Characterization of nuclear material and radioactive waste at SRS

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Summary. — The Savannah River National Laboratory's Nuclear Measurements Group (NMG) provides both radiochemical analyses and non-destructive assay of nuclear material to the ongoing processes at the Savannah River Site (SRS) as well as to other DOE facilities. The radioanalytical capability of the group serves to complement the more-limited services provided by the Savannah River Site production analytical laboratories as well as offsite commercial laboratories. The amounts of radioactivity in sample matrices vary widely, ranging from environmental levels to those with doses high enough to require remote handling and manipulation. For items too large or too inconvenient to transport to the laboratory for analysis, non-destructive assay (NDA) can be performed in-situ. The group also conducts on-site neutron and gamma assays. The group provides technical support for non-destructive gamma, neutron, and calorimetry assay systems installed in various Site facilities. The NMG supports nuclear measurement technology development, collaborating with numerous universities, to address SRS needs as well as to address nuclear measurement shortfalls across the complex. An overview of past and present SRS nuclear processes, including the extensive radiological waste cleanup efforts underway, are described with a focus on how the NMG's operations are currently intertwined with these operations.

1. – Savannah River Site Radiological Processes

The Savannah River Site (SRS) is an 800-square kilometer U.S. Department of Energy (DOE) site located near Aiken, South Carolina. It was established in the early 1950s as part of the US government's efforts to develop nuclear weapons during the Cold War and has been producing nuclear materials since its inception. The SRS originally comprised five reactors and two production-scale, radiologically shielded PUREX chemical separations facilities (F-Canyon and H-Canyon). The reactors were used primarily to produce tritium and plutonium-239 for the US nuclear weapons programs. However, the Site produced numerous additional radionuclides (fig. 1) beyond those produced for the weapon's programs for space exploration, industrial, energy and medical applications. F-Canyon was used primarily to dissolve uranium targets irradiated to produce plutonium-239. The plutonium was purified in the Canyon using the PUREX process, winding down operations around 2005.

Plutonium processes on-Site are currently limited to legacy nuclear materials management. The K-Reactor facility was converted into a storage facility for the nation's excess plutonium and other special nuclear materials. Most of the plutonium oxide stored in the K-Area Complex was originally slated for disposition by being blended into mixed-oxide fuel on Site, and subsequently burned in conventional reactors. That project was abandoned and an alternate process of down blending and disposing of the plutonium oxide is currently underway. The SRS MOX facility is in the process of being repurposed into a facility to produce plutonium weapon pits for the nation.

H-Canyon was used to primarily reprocess the fuel used in the five Site reactors. L-Reactor's Disassembly Basin was re-purposed post reactor shut-down to continue to serve as a spent nuclear fuel (SNF) storage facility. Since 1964, SRS has received more than 2,467 casks containing over 47,880 domestic and foreign SNF assemblies. As a result, H-canyon's SNF reprocessing function has continued long after the Site's reactors shut down, reprocessing aluminum-clad, highly-enriched-uranium, spent nuclear fuel which, for a period, was then blended down to commercial reactor fuel specifications. That blend-down function recently ceased, and the H-Canyon has shifted to a dissolve and dispose function for SNF stored in the L Area Disassembly Basin. The L Area complex is also the storage site for millions of liters of tritiated heavy water that was used for the reactor operations.

Radioactive liquid waste from the two separation canyons is rendered caustic and discharged into SRS's F and H-Area Tank Farms. The Tank Farms contain 51 waste tanks of four distinct types, with capacities ranging from ~ 3 million to 5 million liters. The caustic rendering of the liquid waste caused the waste to separate into two forms, an aqueous layer containing soluble components and a sticky sludge layer containing components that were not soluble in the caustic medium. Over 625 million liters of liquid waste was discharged from the Canyons into the SRS Tank Farms. The aqueous layer was concentrated by evaporation, forming an additional waste form of solid "saltcake". The initial volume of 625 million liters was concentrated to approximately 129 million liters of waste that was stored in the SRS Tank Farms. As of March 31, 2022, the SRS Waste Tank radiological inventory was 227 million curies (30 ZBq) [1]. Of that, $\sim 51\%$ was in the supernate and saltcake form, primarily Cs-137. The remaining 49% was in the sludge form, primarily Sr-90 and its radiological daughter, Y-90. The actinides and lanthanides also partitioned primarily into the sludge component of the waste.

