to be removed safely from the hotcells as determined by the COGNIZANT SCIENTIST.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Balance--readable to at least 0.0001 grams.
- Pipet--type and volume to be specified by the COGNIZANT SCIENTIST.
- Deionized water.
- Vials--leached, volume to be specified by the COGNIZANT SCIENTIST.
- Thermometer--readable to 0.1°C at the hotcell ambient temperature.

4.2 Pipet Calibration and Specific Gravity Measurement

Specific gravity is measured by weighing a known volume of sample

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solution. The sample is pipetted into a tared, leached vial using a calibrated pipet. The specific gravity is calculated using the measured weight and volume.

The ANALYST shall perform the following steps unless otherwise specified.

Step 1) Weigh a specified vial plus cap to 0.0001 g or better.

Step 2) Using a specified pipet, pipet a measured volume of deionized water into the vial.

Step 3) Weigh the vial plus water plus cap to 0.0001 g or better. Record all weights in the LRB.

Step 4) Repeat steps 1), 2), and 3) at least 4 more times for pipet calibration. Repeat two or more times for sample measurements.

Step 5) Measure and record the in-cell ambient temperature.

Step 6) Calculate the volume of the pipet using Section 4.3, Subsections 4.3.1, 4.3.2, 4.3.3 and 4.3.4.

Step 7) Repeat 1), 2), 3), 4), and 5) using sample instead of water.

Step 8) Calculate the specific gravity using Section 4.3, Subsections 4.3.1, 4.3.2, 4.3.3 and 4.3.5.

4.3 Pipet Calibration and Sample Calculations

4.3.1 Weight of Water or Sample Pipetted

$$A = (B)-(C)$$

Where: A = weight of water or sample in grams
B = weight of water or sample plus vial plus cap from Step 3)
C = weight of vial plus cap from Step 1)

4.3.2 Average Weight of Pipettings of Water or Sample

$$\bar{A} = \frac{\Sigma A}{D}$$

Where: $\bar{A}$ = the average weight of water or sample pipetted in grams

ΣA = the sum of all the values of weighed water or sample

D = the number of water or sample weighings done

4.3.3 Relative Standard Deviation of Water or Sample Weights

$$RSD = \sqrt{\frac{\Sigma(A_i - \bar{A})^2}{N-1}}$$

Where: RSD = relative standard deviation of the average water or sample weight

$\Sigma(A_i - \bar{A})^2$ = the sum of the squares of the differences between average weight of water or sample and each weight of water or sample

N = the number of water or sample weighing made

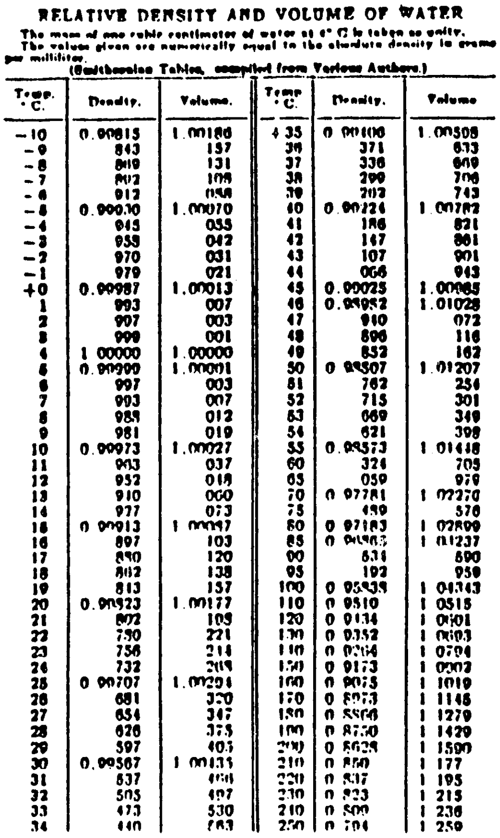
4.3.4 Pipet Volume ± Relative Standard Deviation

$V \pm RSDv = (A \pm RSDA)(T)$

Where: $V \pm RSDv$ = volume of pipet in ml ± relative standard deviation

$A \pm RSD\bar{A}$ = average weight of water (4.3.2) ± relative standard deviation

TABLE 1



RELATIVE DENSITY AND VOLUME OF WATER

The mass of one cubic centimeter of water at 4° C is taken as unity.
The values given are numerically equal to the absolute density in grams per milliliter.

