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Radioanalytical Technology for 10 CFR Part 61 and Other Selected Radionuclides

Literature Review

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Operated by
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Prepared for
U.S. Nuclear Regulatory Commission

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Abstract

A comprehensive literature review and assessment was conducted to identify and evaluate radioanalytical technology and procedures used for measuring 10CFR61 radionuclides and other long-lived isotopes. This review evaluated radiochemical procedures currently in use at a number of laboratories in the US, as well as identifying new advanced methods and techniques which could be adapted for routine radiochemical analyses of low-level radioactive waste. The 10CFR61 radionuclides include ^{14}C, ^{60}Co, $^{59,63}Ni$, ^{90}Sr, ^{94}Nb, ^{99}Tc, ^{129}I, ^{137}Cs, and TRU Isotopes with half-lives greater than five years. The other low-level radionuclides of interest include $^{7,10}Be$, ^{26}Al, ^{36}Cl, ^{93}Mo, $^{109,113m}Cd$, and $^{121m,126}Sn$, which may be present in various types of waste streams from nuclear power stations.

Contents

Figures

Tables

Summary

Since promulgation of 10 CFR Part 61 ("Licensing Requirements for Land Disposal of Radioactive Waste") in 1982, other long-lived radionuclides not specified in Part 61 have been identified which may be of concern in activated metal wastes and perhaps other waste streams going to low-level waste disposal facilities. A more comprehensive radionuclide analysis of activated metal wastes is therefore warranted to ensure that these additional radionuclides do not pose a future problem to the protection of public health and safety. Pacific Northwest National Laboratory (PNNL) will analyze several reactor waste samples for the 10 CFR Part 61 and additional long-lived radionuclides. Several of these additional long-lived radionuclides are gamma emitters and will be determined by measurement of their characteristic gamma ray energies (e.g., ^{108m}Ag, ^{133}Ba, and ^{152,154,155}Eu). However, the remainder decay primarily by low-energy emissions and require radiochemical separations prior to measurement. Appropriate scaling factors for these additional long-lived radionuclides also will be calculated, if they are measured in radioactive waste in significant quantities.

To ensure that PNNL's radioanalytical procedures for these analyses incorporate the latest methodology, a review of the literature was completed. This review was based primarily on an extensive survey of literature pertaining to the radiochemical analyses of 10 CFR Part 61 radionuclides and several additional hard-to-measure, long-lived radionuclides (^{10}Be, ^{36}Cl, ^{93m}Nb, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, ^{121m}Sn, and ^{126}Sn). Procedures and technology currently being used by various laboratories for analysis of reactor wastes are presented, as are other chemical and radiochemical procedures with potential for application to reactor waste analyses. Summaries of PNNL radioanalytical procedures for 10 CFR Part 61 and the additional long-lived radionuclides, as well as references to procedures that might be further adapted to analysis of reactor waste, are included as appendices.

1 Introduction

The technical requirements for disposal of low-level radioactive waste, as specified in the Code of Federal Regulations, 10 CFR Part 61 ("Licensing Requirements for Land Disposal of Radioactive Waste"), necessitate that low-level radioactive waste be characterized and classified before disposal. Waste classification involves the quantification of specified radionuclides (Tables 1.1 and 1.2) in the waste materials to comply with disposal requirements and site performance objectives.

In practice, nuclear power generating stations comply with 10 CFR Part 61 requirements by initially analyzing sufficient samples from each waste stream to demonstrate that concentrations of controlled radionuclides are consistently within error limits set by Part 61, over time, within each waste stream. For subsequent waste disposed of from a waste stream, Part 61 allows the use of scaling factors, derived from the initial analyses, to calculate estimates of the concentrations of the specified, hard-to-measure radionuclides. For calculation of subsequent estimates, the nuclear power stations analyze, onsite, periodic samples from the waste streams for the gamma-emitting radionuclides (e.g., ^{60}Co being representative of activation products and ^{137}Cs being representative of fission products). These qualitative analyses are combined with measurements of waste container dose rates, using hand-held meters, to calculate the gamma-emitting radionuclide inventories within the container using various techniques such as point kernel shielding codes. Each predetermined radionuclide scaling factor is then multiplied by the measured concentration of the appropriate gamma-emitting radionuclide to estimate the concentration of the hard-to-measure radionuclides in the waste being disposed of. The scaling factors for each waste stream are reevaluated annually by commercial laboratory radiochemical analyses of typical samples.

For a number of radionuclides (e.g., ^{14}C, ^{129}I, and ^{99}Tc), the scaling factors used in the nuclear power industry have been overly conservative because the scaling factors were based either primarily on "less-than" values corresponding to the lower limits of detection of the analytical methods used by the commercial laboratories performing the analyses or, alternatively, on a few samples having unusually high concentrations of these radionuclides. These conservative assumptions have not generally influenced the classification status of the waste, but do artificially increase the inventories of ^{129}I and ^{99}Tc within waste containers and, subsequently, the total estimated inventories of these nuclides at disposal sites. The total disposal site inventories of these radionuclides are often the controlling factors for the total quantities of radioactive waste permitted in a low-level waste shallow-land burial facility. Thus, an overly conservative estimate of the concentrations of these isotopes in low-level waste could lead to premature closure of a disposal facility. It is therefore critical that waste generators use the most accurate scaling factors possible.