SRS has brought numerous waste treatment facilities on-line to remediate the various waste forms found in the SRS Tank Farms as well as to process the residues from the on-going H-Canyon operations. In 1996 SRS brought the Defense Waste Processing Facility (DWPF), a high-level-waste vitrification plant, on-line. DWPF initially only vitrified the sludge component from the SRS tank farms. In 2008, the Actinide Removal Process (ARP) & Modular Caustic Side Solvent Extraction (CSSX) Unit (abbreviated in sum as MCU) operations began, decontaminating caustic supernate and dissolved saltcake. The ARP process removes residual Sr-90, actinides and lanthanides from the aqueous feed solutions using a batch contact with monosodium titanate (MST) process. The CSSX process uses centrifugal contactors to extract Cs-137 from the aqueous feed solutions with a solvent-solvent process based on a calixarene extractant. The MST slurry and Cs-137 extract were then sent to DWPF to be vitrified in conjunction with the sludge vitrification process. This process was accelerated with the construction of the Salt Waste Processing Facility (SWPF) which is capable of processing waste at six times the speed of the MCU facility. SWPF was brought on-line in 2020 and is expected at its peak capacity to be able to process up to 9 million gallons of aqueous feed. Decontaminated
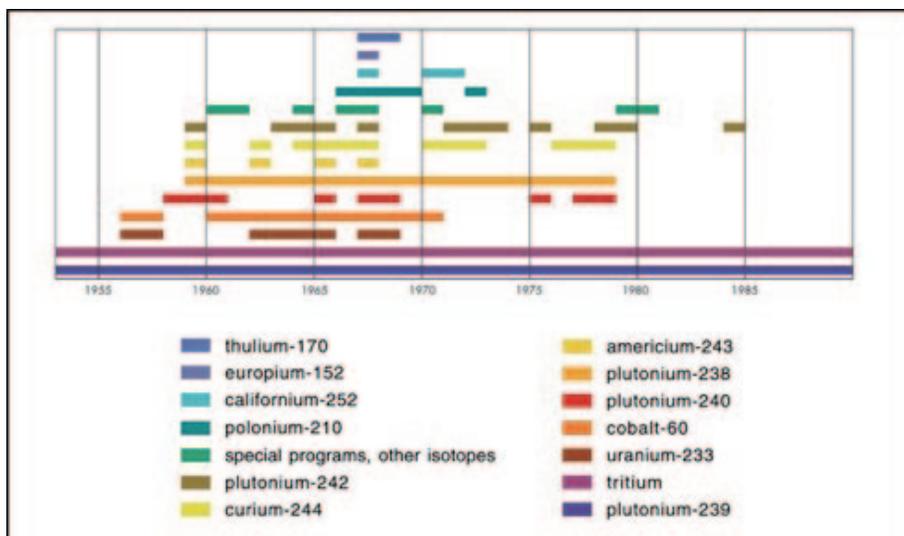
Fig. 1. – Radionuclides produced at the Savannah River Site.

solutions are sent to SRS's Saltstone Production Facility (SPF). The SPF contains tanks and equipment necessary to receive the large decontaminated salt solution DSS stream from SWPF. Saltstone grout is made by mixing the decontaminated feeds from SWPF with fly ash and slag. The grout mixture is then pumped into large concrete permanent disposal units called Saltstone Disposal Units (SDU). Current SDU's under construction can hold up to 125 million liters of Saltstone.

2. – Nuclear Measurements Group

The SRNL Nuclear Measurements Group (NMG) provides several functions to support the Savannah River Site, as well as the larger US Department of Energy community. NMG provides a field-deployed non-destructive assay service to the Site. The NDA team measures radioisotopes in various structures and components in both functioning facilities, and in facilities slated for decommissioning.

The bulk of the NDA work is gamma assay. The gamma assays are calibrated using Monte Carlo N-Particle (MCNP) calibration models generated by the team, or by using Mirion Technologies' In Situ Object Counting System (ISOCS). In addition to gamma assays, the team conducts gamma imaging to map gamma emitting radioisotope contamination in the field. The team makes use of the PHDS Co. GeGI as well as the H3D, Inc. Gamma Imager. The GeGI is a high purity gamma imager that can quicky identify the high concentrations of a radionuclide in the field using Compton Imaging technology or can map the contamination field using pin-hole imaging (fig. 2). The H3D Gamma Imager incorporates a less efficient CdZnTe-based detector, but has a smaller form function that can be easier to handle in the field. The H3D detector can also image with Compton Imaging and maps contamination fields with coded-aperture measurements.