(Smithsonian Tables, compiled from Various Authors.)

Temp. °C.	Density.	Volume.	Temp. °C.	Density.	Volume
−10	0.99815	1.00186	+35	0.99406	1.00598
−9	843	157	36	371	633
−8	869	131	37	336	669
−7	892	108	38	299	706
−6	912	088	39	262	743
−5	0.99930	1.00070	40	0.99224	1.00782
−4	945	055	41	186	821
−3	958	042	42	147	861
−2	970	031	43	107	901
−1	979	021	44	066	943
+0	0.99987	1.00013	45	0.99025	1.00985
1	993	007	46	0.98982	1.01028
2	997	003	47	940	072
3	999	001	48	896	116
4	1.00000	1.00000	49	852	162
5	0.99999	1.00001	50	0.98807	1.01207
6	997	003	51	762	254
7	993	007	52	715	301
8	988	012	53	669	349
9	981	019	54	621	398
10	0.99973	1.00027	55	0.98573	1.01448
11	963	037	60	324	705
12	952	048	65	059	979
13	940	060	70	0.97781	1.02270
14	927	073	75	489	576
15	0.99913	1.00087	80	0.97183	1.02899
16	897	103	85	0.96865	1.03237
17	880	120	90	534	590
18	862	138	95	192	959
19	843	157	100	0.95838	1.04343
20	0.99823	1.00177	110	0.9510	1.0515
21	802	198	120	0.9434	1.0601
22	780	221	130	0.9352	1.0693
23	756	244	140	0.9264	1.0794
24	732	268	150	0.9173	1.0902
25	0.99707	1.00294	160	0.9075	1.1019
26	681	320	170	0.8973	1.1145
27	654	347	180	0.8866	1.1279
28	626	375	190	0.8750	1.1429
29	597	405	200	0.8628	1.1590
30	0.99567	1.00435	210	0.850	1.177
31	537	466	220	0.837	1.195
32	505	497	230	0.823	1.215
33	473	530	240	0.809	1.236
34	440	563	250	0.794	1.259

T = volume factor from Table 1 for the ambient temperature measured, e.g., 25°C = 1.00294

4.3.5 Sample Specific Gravity

$$Sp.G = \frac{\bar{A}}{V} \pm \frac{\bar{A}}{V}\sqrt{\left(\frac{RSDA}{\bar{A}}\right)^2 + \left(\frac{RSDv}{V}\right)^2}$$

Where: Sp.G. = specific gravity of sample at temperature recorded

$\bar{A}$ = average of sample weights from 4.3.2

V = the pipet volume from 4.3.4

RSD$\bar{A}$ = relative standard deviation for average weight of sample from 4.3.3

RSDv = relative standard deviation for volume of pipet from 4.3.4

4.4 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033 . ~~Laboratory Record Books shall be used in accordance with PAP-70-1704~~. LRB's and analytical report cards provide a mechanism for control of most records. Self-calibrated equipment shall be used in accordance with PAP-70-1201.

4.5 Procedure Qualification

This procedure is considered qualified since calibration of the pipetter is carried out at the time of each measurement. In addition, this procedure is considered qualified through an Independent Technical Review.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-536, (Replaces 7-40.30), BULK DENSITY OF HIGHLY RADIOACTIVE FREE-FLOWING GRANULAR SOLIDS

1.0 APPLICABILITY

This procedure applies to the measurement of bulk density of highly radioactive, free-flowing granular solids in a hotcell.

2.0 DEFINITIONS

High radioactive solids are solids that are too radioactive to be removed safely from the hotcell as determined by the COGNIZANT SCIENTIST.