Since promulgation, by the Nuclear Regulatory Commission (NRC), of 10 CFR Part 61 on December 27, 1982, additional long-lived radionuclides (Table 1.3) have been identified that may be of concern in activated metal wastes and perhaps other wastes going to low-level waste disposal facilities. A more comprehensive radionuclide analysis of activated metal wastes is therefore warranted to ensure that these additional radionuclides do not pose a future problem to the protection of public health and safety. Appropriate scaling factors for these additional long-lived radionuclides will be calculated if they are measured in radioactive waste in significant quantities.

To ensure that radioanalytical procedures used by the Pacific Northwest National Laboratory (PNNL)[1] for these analyses incorporate the latest methodology, a review of the literature was completed. This review was based primarily on an extensive survey of literature pertaining to the radiochemical analyses of 10 CFR Part 61 radionuclides and several additional hard-to-measure, long-lived radionuclides (i.e., ^{10}Be, ^{36}Cl, ^{93m}Nb, ^{93}Mo, ^{108m}Ag, ^{113m}Cd, ^{121m}Sn, and ^{126}Sn). These radionuclides are not listed in Tables 1 or 2 of 10 CFR Part 61, but are anticipated as present in nuclear power station waste streams, and may be of concern for land disposal of low-level radioactive waste. Several of these additional long-lived radionuclides are gamma emitters and will be determined by measurement of their characteristic gamma ray energies (e.g., ^{108m}Ag, ^{133}Ba, and ^{152,154,155}Eu). However, the remainder decay primarily by low-energy emissions and require radiochemical separations before measurement.

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[1] Operated for the U.S. Department of Energy (DOE) by Battelle Memorial Institute.

Table 1.1. Radionuclides in Table 1 of 10 CFR Part 61

Nuclide	Half-life (years)	Primary production mode	Principal waste materials
^{14}C	5730	$^{14}N(n,p)^{14}C$ $^{17}O(n,\alpha)^{14}C$	activated metals (AM) dry solids dry active waste (DAW) dewatered resins
^{59}Ni	75000	$^{58}Ni(n,\gamma)^{59}Ni$	AM resins
^{94}Nb	20300	$^{93}Nb(n,\gamma)^{94}Nb$	AM (Inconel, steel)
^{99}Tc	2.13×10^5	$^{98}Mo(n,\gamma)^{99}Mo$ fission	resins activated Inconel dry solids DAW
^{129}I	1.57×10^7	fission	resins dry solids DAW
Alpha TRU		activation	resins, filters, control rod blades, burnable poison rods, resins, DAW, sorbed liquids, dry solids
^{241}Pu	14.4	$^{238}U(n_x \text{ capture})^{241}Pu$ $^{239}Pu(n_x \text{ capture})^{241}Pu$	resins, filters, control rod blades, burnable poison rods, resins, DAW, sorbed liquids, dry solids
^{242}Cm	0.446	$^{241}Pu\ (\beta^- \text{ decay})\ ^{241}Am$ $^{241}Am(n,\gamma)^{242}Am(\beta^-)\ ^{242}Cm$	resins, filters, control rod blades, burnable poison rods, resins, DAW, sorbed liquids, dry solids

Table 1.2. Radionuclides in Table 2 of 10 CFR Part 61

Nuclide	Half-life (years)	Primary production mode	Principal waste materials
^{3}H	12.3	^{6}Li(n,α)^{3}H	dry solids, burnable poison rods, aqueous liquids
		^{2}H(n,γ)^{3}H	water
^{60}Co	5.27	^{59}Co(n,γ)^{60}Co	activated metals (AM), resins, filters, dry solids
^{63}Ni	100.1	^{62}Ni(n,γ)^{63}Ni	AM, resins, filters
^{90}Sr	28.5	fission	resins, DAW
^{137}Cs	30.0	fission	resins, DAW, filters

Table 1.3. Additional radionuclides expected in low-level radioactive waste

Nuclide	Half-life (years)	Primary production mode	Probable waste materials
^{10}Be	1.6×10^{6}	^{10}B(n,p)^{10}Be	B_4C control rods, water
^{36}Cl	3.01×10^{5}	^{35}Cl(n,γ)^{36}Cl	activated concrete, DAW, burnable poison rods
^{93m}Nb	13.6	^{93}Nb(n,n')^{93m}Nb	activated steel, Inconel
^{93}Mo	3500	^{92}Mo(n,γ)^{93}Mo	activated steel, Inconel
^{108m}Ag	127	^{107}Ag(n,γ)^{108m}Ag	Ag-Cd-In control rods
^{113m}Cd	13.7	^{113}Cd(n,n')^{113m}Cd	Ag-Cd-In control rods
^{121m}Sn	55	^{120}Sn(n,γ)^{121m}Sn	activated Zircaloy, resins
^{126}Sn	1×10^{5}	^{124}Sn(n,γ)^{125}Sn(n,γ)^{126}Sn	activated Zircaloy, resins
^{133}Ba	10.54	^{132}Ba(n,γ)^{133}Ba	burnable poison rods, B_4C
^{151}Sm	90	^{150}Sm(n,γ)^{151}Sm	burnable poison rods, B_4C
^{152}Eu	13.33	^{151}Eu(n,γ)^{152}Eu	burnable poison rods, B_4C
^{154}Eu	8.8	^{153}Eu(n,γ)^{154}Eu	burnable poison rods, B_4C
		^{152}Sm(n,γ)^{153}Sm(β^-) ^{153}Eu(n,γ)^{154}Eu	burnable poison rods, B_4C
^{155}Eu	4.96	^{154}Sm(n,γ)^{155}Sm(β^-)^{155}Eu	burnable poison rods, B_4C

PNNL will analyze each reactor sample for all the 10 CFR Part 61 and additional long-lived radionuclides (see Appendix A for a summary of PNNL's radioanalytical procedures).