In addition, the NDA team conducts field neutron assays. The team also supports gamma, neutron and calorimetry measurements in facility locations scattered across the Savannah River Site.
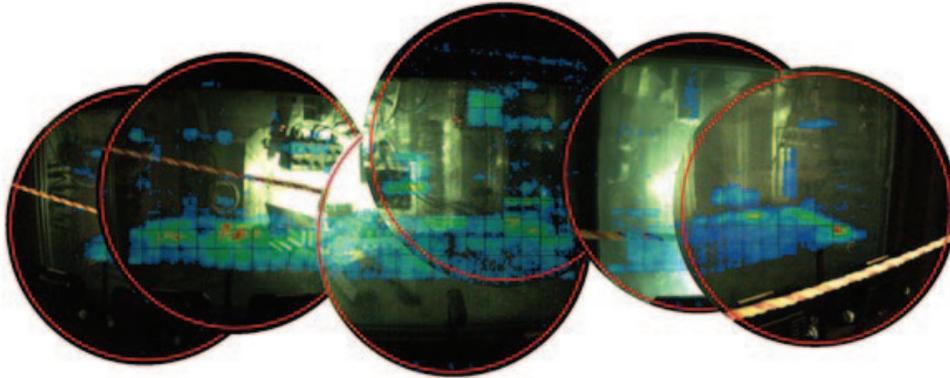
Fig. 2. – Pin-hole image from PHDS GeGI of Pu-238 contamination.

The NMG provides support to the SRS to develop field deployable assay devices to support various Site initiatives. For example, to support SRS Wildlife hunts which are Site-sponsored to reduce vehicle animal collisions on Site, the NMG developed a Cs-137 radiation monitor to screen all harvested animals for Cs-137 prior to allowing the hunters to remove the animals from the Site [2]. The NMG also has recently supplied process control radiation monitors to the Site's Tank Closure Cesium Removal (TCCR) process. This was a small scale, at-tank Cs-137 decontamination process based on a Crystalline Silico Titanate (CST) decontamination process which needed real-time Cs-137 monitoring [3].

The NMG collaborates with numerous universities, conducting research in areas suffering from gaps in technology, and taking advantage of both NMG's ability to handle wide ranges of radioactivity, as well as its stock of various nuclear materials. The group is currently collaborating with Purdue University to develop neutron detectors based on the interaction of neutrons with tensioned fluids (fig. 3). The fluids are tensioned centrifugally (centrifugally tensioned metastable fluid detectors or CTMFD) or they are tensioned acoustically (acoustically tensioned metastable fluid detectors or ATMFD)

The goal of the project is to develop neutron detectors with the sensitivity of He-3 based Bonner Sphere type neutron detectors but at the cost of only a couple hundred US dollars [4-7]. NMG is currently collaborating with a consortium of universities to generate new waste forms to encapsulate various actinides and fission products [8-11]. NMG is collaborating with Florida International University to generate next generation extractants for radiological waste treatment purposes.

3. – The Nuclear Measurements Group Radiochemistry Program

The NMG has an extensive radiochemistry program, conducting 5,000 to 30,000 radiochemical analyses a year supporting SRS radiological processes as well as other customers' characterization needs in the DOE complex. Analyses are customized to the customer's data quality objectives. Analyses for well over 100 radioisotopes have been performed. Radioactivity levels of samples range from environmental, to high activity waste, to hundreds of grams of special nuclear materials such as plutonium. Requests often come in for isotopes to be measured at sub-Bq levels in the presence of radioisotopes 10 orders

Fig. 3. – From left to right CTMFD, He-3 (Ludlum 30-7B), ATMFD.

of magnitude more radioactive. For high dose matrices requiring remote handling, the NMG has access to the SRNL Shielded Cells facility. The SRNL Shielded Cell Facility consists of 16 6x6 foot workstations with shielding designed to be able to remotely handle materials with dose rates up to 100 Sv/h.

For sample matrices low enough in radiological dose to be handled directly, the NMG has 5 sample preparation laboratory modules consisting of 3 gloveboxes, 9 radiological hoods, and 6 radiobenches. The gloveboxes can handle several hundred grams of plutonium-239 equivalent special nuclear material. Samples having contact dose rates up to 15 mSv/h, whole body dose rates at 30 cm of 0.1mSv, and alpha and beta levels up to 1.67E+08 Bq can be routinely handled in the radiobenches and radiohoods. Levels above that require an ALARA (As Low As Reasonably Achievable) review prior to execution of the task.

There are four instrumentation lab modules available to conduct instrumental analyses. There are sixteen gamma spectrometers of various types available to support the radiochemistry program. Some examples of the available detector types follow. Two Changer Labs robotic sample changers are equipped with 50%relative efficient coaxial HPGe gamma spectrometers for routine analyses. One Changer Labs robotic sample changer is equipped with a 70%relative efficient, Mirion LabSOCSs modeled HPGe well gamma spectrometer which provides high detection efficient analyses on small aliquots of sample. A Mirion robotic Gamma Analyst is available to count large volume samples in Marinelli beaker geometries. A high efficiency (140%relative efficiency) HPGe stand-alone detector is also modeled with Mirion LabSOCS. The laboratory has four low-energy gamma spectrometers equipped with either beryllium or carbon composite

windows to measure x-ray or low energy gamma emissions.