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 Equipment and Materials

- Balance - readable to 0.0001 grams.
- Volumetric flask - volume specified by COGNIZANT SCIENTIST. Some options are: 2 ml ± .015 ml, 5 ml ± .020 ml, 10 ml ± .020 ml, 25 ml ± .03 ml and 50 ml ± .05 ml(1)

4.2 Bulk Density Measurement

Bulk density is measured by weighing a measured volume of the material. The volume is measured using a volumetric flask. Since

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(1) NBS Circular No. 602, 1959.

Author Date AC Leaf 8/3/88	Project Mgr. Date N/A	QAD Representative Date LJ Ethridge 8/4/88
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no meniscus is formed by granular solids the flask is filled to calibration mark and made level and even with the mark.

The ANALYST shall perform the following steps unless otherwise specified.

Step 1) Weigh a volumetric flask, specified by the COGNIZANT SCIENTIST, to 0.0001 grams.

Step 2) Transfer the sample to the volumetric flask and fill to the calibration mark. Be sure the material is level and even with the mark.

Step 3) Weigh the flask plus sample to 0.0001 grams.

Step 4) Calculate the bulk density using the calculations in 4.3.

4.3 Calculations

$$BD = \frac{A-B}{C} \pm (EE)$$

Where, BD = bulk density in grams/ml

A = weight of sample plus volumetric flask (Step 3)

B = weight of the volumetric flask (Step 1)

C = volume of volumetric flask

EE = estimated error is estimated at 2 times the volumetric error as given in 4.1

4.4 Records

Records will be maintained and controlled so as to conform with requirements of MCS-033 . ~~Laboratory Record Books shall be used in accordance with PAP-70-1704.~~ LRB's and analytical report cards provide a mechanism for control of most records. Self-calibrated equipment shall be used in accordance with PAP-70-1201.

4.5 Procedure Qualification

This procedure is considered qualified by use of certified volumetric flasks and calibrated balances. In addition, this procedure is considered qualified through an Independent Technical Review.

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-537, (Replaces 7-40.41), PURIFICATION OF LITHIUM BY HOT GETTERING AND FILTRATION

1.0 APPLICABILITY

This procedure is intended for the purification of molten lithium metal by contacting the hot lithium with a zirconium alloy which absorbs carbon and nitrogen. Prior to use the lithium is filtered at low temperature to remove particulate metallic and other non metallic impurities down to near their solubility values. In general, metallic impurities will not be reduced by this procedure. This procedure can be used even more effectively with sodium or potassium. With those metals, oxygen will also be removed by the zirconium alloy.

2.0 DEFINITIONS

NONE

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Analyst

4.0 PROCEDURE

4.1 SAFETY

This procedure involves working with red hot lithium, an extremely reactive metal. Every precaution should be taken to assure that hot lithium does not come in contact with air. Only staff experienced with lithium and glove box operations should use this procedure.

4.2 EQUIPMENT AND MATERIALS

4.2.1 Argon atmosphere glovebox with recirculating purification system for removal of reactive gases.

Author	Date	Project Mgr.	Date	QAD Representative	Date
RF Keough	9/22/89	N/A		GK Gerke	10/3/89
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		WC Weimer	9/22/89	All original signatures on file	

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4.2.2 Heated, iron vessel (figure 1) made of "Armco" high purity iron or equal. Wall thickness to be 0.06" or greater if 500 cc or larger and 0.03" or thicker if smaller than 500 cc capacity. No vessel larger than 2500 cc shall be used and no more than 1000 grams of lithium shall be purified in a batch.

4.2.3 Lithium metal of the highest quality available. For some applications this will include isotopic purity. Dry packed lithium is preferred but oil packed is often the only form available.

4.2.4 Getter alloy chips containing 75% zirconium, 15% vanadium and 10% iron. This material is available from SAES Getters as Alloy 707.

4.2.5 Oil solvent for removing mineral oil from the lithium supply. Petroleum ether or toluene are satisfactory.

4.3 LITHIUM PURIFICATION

4.3.1 Open the sealed lithium container in a hood and quickly lift the block of lithium from the mineral oil and submerge it in oil solvent. Move it around to quickly wash as much oil off as possible.