For this survey, the Hanford Technical Library used two major literature search vendor services that maintain hundreds of data bases from a broad scope of disciplines: Dialog Information Services, Inc. (Dialog) and STN International (STN), in addition to reviewing book catalogs and CD ROMs. Data bases accessed in Dialog include the following:

- **National Technical Information Services (NTIS)**
  - government-sponsored research, development, and engineering, plus analyses prepared by federal agencies, their contractors, or grantees
- **Compendex Plus**
  - machine-readable version of *The Engineering Index*, which provides abstracted information from the world's significant literature of engineering and technology
- **Energy Science and Technology (formerly DOE Energy)**
  - one of the world's largest sources of literature references on all aspects of energy and related topics
- **Nuclear Science Abstracts**
  - comprehensive abstract and index collection of all aspects of international nuclear science and technology literature
- **Analytical Abstracts**
  - covers all aspects of analytical chemistry
- **Chemical Abstracts Search**
  - citations from the literature of chemistry and its applications; contains the basic bibliographic information appearing in the printed volumes of *Chemical Abstracts* (no abstracts available).

Databases accessed in STN include the following:

- **File CA - Chemical** Abstracts
  - covers all areas of chemistry and chemical engineering worldwide (STN, unlike Dialog Chemical Abstracts Search, offers an abstract with most of these records)
- **Analytical Abstracts**
  - covers worldwide literature on analytical chemistry including abstracts for documents reported in the printed volumes of *Analytical Abstracts*.

The search was limited to the period from 1980 to the present. Where appropriate, documented procedures used by individual laboratories were included if they contained unusual chemical separation and/or instrumental methods applicable for measurement of radioisotopes of interest in nuclear power station waste streams. However, commercial laboratory radiochemical analytical procedures are often considered proprietary and thus not referenceable. Thus, this literature review is not presented as being complete or exhaustive.

2 Procedures and Technology Currently Being Used for Radiochemical Analysis of Reactor Wastes

The following compilation summarizes current procedures and technology, in use by several laboratories, that are applicable to the analysis of various types of nuclear wastes for the 10 CFR Part 61 radionuclides and for additional long-lived radionuclides that may be present. The compilation is listed alphabetically by element of interest.

2.1 Aluminum-26

PNNL has measured ^{26}Al in borosilicate glass from a burnable poison rod by instrumental analysis. A triple coincidence gamma ray spectrometric technique is used that measures both 511-keV gamma photons from positron annihilation and the 1809-keV gamma photon. This technique greatly improves the selectivity and sensitivity for the measurement of ^{26}Al (Lepel et al. 1994).

2.2 Americium-Curium

Los Alamos National Laboratory (LANL) has measured americium and curium isotopes by concentrating the lanthanides and actinides using a LaF_3-$La(OH)_3$ precipitation cycle followed by extraction using di-2-ethylhexyl orthophoshoric acid. Final purification of americium and curium is accomplished using anion exchange. Separation of americium from curium is obtained using cation exchange. Americium-243 is used for analytical yield determination, and isotopic concentrations are determined using alpha energy spectrometry (Kleinberg 1990).

PNNL has measured ^{241}Am, ^{242}Cm, and ^{244}Cm in a variety of low-level waste and neutron-activated reactor hardware samples. Because of their very similar chemical properties, americium and curium isotopes are separated and purified in a single procedure. The isotopes are coprecipitated with iron hydroxide and then dissolved in strong HNO_3. Plutonium and neptunium are removed from the solution by sorption onto an anion exchange resin. The americium and curium in the effluent solution are then coprecipitated at pH 3.0 using 1 mg of calcium carrier and oxalic acid. The oxalate precipitate, containing the americium and curium isotopes, is separated from the liquid, dissolved in a weak sulfuric acid solution, and electroplated onto a stainless steel disc. Americium-243 is used for analytical yield determination and isotopic concentrations are determined using alpha energy spectrometry (Robertson et al. 1992).

Science Applications International Corporation (SAIC), now Scientech, Inc. has prepared reactor waste samples for americium and curium analysis by fusing the sample. The fusion cake is dissolved in HCl and the transuranic nuclides are coprecipitated with barium sulfate. The barium sulfate precipitate is separated from the liquid, dissolved, and liquid-liquid extractions are performed, thus separating the radionuclides into three groups: U with Th, Pu with Np, and Am with Cm. Each fraction is electroplated and analyzed using a surface barrier alpha-particle detector (Cline et al. 1985).

