Lockheed
Analytical Laboratory

SAMPLE PREPARATION AND ANALYSIS FOR GAMMA ACTIVITY IN AQUEOUS SAMPLES

LAL-91-SOP-0063

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1.0 PURPOSE

The purpose of this standard operating procedure is to provide instruction and guidance to the staff of the Lockheed Analytical Laboratory on procedures necessary for sample preparation for determining the gamma activity in a water sample.

2.0 SCOPE AND APPLICATION

2.1 ASSIGNMENT OF RESPONSIBILITY

This SOP is to be used by personnel working in the radionuclide section of the laboratory when preparing water samples for determination of gamma activity. This document shall also be regarded as a task specific safety plan.

For all water samples received, it should be indicated on the analysis request as to whether total (soluble plus insoluble), soluble, or separate soluble and insoluble fractions are to be analyzed.

2.2 SUMMARY OF METHOD

Many water samples received contain significant amounts of solids, sludge, or other separate phases. These samples are, for reasons discussed in 2.3, separated by filtration, centrifugation, or other means as necessary. Each fraction is then analyzed individually, either by this procedure or using LAL-91-SOP-0064, Gamma Activity in Solids Sample Preparation.

Some samples will have sufficient activity present to analyze as is. Those with a lower specific activity, however, are concentrated to a smaller volume and counted at a suitable geometry.

A known volume of a homogeneous aliquot of the water sample is placed in a pre-weighed standard geometry container. The weight and density are then determined after reweighing the container and sample. The sample is then passed on to the counting room personnel for gamma measurement.

2.3 INTERFERENCES

Many water supplies contain dissolved solids at such high concentrations (>500 mg/liter) that measurement of gamma activity is affected by self-shielding within the sample. The same will be true for samples containing significant amounts of solid particles or other phases. This problem may be reduced during counting procedures by applying correction factors from a plot of density versus the calculated efficiency for various energies. Further, solids or other phases can concentrate in varying portions of a sample, creating the possibility of non-representative sampling and/or an increase or decrease in the relative counting efficiency of the sample. This may be avoided by sampling and counting only homogeneous samples. In addition, homogeneity can also be affected by adsorption of radionuclides on the walls of the counting container. Acidification of the sample with nitric or hydrochloric acid to a pH of 1-2 in the field or before transfer to the counting container will greatly reduce this effect.

3.0 DEFINITIONS

Homogeneous - uniform throughout in composition.

MSDS - Material Safety Data Sheet.

OHS - Occupational Health Services, Inc. 11 West 42nd Street, 12th Floor, New York, NY 10036.

Specific activity - an activity density of a sample, usually in units of activity/volume for liquids or activity/weight for solids.

Standard geometry container - a container such as a beaker or a bottle, specific in size and shape, used when counting samples for gamma activity.

4.0 SAFETY

4.1 GENERAL

4.1.1 All laboratory personnel must be thoroughly familiar with the Lockheed Analytical Health and Safety Manual and the Lockheed Analytical Laboratory Radiation Safety Manual before undertaking any laboratory work in the radionuclide section of the laboratory. Employees must adhere to all guidelines described in these documents.

4.1.2 Safety glasses and lab coats are available through Lockheed and must always be worn in the laboratory. In addition, appropriate gloves must be worn when handling any chemicals or samples.

4.1.3 Personnel must be aware of the location of the nearest emergency wash facilities, including an eye wash fountain and a quick drench shower, and must be familiar with the operation of each facility.

4.1.4 Care must be exercised in handling solvents, standards, and samples. Analysts must be familiar with the Material Safety Data Sheets for all chemicals used. MSDS information is available from the Designated Safety Representative, and will be thoroughly reviewed before performing this sample preparation procedure.

4.1.5 In consideration of the radioactivity and/or chemical composition of samples, all samples must be treated as a potential health hazard. Exposure to these hazards must be reduced to the lowest practicable levels. The use of fume hoods and appropriate gloves are of utmost importance.

4.1.6 All procedures that have a potential to generate airborne radioactivity must be performed in a fume hood.

4.1.7 All radioactive wastes must be handled according to LAL-91-SOP-0083, Disposal of Radioactive Materials.

4.2 SPECIFIC

4.2.1 **Nitric acid** is a colorless to pale yellow liquid with a suffocating odor. It is a strong oxidizer, and may ignite other combustible materials (wood, paper, oil, etc.). It reacts violently with water and fuels. Thermal decomposition products may include toxic oxides of nitrogen, and runoff to sewer may create fire or explosion hazard. It is TOXIC BY INHALATION AND INGESTION, and is corrosive upon inhalation, ingestion, and by skin and eye contact. Persons with impaired pulmonary function and pre-existing eye and skin disorders are at increased risk from exposure. It is incompatible with many other chemicals, and should be handled in a hood while wearing a faceshield or with the hood sash pulled down as far as possible to shield the operator's face.