4.3.2 Remove the lithium from the contaminated solvent and repeat the washing in two more batches of solvent.

4.3.3 Blot residual solvent from the lithium block and quickly transfer it to the vacuum chamber of the glovebox. Evacuate to remove traces of remaining solvent.

4.3.4 Take the lithium into the argon atmosphere of the glovebox and melt it in a stainless steel beaker. Do not exceed 250°C. With the lithium at 200-220°C, skim off any dross.

4.3.5 Pour the lithium into the iron vessel, which should be preheated to 200-300°C. Do not fill the vessel more than 75% full to allow for expansion on heating. Visually estimate the lithium volume.

4.3.6 Add about 1 gram of SAES 707 alloy chips to the vessel for each 20 cc of lithium.

4.3.7 Cap the vessel and heat to 500-600°C. Loosen the cap briefly to relieve any pressure, then heat to 800-825°C. Caution, do not attempt to manipulate the vessel at temperatures above 600°C.

4.3.8 Heat the vessel at least 12 hours at 800-825°C.

4.3.9 Cool to 200-250°C prior to analysis or use. For both analysis and use, the lithium must be passed through a 5 micron stainless steel filter at 200-250°C.

4.3.10 Obtain chemical analyses by suitable procedures as required to establish concentrations of any specified impurities.

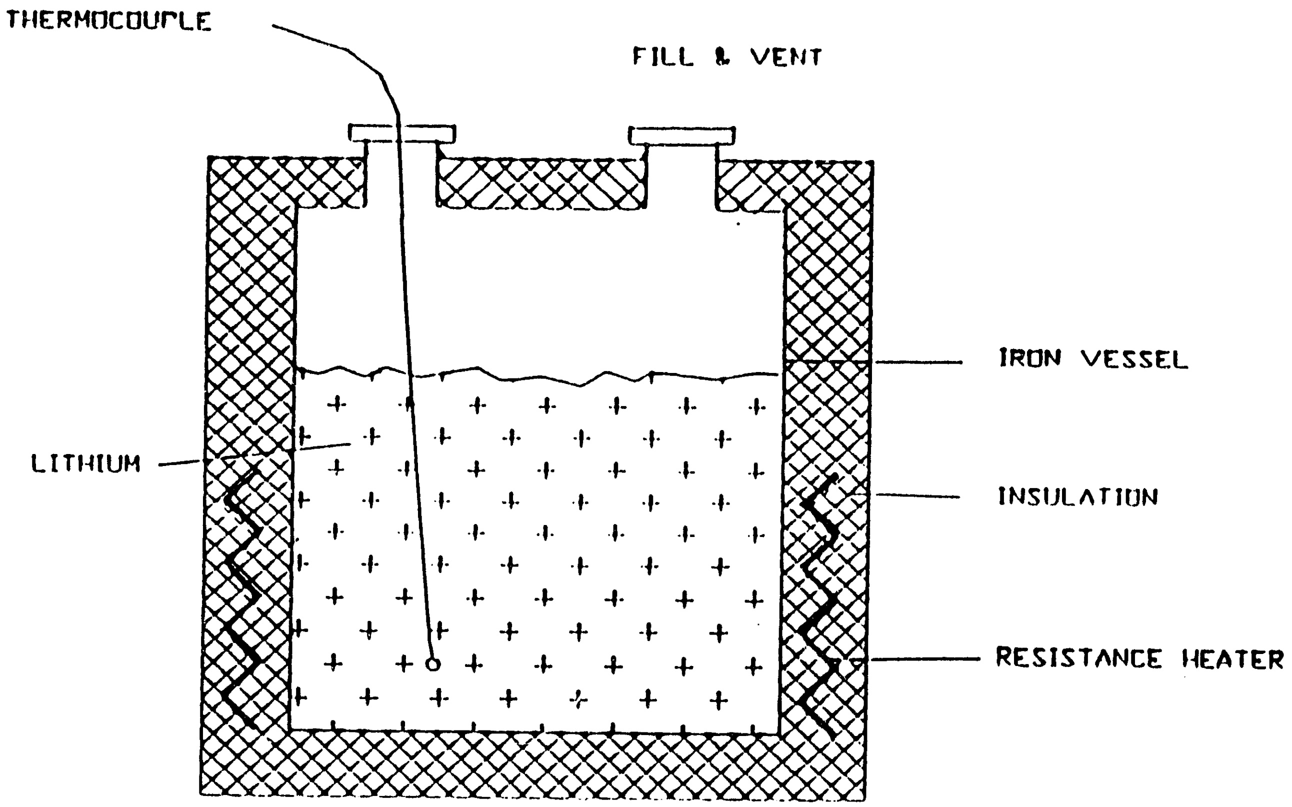
4.3.11 In the event that carbon or nitrogen levels remain above the acceptable limits established by the test engineer or TDD, repeat steps 4.3.8 and 4.3.9. If other impurities are at unacceptable levels, the batch must be rejected.