Thermo Analytic, Inc. (TMA)[1] has separated americium and curium in reactor waste samples. Treatment of the samples with an anion exchange column separates Pu and other species. Am, Cm, and Y carriers are separated as a group by oxalate precipitations and by extraction with the bidentate organophosphorus extractant, dibutyl-N,N-diethylcarbamoylphosphonate (DDCP). Am, Cm, and Y are back extracted into 2 M nitric acid and reduced to a low volume by boiling. Am and Cm, in a mixed alcohol-nitric acid solution, are separated from Y on an anion exchange column. Am and Cm are eluted with 40% 6 M nitric acid—60% methanol followed by 8 M nitric acid. Further purification is obtained using a cation exchange column. Am and Cm are electroplated, and ^{241}Am and ^{244}Cm are measured using an alpha energy spectrometer. ^{243}Am is used as a yield tracer.

2.3 Beryllium-7,-10

LANL has separated ^{7}Be from fission products by extracting the beryllium acetylacetone complex from a solution of disodiumethylenediaminetetraacetate (EDTA), at a pH of 7.7, into CCl_4. This is followed by an anion exchange column separation, NaOH precipitation scavenge, lanthanum fluoride precipitation scavenge, and final precipitation as $BaBeF_4$. Beryllium-7 is measured using gamma-ray spectrometry (Kleinberg 1990).

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[1] Arthur Li, Thermo Analytic, Inc., private communication, February 1992.

PNNL has measured the concentration of ^{10}Be in the borosilicate glass of a burnable poison rod and the boron carbide of a cruciform control rod. Beryllium carrier and ^{7}Be tracer are added to the aliquots of solid samples, the samples are alkali fused, and the residues are dissolved and then precipitated as $Be(OH)_2$. The precipitate is dissolved in dilute nitric acid, adjusted to pH 5, extracted with acetylacetone into chloroform, and back extracted into nitric acid. Beryllium is precipitated as the hydroxide and then as $BaBeF_4$. Beryllium-10 is measured in a scintillation spectrometer (Lepel et al. 1994).

2.4 Cadmium 109,-113m

LANL has separated cadmium isotopes from fission products by scavenging with sequential CdS, acid sulfide, and $Fe(OH)_3$ precipitations. The cadmium, in 4 M HCl, is then placed on an anion exchange resin and eluted with 1.5 M H_2SO_4. The cadmium is converted to the elemental form by electroplating. The isotopes are quantified by counting on an appropriate detector (Kleinberg 1990).

PNNL has measured ^{113m}Cd and ^{109}Cd in the Ag-Cd-In alloy of a spent rod cluster control assembly (RCCA). The solid sample is dissolved in nitric acid and repeatedly scavenged by AgCl precipitations. Cadmium-115 is used as tracer. Cadmium is then extracted from a highly basic solution with dithizone in chloroform, back extracted into HCl, loaded on an anion resin, and washed with 1 M HCl and then with 0.5 M HBr. Cadmium is eluted with 7.5 M NH_4OH and precipitated as the sulfide with thioacetamide, and the cadmium isotopes are beta counted in a liquid scintillation spectrometer (Lepel et al. 1994).

2.5 Carbon-14

PNNL has separated ^{14}C for radiochemical analysis either by acid distillation, in the case of inorganic carbonates, or by oxidation/combustion at high temperatures in the case of organic carbon compounds or carbides. In either instance, the distilled carbon dioxide is trapped in a caustic solution. Analytical yields are determined Carbon-14 is quantified by beta counting in a liquid scintillation spectrometer (Robertson et al. 1992).

PNNL has analyzed for total ^{14}C in irradiated metals, such as Zircaloy cladding and stainless steel components. The method involves total combustion in oxygen in an induction furnace within shielded hot cells, collection of the ^{14}C in NaOH collection bubblers, and measurement by liquid scintillation counting. Yields are determined by using suitable National Institute of Standards and Technology (NIST)-traceable ^{14}C metal standards (Baldwin 1992).

SAIC has separated ^{14}C from liquid and solid reactor samples. Oxidizing distillation techniques are employed for liquid or solid samples, which convert greater than 97% of all carbon species to carbon dioxide. The CO_2 is absorbed in a liquid scintillation cocktail and analyzed for ^{14}C content by liquid scintillation beta counting (Cline et al. 1985).

TMA[1] has separated ^{14}C from solid reactor waste samples by combusting in a furnace and passing the gas stream over a catalyst. Liquid reactor waste samples are distilled from an HCl solution. Both methods collect the ^{14}C as the carbonate and measure the activity in a beta scintillation spectrometer.

2.6 Chlorine-36

LANL has separated chlorine isotopes from fission product samples by scavenging with $Fe(OH)_3$ and AgI precipitations from an ammoniacal solution. AgCl is then precipitated in the presence of EDTA. The chlorine is removed as HCl by treatment with concentrated H_2SO_4. Chlorine is precipitated as mercurous chloride and counted in a beta counter (Kleinberg 1990).

PNNL has measured ^{36}Cl in the borosilicate glass from a burnable poison rod assembly. A glass sample is spiked with ^{38}Cl tracer and alkali fused. The residue is dissolved in acid and the solution is scavenged by ferric hydroxide precipitation. Chlorine is precipitated as silver chloride, and ^{36}Cl is counted in a liquid scintillation spectrometer (Lepel et al. 1994).

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[1] Arthur Li, Thermo Analytic, Inc., private communication, February 1992.