For production alpha spectrometry applications, 36 solid-state alpha silicon detectors in Mirion technologies Alpha Analyst systems, or in Canberra Quad Alpha systems are available. In addition to the routine alpha spectrometer systems there are 32 environmental-level alpha spectrometers. There are also 100 spectrometers maintained in standby mode.

The modules have 4 available liquid scintillation counters; a Perkin Elmer Quantulus GCT 6220 system for ultra-low-level analyses, a Perkin Elmer Tri-Carb 5110 TR for production analyses, and a HIDEX 300SL and 600 SL for applications requiring superior alpha/beta discrimination or triple coincidence liquid scintillation counting. For gross alpha and beta counting applications, the laboratory also has several Gamma Products and Mirion Alpha/Beta gas flow proportional counters.

The radiochemistry laboratory has two neutron irradiation sources available for various applications. The sources are used to generate radiological tracers for the radiochemistry program as well as for neutron activation analysis (NAA). The SRNL Cf-252 NAA facility was once stocked with up to 200 mg of Cf-252. The most recent Cf-252 charge was a 50mg source added to its inventory in 2002. It is currently down to less than 1mg of Cf-252, with thermal neutron fluxes available up to 5E6 n/s/cm2. To augment the capabilities of the decaying Cf-252 source, an Adelphi Technology (D,D) neutron generator was recently installed. The neutron generator has thermal neutron fluxes of up to 2.5E7 n/s/cm2. For higher fluxes, when needed, SRNL make use of collaborations with university research reactors.

Supporting the Radiochemistry laboratory there are also multiple non-nuclear analytical instruments, including quadrupole and triple quadrupole ICP-MS as well as ICP-AES instrumentation available.

4. – Tank Closure Processes and NMG Radiochemistry Methodologies

These SRS waste treatment processes have been established to empty and close the 51 legacy SRS waste tanks. Once a waste tank's bulk components of salt and sludge waste have been removed from the waste tank, but before tank closure, the residues of the waste tank must be characterized to establish the radiological inventory being grouted in place and left in South Carolina. A performance assessment is conducted for each tank being closed. Each waste tank's inventory is unique. The different purposes of the two separation canyons resulted in two different radiological compositions being discharged into the F and H tank farms. The Site also conducted a number of boutique isotope production campaigns, and the residue discharges went to certain waste tanks. The chemical processes also varied between the two canyons. For example, H-Canyon used significant quantities of mercury as a catalyst in the digestion process of the aluminum fuel cladding. There were also records of transfers of waste between the tank farms, as they made space for more waste. These histories are studied to generate a performance assessment of the waste tank being closed. From the performance assessment, a list of radioisotopes requiring quantification, and their required detection limits, is generated.

From 2010–2016, six waste tanks were characterized and then operationally closed by being filled with grout. The first tanks in the series to be characterized, starting in 2010, were Tanks 18F and 19F. These were type IV tanks, of which four were constructed at SRS between 1953 and 1963. Type IV tanks were single walled tanks with no installed cooling capability, each with a storage capacity of 4.9 million liters. The tank residues in Tanks 18F and 19F were a mineral zeolite type material, with conventional SRS type

H-3	C-14	Ni-59	Ni-63	Co-60	Se-79
Sr-90	Y-90	Tc-99	Sn-126	Sb-126	Cs-135
Cs-137	Ba-137m	Sm-151	Eu-152	Eu-154	Eu-155
Th-229	Th-230	U-232	U-233	U-234	U-235
U-236	U-238	Np-237	Pu-238	Pu-239	Pu-240
Pu-241	Pu-242	Pu-244	Am-241	Am-242m	Am-243
Cm-243	Cm-244	Cm-245	Cm-247	Cm-248	Cf-249
Pa-231	Ra-226	Pm-147	Ac-227	Al-26	Zr-93
Nb-94	I-129	Cl-36	K-40	Pd-107	Pt-193m

Fig. 4. – Typical radioisotope suite requested for tank closure campaigns.

sludge mixed in. To clean the tanks and remove as much residual material as possible, grinders were lowered into the tanks to grind and vacuum material out of the tanks. Tank 19F residues were 5E7 Bq/g beta, 3.3E4 Bq/g alpha.

The second set of tanks to be characterized and closed were Tanks 5F and 6F. These were Type 1 tanks, built between 1951 and 1953. Type 1 tanks are double-walled tanks, cooled with an extensive network of cooling coils. Each tank had a capacity of 2.8 million liters. These tanks were cleaned with a chemical cleaning treatment, unlike the mechanical cleaning of Tanks 18F and 19F. The tanks were cleaned with an oxalic acid based chemical cleaning. Oxalic acid dissolved a large volume of the non-radiological materials in the tanks, significantly reducing volumes. It was less effective in dissolving some of the radiological constituents such as Sr-90. As a result, Tanks 5F and 6F residues were substantially more radioactive than Tanks 18F and 19F. Tank 5F was nominally 8.5E8 Bq/g beta, and 5E5 Bq/g alpha. Tank 6F was nominally 1.2E9 Bq/g beta and 5E5 Bq/g alpha.