5.0 APPARATUS/MATERIALS/STANDARDS

5.1 APPARATUS

5.1.1 Centrifuge.

5.1.2 Filter membranes, 47 mm diameter, 0.45 μm pore size or glass fiber filters, such as Gelman Type A/E or Millipore Type AP.

5.1.3 Separatory funnel.

5.1.4 Standard geometry counting containers (1 or 4-liter polypropylene Marinelli beaker or 4 oz. polypropylene bottle or other approved container) labeled for contents, marked with a liquid level line, and pre-weighed. Liquid level lines are marked for the corresponding container size as follows:

4 oz	75 ml liquid level line
1 liter	1 liter liquid level line
4 liter	3.5 liter liquid level line
other as required	

5.1.5 Top-loading balance capable of measuring 4.4 kg at an accuracy of ± 0.1 grams.

5.2 MATERIALS

5.2.1 Nitric acid, conc. (HNO_3, 70%).

5.3 STANDARDS

5.3.1 Multi-nuclide standards

9-nuclide reference standards consisting of:

Nuclide	Energy KeV
Cd-109	88
Co-57	122
Ce-139	166
Hg-210	279
Sn-113	392
Sr-85	514
Cs-137	662
Y-88	898
Co-60	1173
Co-60	1333
Y-88	1836

Available from Amersham, Analytics, or Isotope Products Laboratory.

Long Lived Mixed Radionuclide

Nuclide	Energy (KeV)
Eu-154 and 155	43
Eu-155	87
Eu-155	105
Eu-154	123
Sb-125	176
Eu-154	247
Sb-125	428
Sb-125	463
Eu-154	592
Sb-125	601
Sb-125	636
Eu-154	723

Eu-154	873
Eu-154	996
Eu-154	1005
Eu-154	1274

Available from NIST

5.3.2 Single Nuclide Standards

Nuclide	Energy (KeV)
Se-75	97
Se-75	121
Se-75	136
Se-75	265
Se-75	280
Se-75	401
Am-241	60
Pb-210	46
I-129	29
I-129	40

Available from the above mentioned sources.

The above nuclides will be placed in solution in various density solutions in the exact geometry of the sample. Alternatively, commercially produced solid matrix standards may be utilized.

6.0 PROCEDURE

If the sample contains significant solids or is multiphasic, or if stated on the analysis request, the sample should be separated by centrifuging, filtering, or other means. Each fraction should be analyzed separately, with liquid samples prepared as follows.

6.1 Typical Samples

This procedure is to be followed if the specific activity of the homogeneous sample is suitable to count the sample as is in a standard geometry container. All samples should be thoroughly mixed immediately before aliquoting into a pre-weighed, labeled, and marked standard geometry container.

6.1.1 Fill a prepared standard geometry container to the mark with a representative sample aliquot. Cap the container and wipe with a clean paper towel.

6.1.2 Reweigh the container and its contents, then determine and record the density of the sample -- (Gross weight - Tare weight)/(Volume).

6.1.3 Seal the sample with silicon sealant (or equivalent) and/or electrical tape and place in an appropriately sized plastic containment bag.

6.1.4 Place the labeled sample with proper documentation in the appropriate location for retrieval by counting room personnel.

6.2 Concentration of Low-Level Sample

This procedure is to be followed if the sample specific activity is too low to count the sample as is in a standard geometry container.

6.2.1 Mix the sample thoroughly to ensure representative sampling.

6.2.2 Pour an aliquot of the sample, to the nearest 100 mL (up to 1000 mL), into a clean, dry 1000 mL graduated cylinder. The aliquot taken should not be more than half the total volume of the sample to be analyzed. Record the aliquot volume.

6.2.3 Transfer the aliquot to a clean 1000 mL beaker, using several washings of 8 M HNO_3.

6.2.4 Place the beaker on a hot plate and cover with a ribbed watch glass. Evaporate the aliquot to approximately 40 to 50 mL.

6.2.5 Transfer the sample to a prepared 4 oz standard geometry container, rinsing the beaker with 1 N HNO_3. Use a rubber policeman, if necessary, to ensure transfer of any residues. Fill the container to the marked level with 1 N HNO_3.

6.2.6 Cap the container securely, and wipe the outside of the bottle with a clean paper towel.

6.2.7 Reweigh the container and its contents, then determine and record the density of the sample -- (Gross weight - Tare weight)/(Volume).