Xinqi, et al. (1991) described the measurement of ^{36}Cl in nuclear power reactor primary coolant water and primary cleanup resin using either liquid scintillation counting (LSC) or accelerator mass spectrometry (AMS). The ^{36}Cl was radiochemically purified in the water samples by ion exchange chromatography or by AgCl precipitations. The ^{36}Cl was separated from the resin samples by a distillation technique.

2.7 Iodine-129

PNNL has measured ^{129}I in reactor samples by separating it onto anion exchange resin. Elution from the resin is achieved by oxidation with NaOCl. Iodine is further purified by solvent extraction using carbon tetrachloride and hydroxylamine-hydrochloride, and is back extracted into a water-sulfite solution. The iodine is then coprecipitated with palladious chloride. Iodine-129 is quantified using a thin-window intrinsic germanium detector through measurement of the xenon x-rays. Iodine-131 is utilized as a yield tracer during the purification procedure (Robertson et al. 1992).

SAIC has separated ^{129}I from liquid and solid reactor waste samples. Aliquots of liquid samples are used for analysis, but solid samples are first dissolved by alkaline fusion to prevent volatilization and loss of iodine. Subsequent solutions are stirred with anion exchange resin in batch form to remove iodine. The iodine is extracted from the resin and liquid-liquid extractions are performed. The purified iodine is precipitated as CuI and counted on a thin-window NaI(Tl) detector (Cline et al. 1985).

TMA[1] has measured ^{129}I in solid and liquid reactor waste. Solid samples are fused with KF, KOH, and K_2CO_3 containing sodium hypochlorite. Iodine is purified by a series of extractions into carbon tetrachloride and toluene. Iodine is then back extracted into water with bisulfite, and ^{129}I is measured using a scintillation counter.

PNNL has also measured ^{129}I in reactor waste samples by neutron activation analysis (NAA) and thermal emission negative ion mass spectrometry (TEMS). Samples are spiked with ^{125}I for chemical yield determination, and liquid samples are concentrated by anion exchange. The anion exchange resin containing the separated iodine is then processed the same as for a solid sample. Solid samples are directly combusted and the iodine in the combustion off-gas is trapped on charcoal. The iodine is volatilized from the charcoal by heating and is collected in a small volume of dilute ammonia solution and then prepared for either NAA or TEMS analysis (Brauer 1989).

2.8 Molybdenum-93

LANL has measured molybdenum isotopes in a fission product mixture by removing Mo^{+6} onto an anion resin column from a 5 to 9 M HCl solution. The resin is washed with a mixture of dilute HCl and HF and with 3 M NH_4OH. Molybdenum is eluted from the column with 6 M $NH_4C_2H_3O_2$, precipitated with alphabenzo inoxime, converted to MoO_3 by ignition, and then counted (Kleinberg 1990).

PNNL has measured ^{93}Mo in activated reactor hardware by scavenging the dissolved sample repeatedly with Fe-Co-Ni-Nb hydroxide precipitates from a weak NaOH solution containing a trace of $NaNO_2$. Molybdenum is then precipitated as lead molybdate. Molybdenum-93 is quantified using a thin-window intrinsic-germanium detector through measurement of the niobium x-rays. The recovery is determined using ^{99}Mo as yield tracer. Since ^{93}Mo and ^{93m}Nb decay emitting x-rays of identical energy, ^{95}Nb was added as a tracer to ensure that no ^{93m}Nb is carried through the procedure (Lepel et al. 1994).

2.9 Neptunium-237

LANL has separated ^{237}Np from fission product mixtures by extracting the neptunium from 1 M HCl using 0.5 M thenolytrifluoroacetate (TTA) in xylene. Neptunium is stripped from the organic phase with 8 M HNO_3. Further purification is accomplished by anion exchange resin columns. Neptunium is loaded onto the column from a 12 M HCl solution, is washed with 12 M HCl—0.06 M HF, and then with an HI-HCl solution. Neptunium is eluted with 6.5 M HCl—0.004 M HF and electroplated, and then ^{237}Np is measured using alpha energy spectroscopy (Kleinberg 1990).

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[1] Arthur Li, Thermo Analytic, Inc., private communication, February 1992.

PNNL has separated ^{237}Np from nuclear waste samples onto anion exchange resin from a strong nitric acid solution. The anion column is then washed with strong HCl. Neptunium is eluted using HCl-HF acid, evaporated to dryness with nitric acid, and subsequently electroplated from a dilute sulfuric acid solution. The separated and purified ^{237}Np is quantified using an alpha energy spectrometer. Neptunium-239 is utilized during the separation procedure as a yield tracer (Robertson et al 1992).

SAIC has separated ^{237}Np from reactor waste samples. The sample is dissolved by fusion techniques, the fusion cake is dissolved in HCl, and the transuranic nuclidesare coprecipitated with barium sulfate. The barium sulfate is dissolved and liquid-liquid extractions are performed, separating U with Th, Pu with Np, and Am with Cm. Each of the three fractions is electroplated and analyzed separately using a surface barrier alpha-particle detector (Cline et al. 1985).

TMA[1] has separated ^{237}Np from solutions of reactor waste. Neptunium-239, in equilibrium with ^{243}Am, is added as yield tracer to a liquid aliquot and adjusted to 8 N HNO_3. The solution is oxidized and passed through an anion column. The Np is eluted with dilute HCl. Neptunium is then carried on an $Fe(OH)_3$ precipitate, dissolved in HCl, and extracted into a benzene—TTA solution. Neptunium is back extracted with 8 N HNO_3, evaporated, and electroplated. The Np yield is determined by counting the ^{239}Np beta activity on a low-background beta counter.