4.4 DOCUMENTATION

Record all available information on the lithium in a laboratory notebook. This information may include manufacturer, lot number, manufacturer's purity designation, lot analysis, purification date, quantity purified, and any PNL final analysis.

4.5 PROCEDURE QUALIFICATION

This procedure is considered self-qualifying due to the dependance on a final chemical analysis to verify the purity prior to use of the product. In addition, it has received an independent technical review.



LITHIUM PURIFICATION POT

FIGURE 1

PNL TECHNICAL PROCEDURE

TITLE: PNL-ALO-538, (Replaces 7-40.68), LITHIUM FILLING OF MOTA CAPSULES

1.0 APPLICABILITY

This procedure is intended for the filling of MOTA capsules with molten lithium under vacuum. With size modifications it could be used for other types of open capsules.

2.0 DEFINITIONS

MOTA - Materials Open Test Assembly; an FFTF irradiation test item.
JSA - Job Safety Analysis
LRB - Laboratory Record Book

3.0 RESPONSIBLE STAFF

Cognizant Scientist
Technician

4.0 PROCEDURE

4.1 Safety

Observe the general safety rules and any applicable JSA's.

4.2 Quality Assurance

The experimenter may impose general QA requirements and/or specific tolerances, impurity limits, inspection points or other restrictions, depending on the test needs. These requirements will be documented, generally in a traveler, memo or letter of instruction.

4.3 Equipment and Supplies

(a) Argon Atmosphere Glovebox
(b) Pure Lithium Supply

Author	Date	Project Mgr.	Date	QAD Representative	Date
RF Keough	7/10/91	N/A		GK Gerke	7/11/91
Technical Reviewer	Date	Line Mgr.	Date	Other	Date
N/A		MW Urie	7/15/91	All original signatures on file	

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(c) Test Capsule
(d) Capsule Heater
(e) Vacuum Pump

4.4 Apparatus Setup and Fill Procedure

4.4.1 Assemble the apparatus as shown in Figure 1. Use heat tapes to assure that all connecting tubing is maintained above the melting point of lithium (181°C).

4.4.2 Evacuate and heat the capsule to at least 300°C. Heat the lithium to 200-250°C. During the lithium heat up, use the melting point of lithium to confirm all temperature readouts are accurate to within 2°C unless they have been checked in the last week and documented in the LRB.

4.4.3 With the capsule under vacuum, open the valve slightly and allow lithium to enter the bottom of the capsule until it can be seen through the glass view port, rising through the test items.

4.4.4 If necessary, shake or vibrate the capsule through the capsule heater to get uniform distribution of lithium. If wetting is required, the temperature may have to be raised to about 400°C to speed up the process.

4.4.5 When the lithium has reached the proper level, as established by the experimenter, stop the lithium addition and allow the capsule to cool.