6.2.8 Seal the sample with silicon sealant (or equivalent) and/or electrical tape and place in an appropriately sized plastic containment bag.

6.2.9 Place the labeled sample with proper documentation in the appropriate location for retrieval by counting room personnel.

6.3 SAMPLE COUNTING

6.3.1 Count the sample following LAL-91-SOP-0075, Calibration, Maintenance, and Operation of a High-Resolution Gamma Spectroscopy System.

6.4 CALCULATIONS

6.4.1 Calculate activity concentration of each nuclide in sample as follows:

$$Activity(pCi/L) = \frac{C_{SPL} - C_B}{E_s * Y * V * 2.22}$$

where:

C_{SPL} = sample gross CPM
C_B = background CPM
E_s = efficiency at nuclide peak energy
V = aliquot size in L
Y = branching intensity of gamma at peak energy
2.22 = Conversion factor from CPM to pCi

6.4.2 Lower Limit of Detection (LLD)

$$LLD(pCi/L) = \frac{4.66 * (\sigma_{BKGD})}{2.22 * E * Y * V}$$

Where:

4.66 = a statistical factor ($2\sqrt{2k}$ at the 95% confidence level)
σ_{BKGD} = standard deviation of the background which may be approximated by $(C_{BKGD})^{0.5}/T$
C_{BKGD} = background gross count
T = background count time
2.22 = conversion factor to pCi
E = efficiency from efficiency curve
Y = branching intensity of gamma at peak energy
V = volume of the sample aliquot in liters

6.4.3 Minimum Detectable Activity (MDA)

$$MDA\,(pCi/L) = \frac{4.66 * (\sigma_{BLK})^{0.5}}{2.22 * E * Y * V}$$

Where:

4.66 = a statistical factor ($2\sqrt{2k}$ at the 95% confidence level)
σ_{BLK} = standard deviation of the reagent blank which may be approximated by $(C_{BLK})^{0.5}/T$
C_{BLK} = reagent blank gross count
T = reagent blank count time
2.22 = conversion factor to pCi
E = efficiency from efficiency curve
Y = branching intensity of gamma at peak energy
V = volume of the sample aliquot in liters

6.4.4 Counting Error (CE) at the 95% confidence level

$$CE(pCi/l) = 1.96 * \frac{\sqrt{\frac{C_s}{T_s^2} + \frac{C_B}{T_B^2}}}{2.22 * E * Y * V}$$

Where:

C_s = gross counts of the sample
T_s = count time of the sample
C_B = gross counts of the blank
T_B = count time of the blank
2.22 = conversion factor to pCi
E = efficiency from efficiency curve
Y = branching intensity of gamma at peak energy
V = volume of the sample aliquot in liters

7.0 QUALITY ASSURANCE

7.1 CONTINUING CALIBRATION VERIFICATION

7.1.1 Instrument background will be counted at a minimum of once per week per the instrument operating procedure. The limits are incorporated in the instrument operating procedure.

7.1.2 Instrument check standards will be counted at a minimum of once per week per the instrument operating procedure. The limits are included in the instrument operating procedure.

7.2 REAGENT BLANKS

7.2.1 A minimum of one reagent blank must be analyzed with each batch of samples. The minimum frequency of reagent blanks will be 5%.

7.2.2 If the reagent blank is greater than two times the LLD, the analysis must be considered to be out of control.

7.3 REPLICATES

7.3.1 Replicate analysis must be performed at a minimum of once with each batch of samples. The minimum frequency of replicates is 10%.

7.3.2 The replicates will be analyzed using the same aliquot and count time as the original sample.

7.3.3 Replicates will agree within the 95% confidence level based upon the summed error of the analysis.

7.4 LABORATORY CONTROL SAMPLES

7.4.1 A minimum of one LCS must be analyzed per batch of samples. The minimum frequency of LCS analyzed must be 5%.

7.4.2 The LCS control limit must be set at 3 standard deviations. If the LCS is not within 3 standard deviations of the known value the analysis is considered to be out of acceptance limits.

7.4.3 The LCS warning limit must be set at 2 standard deviations from the known value. Two consecutive LCS results more than two standard deviations from the known value will be considered out of acceptance limits.

7.4.4 Seven consecutive LCS on the same side of the true value will indicate an analytical bias and an out-of-control condition.

7.5 MATRIX SPIKE AND MATRIX DUPLICATES

7.5.1 A matrix spike (MS) and matrix spike duplicate (MSD) will be performed the first time each matrix is analyzed using this method. More MS and MSD may be required by a sample specific QAPP or specified by a customer.

7.5.2 The matrix spike recovery must be between 80 and 120 percent.

7.5.3 The percent relative standard deviation of the matrix spike and the matrix spike duplicate must be less than 20 percent.