2.10 Nickel-59,-63

LANL has separated nickel radionuclides from fission products by precipitating with dimethylglyoxime from an ammoniacal medium in the presence of citrate ion. The Ni-dimethylglyoxime is then extracted into chloroform, back extracted into dilute HCl, electroplated, and counted on an appropriate detector (Kleinberg 1990).

PNNL has separated nickel radionuclides from reactor waste by successive steps of chelating iron with citric acid and precipitating the nickel as dimethylglyoxime. The final dimethylglyoxime precipitate is weighed and mounted for measurement of the ^{59}Ni x-rays with a low-energy gamma spectrometer. The precipitate is then carefully dissolved in nitric acid and taken to dryness. The residue is dissolved in weak HCl and prepared for beta counting in a liquid scintillation spectrometer for ^{63}Ni. Yields are determined gravimetrically (Robertson et al. 1992).

SAIC has separated ^{59}Ni and ^{63}Ni from reactor waste samples. Solid samples such as sludge and resins are dissolved with mixed strong acids. Aliquots of the dissolved solids or of the liquid samples are taken for analysis. Nickel is separated from contaminating radionuclides by precipitating $Fe(OH)_3$ with NH_4OH. Nickel remains in solution as an ammonium complex. Further decontamination is accomplished by specific precipitations of Ni with dimethylglyoxime (Ni-DMG).

The complex is dissolved and the organic destroyed with 1:1 HNO_3:$HClO_4$ and by heating to dryness. The salts are dissolved and volumetrically diluted to 10 mL. Yield is determined by atomic absorption. The ^{63}Ni is determined by liquid scintillation counting; the ^{59}Ni activity is measured using a thin-window NaI(Tl) detector (Cline et al. 1985).

TMA[1] has separated ^{63}Ni from reactor waste samples using a multi-step purification procedure which includes precipitation and extraction of the dimethylglyoxime complex into benzene, and back extraction into HCl solution. The Ni-DMG precipitate is corrected for yield by gravimetric means and then dissolved in a cocktail for counting by liquid scintillation spectrometry. Counting efficiency is determined by spiking techniques. Chemical purification for ^{59}Ni is similar to that for ^{63}Ni. The Ni is then electrodeposited on a copper disc, weighed for yield, and counted on a thin NaI(Tl) detector for x-ray spectrometry.

2.11 Niobium-93m,-94

LANL has separated niobium from fission products by scavenging with $Ba(ZrF_6)$, then extracting the niobium cupferron derivative into $CHCl_3$ from a boric acid—1 M HCl solution. The $CHCl_3$ is destroyed by digesting in H_2SO_4-HNO_3 solution and the niobium is precipitated as the basic hydrous oxide. The precipitate is dissolved in sulfuric acid and scavenged with a sulfide precipitation. Niobium is finally precipitated as the cupferrate, ignited, weighed, and counted on an appropriate detector (Kleinberg 1990).

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[1] Arthur Li, Thermo Analytic, Inc., private communication, February 1992.

PNNL has measured ^{94}Nb and ^{93m}Nb in neutron-activated reactor hardware, after dissolution of the metal sample, by precipitation of niobic oxide in concentrated nitric acid. Both stable niobium carrier and ^{95}Nb tracer are added during the separation. Niobium-94 is measured by gamma-ray spectrometric techniques while ^{93m}Nb is determined by measuring the niobium x-rays Using a thin window intrinsic germanium detector. Yields are determined by measuring the ^{95}Nb tracer by gamma-ray spectrometry (Robertson et al. 1992).

SAIC has separated ^{94}Nb from solid and liquid reactor wastes. Solid samples, such as sludge or resins, are dissolved or leached with mixed strong acids. Aliquots of the dissolved solid or liquid samples are taken for analysis. Carrier is added and niobium is precipitated with NH_4OH. Washing the precipitate with hot nitric acid provides some decontamination. Niobium is dissolved; cobalt and barium are used to scavenge contaminants. The solution containing niobium is further purified by elution from an anion exchange column. Niobium is precipitated as the oxide and ^{94}Nb is measured by gamma ray analysis using a Ge detector (Cline et al. 1985).

TMA[1] has separated ^{94}Nb from reactor waste samples. The samples are vigorously dissolved in strong acids (e.g., HF, HNO_3) with addition of Nb and Zr carriers. Zirconium is scavenged by precipitating $BaZrF_6$. Then Nb_2O_5 is precipitated, and dissolved as the oxalate complex, and Nb_2O_5 is again precipitated. The oxide is dissolved in fuming H_2SO_4, followed by a $BaSO_4$ precipitation scavenge. The niobium is absorbed on an anion exchange column and eluted as the oxalate complex. Nb_2O_5 is again precipitated, ignited, and weighed for yield. Niobium-94 is counted either on a beta counter or is analyzed on a germanium detector by gamma-ray spectrometry.

2.12 Plutonium-238,-239,-240,-241

LANL has measured $^{239-240}$Pu in fission products by separating plutonium onto anion exchange resin from nitric acid media. Plutonium is eluted from the resin with an HI-HCl solution and electroplated for counting. Plutonium-236 is used as a yield tracer and $^{239-240}$Pu is measured with an alpha energy spectrometer (Kleinberg 1990).