Unlike the previous tanks, Tank 16H was an H-Tank Farm tank, so was filled by H canyon processes. This tank was a Type II tank, built between 1955 and 1956. This tank was a double-walled tank, cooled like the Type I tanks. Type II tanks had a capacity of 3.8 million liters. Tank 16H had begun to leak into its annulus in the 1980s, and the tank was emptied and aggressively cleaned at the time. Most of the radioactive sludge residue had migrated out of the primary tank and into the annulus. For the closure campaign, the residues in the primary tank consisted of rusted coil elements, scattered across the floor of the tank, coated in high activity sludge, making a rather unique material type for a tank closure project. The primary tank residues were roughly 2.2E8 Bq/g beta, 5E5 Bq/g alpha. The annulus was 1.5 Bq/g beta, 1.5E5 Bq/g alpha.

The final tank to be closed as part of this campaign of 6 tanks was Tank 12H, a Type 1 tank. Tank 12H did not have any chemical cleaning performed. Tank 12H also had an unusual history in that it had deposits from some of the experiments the Site had conducted using thorium fuel. As a result, the cooling coils and tank floor were coated in mercury from the H Canyon spent nuclear fuel dissolving process. Also, the solid residues in this tank were roughly 7 weight percent thorium.

Characterization methods were initially designed for Tanks 18F and 19F, but the methods had to continually evolve for the remaining tanks due to their unique matrices. Figure 4 contains a typical list of isotopes for which measurements were requested. The bulk of this list was fairly constant across this program; however some isotopes were added while others were removed for each individual tank. A brief summary of the methodology used for the isotopes follows.

Sample preparations. – Initial sample digestions were conducted either in the SRNL Shielded Cells facility or in radiohoods, depending on the dose rates. Sample aliquots were initially digested by a pressurized mixed-acid digestion for certain volatile radionuclides such as tritium, Se-79, Ni-59, Ni-63, and Tc-99. As the tank residues varied from tank to tank, the mixed-acid recipe also changed. For the Tanks 18F and 19F, with the zeolite residues, the mixed-acid used was an HF/HNO3 mixture. For the other tanks, the mixed-acid was aqua regia. For the non-volatile analytes, *i.e.*, the actinides, lanthanides, Sr-90, etc., the initial digestions were conducted using an alkali fusion digestion. As these matrices were so different, and no time was allocated in these programs for method development, every separation was traced with a chemical or radiotracer to confirm analyte chemical recoveries. Each batch underwent a redox treatment to ensure the oxidation and chemical states of the tracers and the analytes were identical, when necessary. Adjustments were made to the radiochemistry protocols, as needed, to meet program data quality objectives. Batch QC consisting of method blanks and spikes were included. Program data quality objectives and documentation requirements for each tank campaign were defined with all of the program stakeholders prior to initiation of analytical work. Overviews of the radiochemistry methodologies used are covered in the following sections.

Gamma Counting for Cs-137/Ba-137m and Gamma Counting following Cs-137 Removal for Co-60, Eu-152, Eu-154, Eu-155, Am-241, Al-26, Nb-94, K-40. – The gamma spectra of these waste forms are dominated by Cs-137. Cs-137 and its radiological daughter Ba-137m are directly measured using HPGE gamma spectrometers on aliquots of digestion. Other isotopes' gamma emissions are either obscured by the Cs-137 gamma continuum, or dilutions required due to the high levels of Cs-137 in the sample reduce the sensitivity of the gamma analysis below DQOs for those isotopes. To measure the non-Cs gamma-emitting isotopes, a Cs-removal process is conducted on aliquots of the alkali fusion digestion. Aliquots are treated with two separate batch additions of a Bio-Rad industries ammonium phosphomolybdate (AMP) resin to selectively remove the Cs-137. The Cs-removed aliquots are then assayed on HPGe spectrometers. Radiochemistry can be conducted to isolate/concentrate isotopes in cases where DQOs have not been meet by this approach.

H-3. – Tritium analyses are conducted using aliquots of the mixed-acid digestions. Tritiated hydrogen oxide is separated from radiological interferences using a steam distillation process. Aliquots of distillate are added to liquid scintillation cocktail and analyzed by liquid scintillation analysis. The liquid scintillation counters are calibrated with tritium quench curves.