7.6 As discussed in section 2.3, self-shielding within a sample may create counting problems. If the density of the sample in the counting container falls outside that obtainable from the standard curves, results cannot be considered to be reliable.

8.0 CORRECTIVE ACTION

8.1 INSTRUMENT OUT OF CONTROL

8.1.1 If the counting instrument background or instrument check standard is out of control limits, no samples will be counted using the instrument until the problem is investigated and the instrument is brought back into control using the instrument operating procedure. All problems will be documented in the appropriate logbook.

8.2 REAGENT BLANK OUT OF CONTROL

8.2.1 If the reagent blank is out of control, two additional blanks will be prepared and counted.

8.2.2 If the average of the three is within the control limit, the method is considered to be in control.

8.2.3 If the average of the three reagent blanks is out of control, the cause of the contamination must be eliminated prior to the analysis of more samples.

8.2.4 The samples counted with the contaminated blanks will either be tagged or reprepared and reanalyzed depending upon the customers needs.

8.3 LABORATORY CONTROL SAMPLE OUT OF CONTROL

8.3.1 If the LCS is out of control limits, two more LCS samples will be prepared and counted.

8.3.2 If the average of the three LCS is within the two standard deviation limit, the analysis is considered to be in control.

8.3.3 If the average of the three LCS is not within the two standard deviation limit but the two repeated samples are within the two standard deviation warning limit the out of control LCS is considered to be a true outlier and the analysis is in control. The data will be flagged as to the out of limits LCS.

8.3.4 If the analysis is still out of control, the cause of the loss of control must be investigated and eliminated prior to any more sample analysis.

8.3.5 The data generated with the out of control LCS will either be flagged or repeated according to the requirements of the customer.

9.0 DOCUMENTATION REQUIREMENTS

On the Gamma Spectrum Analysis Sample Preparation Worksheet record the following:

At the top of the page:
- PWO
- Customer Batch Number
- LAL Batch Number
- Date Assigned
- Date Due
- Assigned Analyst Name

In tabular format:
- Sample ID number
- Screening Analysis results
- Aliquot used
- Tare weight of the container
- Gross weight of container
- Any applicable comments

At the bottom of the page:
- Date Completed
- Analyst's Signature
- Supervisor's Initials

Upon completion of the worksheet make two copies of the worksheet. Tape one copy in the sample preparation logbook for the laboratory where the preparation was performed. Give one copy and the original to the counting room for documentation of sample preparation. The original will be given to Document Control with the data package.

10.0 REFERENCES

10.1 Calibration and Performance of a High-resolution Gamma Spectroscopy System. UNC-020.

10.2 Gamma-ray Emitting Nuclides in Water, Nondestructive Spectrometric Method. OR-020.

10.3 Preparation of Environmental Samples for Gamma Spectroscopy Analysis. ANL-020.

10.4 Prescribed Procedures for Measurement of Radioactivity in Drinking Water, August 1980. Method 901.1, EPA-600/4-80-032.

10.5 OHS MSDS #OHS16550 (Nitric acid).

STANDARD OPERATING PROCEDURE
CHANGE FORM

SOP NUMBER:	ORIGINATOR/AUTHOR:
LAL-91-SOP-0063 Revision 0	NUNN Nathan J. Nunn
DOCUMENT TITLE: SAMPLE PREPARATION FOR GAMMA ACTIVITY IN AQUEOUS SAMPLES	DATE IMPLEMENTED: 11/21/94

SECTION/CHAPTER: 4.0 SAFETY
PAGE NUMBER:

CHANGE:
This SOP was reviewed for safety/waste management issues.
Delete
4.1 to 4.1.4
Change
4.1.5 to 4.3
4.1.6 to 4.4
4.1.7 to 4.5
4.2 to 4.6
4.2.n to 4.6.n (n = appropriate subsection number)
Add
4.1 Personnel will adhere to the policies in the LAS Environmental Safety and Health Operations Manual and Radiation Safety Manual. Personnel who have been trained as per this SOP have read the Material Safety Data Sheets (MSDSs) for all materials used and are familiar with the contents and hazards listed on the MSDSs.
4.2 The minimum level of hand protection when handling samples or hazardous chemicals is Nitrile™ gloves.
Include in section 4.5
Waste acids will be collected in either 120 liter poly drums or 20 liter poly carboys with red "Hazardous Waste" labels. The waste code D002 will be written on the waste containers. Care must be taken to properly vent the 120 liter waste drum when adding waste to the container.

APPROVAL

Section Supervisor [signature] QA Manager S. K. Aleckson 12-15-94