PNNL has measured ^{238}Pu, $^{239-240}$Pu, and ^{241}Pu in reactor waste samples by separation onto anion exchange resin from a nitric acid media. Plutonium isotopes are eluted from the resin with a hydrochloric acid—ammonium iodide solution. The plutonium is electroplated from a dilute sulfuric acid solution onto a stainless steel disc. Plutonium-242 is used as a yield tracer, and $^{239-240}$Pu and ^{238}Pu are determined by alpha energy spectrometry. Plutonium isotopes are then dissolved from the disc and the solution is measured for beta activity from ^{241}Pu in a liquid scintillation spectrometer (Robertson et al. 1992).

SAIC has separated plutonium from solid and liquid reactor waste samples. The sample is dissolved by a fusion technique. The fusion cake is dissolved in HCl and the transuranic nuclides are coprecipitated with barium sulfate. The barium sulfate is dissolved and liquid-liquid extractions are performed, separating U with Th, Pu with Np, and Am with Cm. Each of the three fractions is electroplated and analyzed using a surface barrier alpha-particle detector. A fraction of the separated Pu is counted in a liquid scintillation counter. Plutonium-241 is counted in the tritium energy window, and alpha-emitting $^{238-239}$Pu is counted in the energy window above tritium. Plutonium-236 tracer yield is determined from the ratio of ^{236}Pu to total alpha/plutonium and is applied to the liquid scintillation alpha count (Cline et al. 1985).

TMA[1] has separated plutonium in reactor waste samples from an 8 N HNO_3 solution using anion exchange resin. Plutonium is eluted from the resin with HF-HNO_3 acid solution. The anion exchange column is repeated, adding an HCl wash, and Pu is eluted with a solution of hydrochloric acid and ammonium iodide. The eluate is reduced to a low volume and electroplated from an ammonium sulfate electrolyte (pH 2, 1.2 amps, 30 min) onto a stainless steel disc. Plutonium is counted in an alpha spectrometer.

2.13 Strontium-90

LANL has separated ^{90}Sr from other fission products by successive fuming nitric acid precipitations. The precipitate is dissolved and scavenged with $BaCrO_4$ precipitation, and strontium is precipitated as the carbonate. After an ingrowth period, ^{90}Sr is then calculated from the separated ^{90}Y daughter measurements. Yields are determined gravimetrically (Kleinberg 1990).

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[1] Arthur Li, Thermo Analytic, Inc., private communication, February 1992.

PNNL has separated ^{90}Sr from reactor wastes by consecutive precipitations of basic carbonates followed by precipitation in fuming nitric acid. After an ingrowth period, an ^{90}Y separation is performed, and ^{90}Sr is calculated from the separated ^{90}Y daughter measurements. Strontium-85 is used as a yield tracer, and is counted by gamma-ray spectrometry (Robertson et al. 1992).

SAIC has separated ^{90}Sr from solid and liquid reactor waste samples. Solid samples, such as sludge and resins, are dissolved or leached with mixed strong acids. Aliquots of the dissolved solids or liquid samples are taken for analysis. A combination of precipitation and scavenging techniques is used for decontamination. Yttrium is separated and strontium is precipitated as the carbonate and counted. A 2-week ingrowth period is allowed before the carbonate is dissolved and the yttrium is separated, purified, and counted. The ^{90}Sr concentration is derived from ^{90}Sr beta counting (Cline et al. 1985).

TMA[1] has measured ^{90}Sr in reactor waste samples by adding ^{85}Sr as a tracer and purifying by $Sr(NO_3)_2$ precipitations, followed by $Fe(OH)_3$ and $Ba(CrO_3)$ scavenge precipitations. The oxalate is precipitated and dissolved, and $SrCO_3$ is precipitated and counted for ^{85}Sr. After an ingrowth period, ^{90}Y is removed by sequentially precipitating as the hydroxide, fluoride, and oxalate. The oxalate is ignited to the oxide and weighed for yield. Yttrium-90 is counted in a low-background beta counter and confirmed by radioactive decay measurements.

2.14 Technetium-99

PNNL has separated ^{99}Tc from reactor waste with repeated iron hydroxide coprecipitations followed by coprecipitation with rhenium carrier, using tetraphenyl arsonium chloride reagent. Technetium-99 is quantified using a thin-window beta proportional counter. Absorption curves are determined for all samples to confirm the presence of ^{99}Tc. Technetium-95 is used as a tracer for analytical yield (Robertson et al. 1992).

SAIC has measured ^{99}Tc in solid and liquid reactor wastes. Rhenium is substituted for technetium as a carrier. Aliquots of liquid samples are used for analyses. Solid samples are dissolved by alkaline fusion to prevent volatilization and loss of technetium. The fused salts are dissolved in 8 M HNO_3 and the solution is boiled to remove iodine. Cobalt is repeatedly used as a precipitation scavenging agent to remove radiocobalt and other multiple distillation of tritium oxide and beta measurement in a liquid scintillation spectrometer (Robertson et al. 1992).