C-14. – Organic and inorganic carbon species in tank residues are oxidized to carbon dioxide using a process involving sulfuric acid catalyzed with silver nitrate wet ashing. The liberated carbon dioxide is captured either directly onto an amine (Perkin Elmer Carbosorb), or is absorbed in sodium hydroxide, liberated by acidification and re-captured

on Carbosorb. The Carbosorb is added to liquid scintillation cocktail and analyzed by liquid scintillation counters calibrated with C-14 quench curves.

59/Ni-63. – Aliquots of pressurized mixed acid-digestion are spiked with a stable nickel chemical carrier. Ni species are then extracted from the sample matrix with a solid-state nickel dimethylglyoxime complexation using Eichrom Technologies' Nickel Resin cartridges mounted on vacuum boxes. Each cartridge run typically removes roughly 3 orders of magnitude of radiological interferences, so for matrices such as these waste tank residues, the separation is run thru two cycles of extraction to get the necessary purification. An aliquot of nickel extract is mounted on a planchet and analyzed by semiplanar, Be-windowed HPGe low energy gamma spectrometry spectrometers. An aliquot of nickel extract is added to liquid scintillation cocktail and analyzed by liquid scintillation counters calibrated with Ni-63 quench curves. An aliquot of nickel extract is analyzed by ICP-AES to measure the chemical recoveries.

Se-79. – The methodology used was detailed in [12]. Aliquots of pressurized mixed-acid digestion are spiked with a stable Se-79 chemical carrier. Selenium is initially reduced, precipitated as selenium metal, and the precipitate washed. The selenium is further purified using a tributyl phosphate extraction following a digestion of the metal. Aliquots of selenium extract are added to LSC cocktail and analyzed by LSC counting with a C-14 quench curve, which has a beta endpoint similar in energy to Se-79. An aliquot is also analyzed by neutron activation analysis to determine selenium chemical recoveries which are then applied to the radiometric Se-79 analysis.

Sr-90/Y-90. – Aliquots of each sample from the alkali fusions are spiked with stable Sr carrier and a stable Ce carrier. The Sr carrier is used for separation yielding purposes and the Ce carrier is used to enhance the separation rates of undesirable isotopes such as Y-90, the lanthanides or the actinides. The Sr in the samples is extracted using commercially available crown ether solid state resin (Eichrom Sr Resin). This resin also extracts some of the Pu under the conditions used to extract the Sr; therefore, the Pu is washed from the resin using an oxalic acid/nitric acid mixture. The Sr is eluted from the resin, and the resulting solution concentrated. An aliquot of the purified Sr solution is neutron activated in a Cf-252 neutron activation facility at SRNL to determine the strontium chemical recovery. A second aliquot of each of the Sr fractions is stored for five to seven days to allow for Y-90 in-growth. Each fraction is then counted by liquid scintillation analysis to determine the Y-90 activity, which is used to calculate the Sr-90 beta activity. The yields of the stable Sr carriers are applied to the Sr-90 beta activity results to determine Sr-90 activities in the original aliquots of the solutions.

Tc-99. – The methodology used is detailed in [13]. Ammonium molybdate is activated in the SRNL Cf-252 NAA facility to generate Mo-99. The resulting Tc-99m is extracted from the dissolved, activated ammonium molybdate. Aliquots of pressurized mixed-acid digestion are spiked with the Tc-99m tracer and oxidized to the pertechnetate form with nitric acid. The technetium is then extracted from the matrix using two stages of a quaternary amine-based solid phase extraction (Eichrom TEVA resin). The final TEVA extraction uses TEVA in a disc form; the disc then being added to liquid scintillation cocktail. The LSC vials are initially counted on well geometry gamma spectrometers to measure the short-lived Tc-99m, which is used to calculate recoveries. The short-lived Tc-99m is allowed to decay and the Tc-99 is then measured using liquid scintillation counters calibrated with Tc-99 standards.

Cs-135. – All reagents used are purified of cesium and barium with a pre-treatment using crystalline silico titanate. Cs-135 is extracted from aliquots of mixed-acid digestion using spherical resorcinol formaldehyde resin. The resin is prewashed with deionized water to remove any cesium or barium interferences. The extracted cesium is analyzed by mass spectrometry to measure cesium masses 133, 135, 137. The initial gamma-measured Cs-137 value is multiplied with the Cs-135/Cs-137 activity ratio measured by mass spectrometry to determine the sample's Cs-135 concentration.