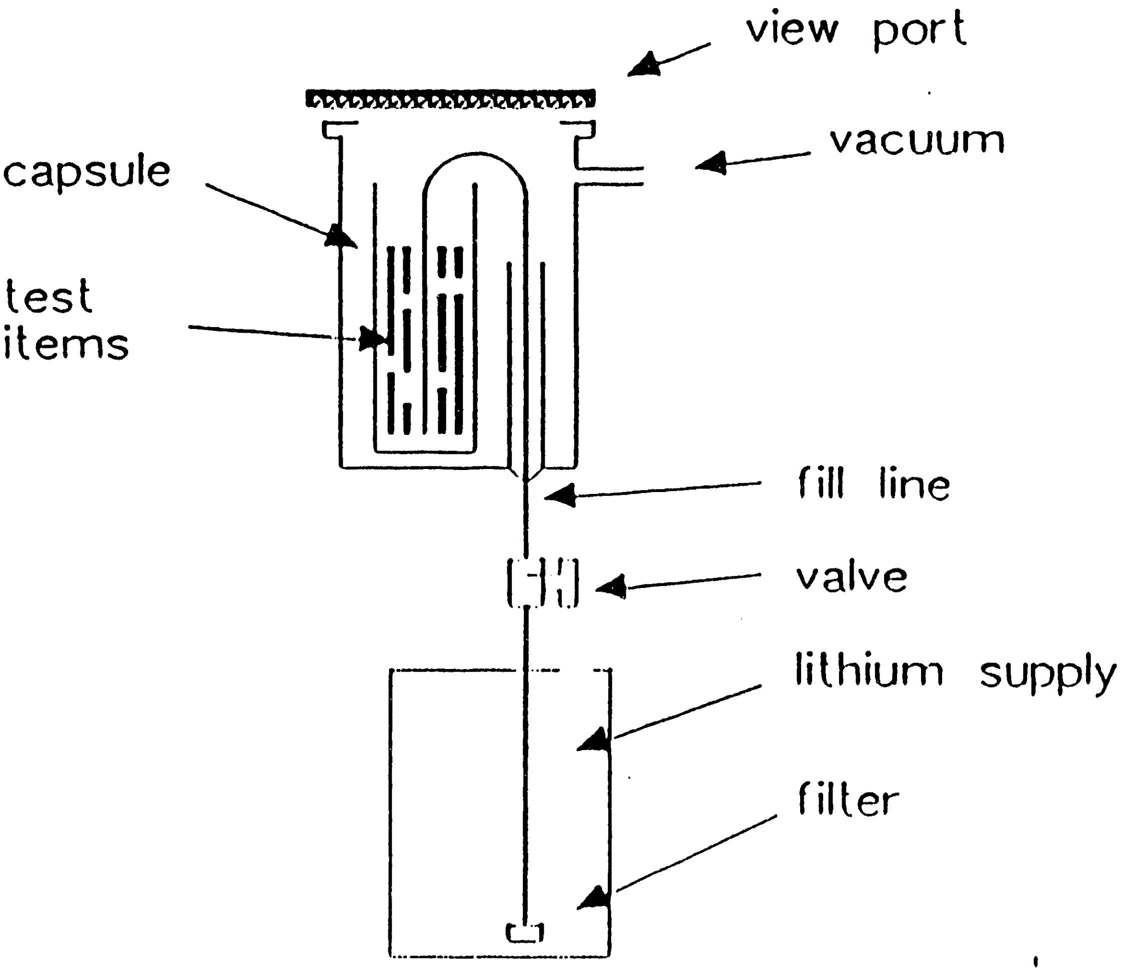
4.4.6 With the lithium frozen, release the vacuum and cut the fill tube as close to the lithium surface as practical. The capsule can now be removed and packaged for shipment to the welding facility for final sealing.

5.0 RECORDS

A Laboratory record book (LRB) and the experimenters traveler will be the recording mechanisms for this procedure. The LRB will be used in accordance with Management Guide 3.8.

6.0 PROCEDURE QUALIFICATION

Not Required. This procedure is considered self qualifying due to its dependence on visual inspection of the end product by the experimenter or his/her representative.



CAPSULE FILLING APPARATUS

FIGURE 1

END

DATE FILMED

9/30/93