Sm-151, Pm-147. – The methodology used is detailed in [14]. Aliquots of each sample from the alkali fusions are spiked with a stable Sm carrier. The spiked sample aliquots are initially oxidized using nitric acid. The Sm and Pm, along with other trivalent species in the samples, are extracted using Eichrom RE resin. The Sm and Pm are then extracted from the other radionuclides present using Eichrom Ln resin. A portion of the purified Pm/Sm solution is neutron activated in a Cf-252 neutron activation facility at SRNL to determine the total Sm and to calculate the fraction of Sm isolated by the procedure. A second portion of each of the Pm/Sm fractions is then counted by liquid scintillation analysis to determine the Pm-147 and Sm-151 activity. The Pm-147 measurement is conducted using a higher energy beta window which is free of any interference from the low-energy Sm-151 beta. The Sm-151 beta result is corrected for any Pm-147 events occurring in its beta counting window when necessary. The yields of the stable Sm carriers are applied to the Sm-151 and the Pm-147 beta activity results to determine Sm-151 and Pm-147 activities in the original aliquots. A Pm-147 spiked sample is run through the process to monitor and correct for any slight differences in the chemical recoveries of Sm and Pm.

Th-229, 230, Ac-227. – Aliquots of each sample from the alkali fusions are run through a thorium separation procedure. The Th species are extracted from the matrix using two stages of a quaternary amine-based solid phase extraction and purified further via co-precipitation with cerium. Th-229 and Th-230 concentrations are measured using passivated, implanted, planar silicon (PIPS) alpha spectrometers. The Th separation is yielded by measuring the Th-232 activities in the separated fractions, and comparing those activities to the Th-232 concentrations measured directly from aliquots of digestion by the ICP-MS. The Th-232 yields are used to correct the various analytes for any Th losses from the radiochemical separations.

U-232, 233, 234, 235, 236, 238. – U-238 and U-235 concentrations are initially measured by ICP-MS on diluted aliquots of alkali fusion digestions. To lower detection limits for the minor uranium isotopes , aliquots of digestion are purified with a diamyl, amylphosphonate DAAP based solid phase extraction (Eichrom UTEVA). The purified aliquots are analyzed by the ICP-MS to measure U-233,234, 236 to U-238 mass ratios. Aliquots of uranium extract are also co-precipitated and analyzed by alpha spectrometry to measure U-232/U-238 ratios. The ratios are then applied to U-238 concentrations measured by the ICP-MS directly on aliquots of digestion to quantify the minor uranium isotope concentrations.

Np-237. – Aliquots of each sample from the alkali fusions are spiked with a Np-239 tracer. The Np species are extracted from the sample matrix using two stages of a quaternary amine based solid phase extraction (Eichrom TEVA). An aliquot of extract is analyzed for Np-239 by gamma spectrometry to determine Np chemical recovery. An aliquot of extract is measured by ICP-MS to determine Np-237 concentrations. The Np

yields from the Np-239 measurements are applied to the Np-237 measurements to correct for any Np losses from the radiochemical separations.

Pu-238, 239, 240, 241, 242. – Pu-238 and the sum of Pu-239+Pu-240 are measured by alpha spectrometry following a solvent-solvent 2- thenoyltrifluoroacetone (TTA) extraction procedure. Aliquots of sample digestion are first spiked with a Pu-236 tracer. The plutonium extracts are analyzed by alpha spectrometry, and the recoveries of the Pu-236 tracers are applied to quantify the Pu-238 and Pu-239+Pu-240 activities in the sample. The Pu species are also extracted from the sample matrix using two stages of a quaternary amine based solid phase extraction (Eichrom TEVA). Aliquots of plutonium extract are assayed by liquid scintillation analysis to determine the ratio of Pu beta (Pu-241) to the plutonium alpha. That ratio is applied to the total plutonium alpha measured from the TTA analysis. An aliquot from the TEVA extraction is also analyzed by ICP-MS to measure the long-lived plutonium isotopes (Pu-242, 244) as well as to determine the Pu-239 and Pu-240 activities.

Am, Cm, Cf isotopes. – This method is used for Am-241, Am-242m, Cm-242, Am-243, Cm-243, Cm-244, Cm-245, Cm-246, Cm-247, Cm-248, and Cf-249. Of these isotopes, the Am-241 can be easily and accurately analyzed directly by extended gamma counting of the dissolved sludge. For the other radionuclides listed above, a separation method has been developed for isolating Am, Cm, and Cf. Tank residues are digested in the Shielded Cells with an alkali fusion. The trivalent actinides are then extracted from the digestion filtrate using a commercially available ion exchange resin (Eichrom DGA). As Y-90 coextracts with the trivalent actinides on DGA resin, the treated samples were held in the Shielded Cells for nine days to allow the Y-90 to decay before they are removed and submitted for analysis. The solutions are purified further with a second RE resin extraction followed by an Eichrom Ln resin extraction. The Am, Cm, Bk, and Cf extracts are then analyzed by alpha and low energy gamma counting techniques as well as by ICP-MS. The radionuclides Cm-242, Am-242m, and Cm-244 are measured by alpha spectroscopy. Am- 241, Am-243, Cm-243, and Cf-249 are measured by low-energy gamma spectroscopy. Cm-245, Cm-246, Cm-247, Bk-247, and Cm-248 are measured by ICP-MS. The fraction of each actinide element isolated by this ion exchange technique is determined by comparing the measured concentrations of Am-241 in the eluted solutions with their respective concentration in the original dissolved slurry that was measured by direct gamma counting of Cs-137-removed aliquots of the dissolved material.

Pa-231. – Aliquots of each sample from the alkali fusions are run through a Pa separation procedure traced with Pa-233 tracer. The aliquots are decontaminated with AMP to improve the clean-up from Cs-137, avoiding jeopardizing the Pa-233 tracer measurement. Protactinium species are then extracted from the matrix using an octanol-based solid phase extractant (Triskem Technologies Tk400 resin). Pa-233 tracer concentrations are measured using high purity germanium spectrometers to determine separation yields. Pa-231 is measured using the ICP-MS. The Pa-233 tracer yields are decay corrected and then used to correct the Pa-231 analyses for any losses from the radiochemical separations.

Ra-226. – This method is detailed in [15]. Aliquots of alkali fusions are decontaminated with a number of resin treatments. Radium is extracted from the matrix using an Empore-Radium-Disk-based extraction. Sample aliquots matrix-spiked with Ra-226 are also run through the procedure for chemical yielding purposes. The disks containing

extracted radium are then analyzed three days following the extraction and 14 days following the extraction to allow for daughter ingrowth. Sample Ra-226 results are corrected with matrix spike recoveries.

Zr-93. – Aliquots of alkali fusion digestions are spiked with Zr-95 tracer. Samples are decontaminated of Cs-137 with an AMP resin treatment. Samples are also decontaminated of Nb-93 with an anion exchange clean-up. Zirconium is extracted with a octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO)/tributyl phosphate (TBP) based solid-phase extraction (Eichrom Technologies RE resin). The Zr extract is analyzed by gamma spectrometry to determine Zr-95 chemical recoveries. The Zr extract is then analyzed by ICP-MS to determine Zr-93 concentrations.

I-129. – Aliquots of as-received residues are spiked with a known amount of stable KI to act as an iodine tracer/carrier. The samples are digested with 8M nitric acid. The traced samples are then rendered caustic, precipitating out the actinides, lanthanides, Sr-90 and Y-90, among some other radioactive species. MST is added to further decontaminate the caustic digestions from Sr-90, Y-90, the actinides and the lanthanides. CST is added to reduce levels of Cs-137. The treated solutions are filtered, and the decontaminated filtrate is then removed from the Shielded Cells for further work in the laboratory. The samples are decontaminated a final time with a resin treatment to remove Cs-137 and the actinide elements. The solution is then treated with AgNO3 to precipitate the iodide ion as AgI. The precipitate is analyzed by low energy photon spectrometry to determine the amount of I-129 present. I-129 is detected by its characteristic gamma and x-ray emissions. The precipitate is then neutron activated in a Cf-252 neutron source at SRNL to determine the total amount of iodine present in order to calculate the recovery of I-129 in the radiochemical separation.

Cl-36. – Aliquots of aqua-regia digestion are initially rendered caustic and subjected to two Monosodium Titanate (MST) and Crystalline Silico-Titanate (CST) based decontamination steps. The resins and insoluble elements (*i.e.*, Actinides, lanthanides, strontium and yttrium) are filtered off, decontaminating the solution. The solutions are then acidified with nitric acid and further decontaminated with Bio-Rad AMP and Eichrom Diphonix resins. The Cl in the samples is subsequently precipitated as AgCl. The AgCl precipitate is counted using gas flow proportional counter analysis. The AgCl precipitate is then activated by neutron activation analysis to determine Cl losses during the processes. The HCl used to digest the samples initially is used to trace Cl-36 throughout the processes. The chlorine yields are used to correct Cl-36 results for any losses.

Pd-107. – Aliquots of each sample from the aqua regia digestion are spiked with elemental Pd. Pd is then extracted from the samples using a DMG based extractant (Eichrom Technologies Nickel Resin). Pd-107 levels are measured using the ICP-MS, and the results are yielded from stable Pd recoveries as measured by the ICP-MS.

193m. – Aliquots of alkali fusions are spiked with a platinum chemical carrier. A Bio-Rad AMP strike is conducted to reduce Cs-137 levels. Platinum is extracted from the sample matrix using two stages of a quaternary amine based solid phase extraction (Eichrom TEVA). An aliquot of extract is analyzed for Pt-193m by low energy gamma/x-ray spectrometry to measure Pt-193m concentrations. An aliquot of extract is measured by ICP-AES to determine Pt chemical recovery.

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