PNNL has measured total tritium in Zircaloy cladding and other metals which are nonvolatile at 2600°C. The method uses a LECO Impulse resistance furnace, transition metal radionuclides. The Re(Tc) is precipitated as a complex with tetraphenyl arsonium chloride, by Model EF-10. The sample is melted in a graphite crucible in the furnace for 2 to 3 minutes in a flowing stream of 6% hydrogen in helium. The gas stream is routed through a hot copper oxide column to convert tritium gas to water. This tritiated water is collected in a bubbler trap and the carrier gas is routed back into the cell. Tritium is measured by liquid scintillation counting (Baldwin 1989).

SAIC has separated tritium from liquid reactor waste samples. Tritium is separated and purified from activation and fission product activities by distillation. An alkaline permanganate solution is used to provide an oxidizing environment. The halogens and other elements are rendered nonvolatile and remain in the oxidizing solution. The purified tritium is collected as the distillate. The tritium is beta counted in a liquid scintillation counter (Cline et al. 1985).

TMA[1] has measured tritium in reactor waste solid and liquid samples. Solid sample aliquots are combusted in a tube furnace and an O_2 gas stream is passed over a CuO catalyst. Tritiated compounds are converted to tritiated water (HTO). The product is collected as water in a dry ice—methanol cold trap. The HTO is distilled from the cold trap, and measured aliquots of distillate are added to a scintillant and counted on an automatic liquid scintillation spectrometer. The efficiency is determined by internal spiking. Liquid samples are distilled in the presence of appropriate hold-back carriers from a slightly basic solution. The condensate is weighed, hold-back carriers are added, and the distillation is repeated. A scintillant is added and the sample is counted as above.

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[1] Arthur Li, Thermo Analytic, Inc., private communication, February 1992.

2.15 Liquid Scintillation

PNNL has recently installed a new liquid scintillation spectrometer for beta measurements of ^{241}Pu, ^{3}H, ^{14}C, ^{63}Ni, and in some cases other low- energy x-ray and beta-emitting isotopes. Background count rates for ^{3}H and ^{241}Pu are about 4 counts per minute (cpm), while background for ^{14}C is 14 cpm and for ^{63}Ni is 10 cpm.

Resolution for a 75-keV e^- is about 18 keV full-width-at-half-maximum-peak-height (fwhm), while for the 624-keV e^- of ^{137}Cs, resolution is about 50 keV. The spectrometer has a system for separating alpha pulses from beta, gamma, or e^- pulses. Alpha pulse resolution (fwhm) varies from about 300 keV for ^{238}U to about 400 keV for ^{241}Am (Lepel et al. 1994). See Figures 2.1 and 2.2 for examples of spectra from this spectrometer.

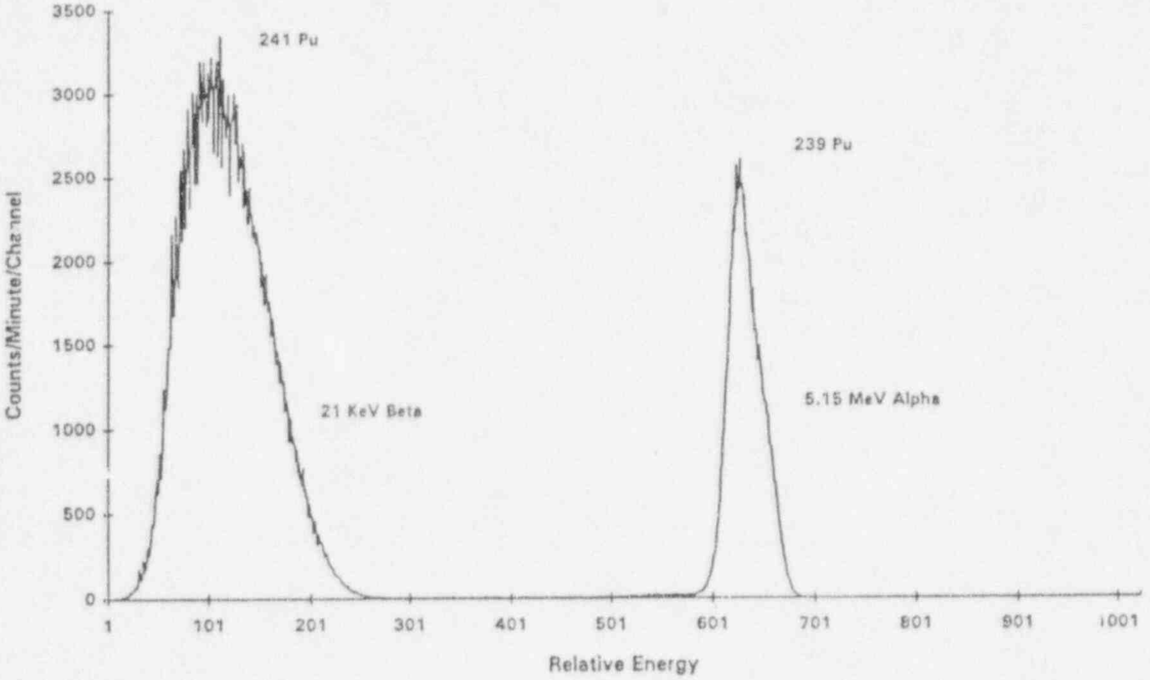

Figure 2.1. Liquid Scintillation Spectrum Showing Separation of ^{239}Pu Alpha and ^{241}Pu Beta

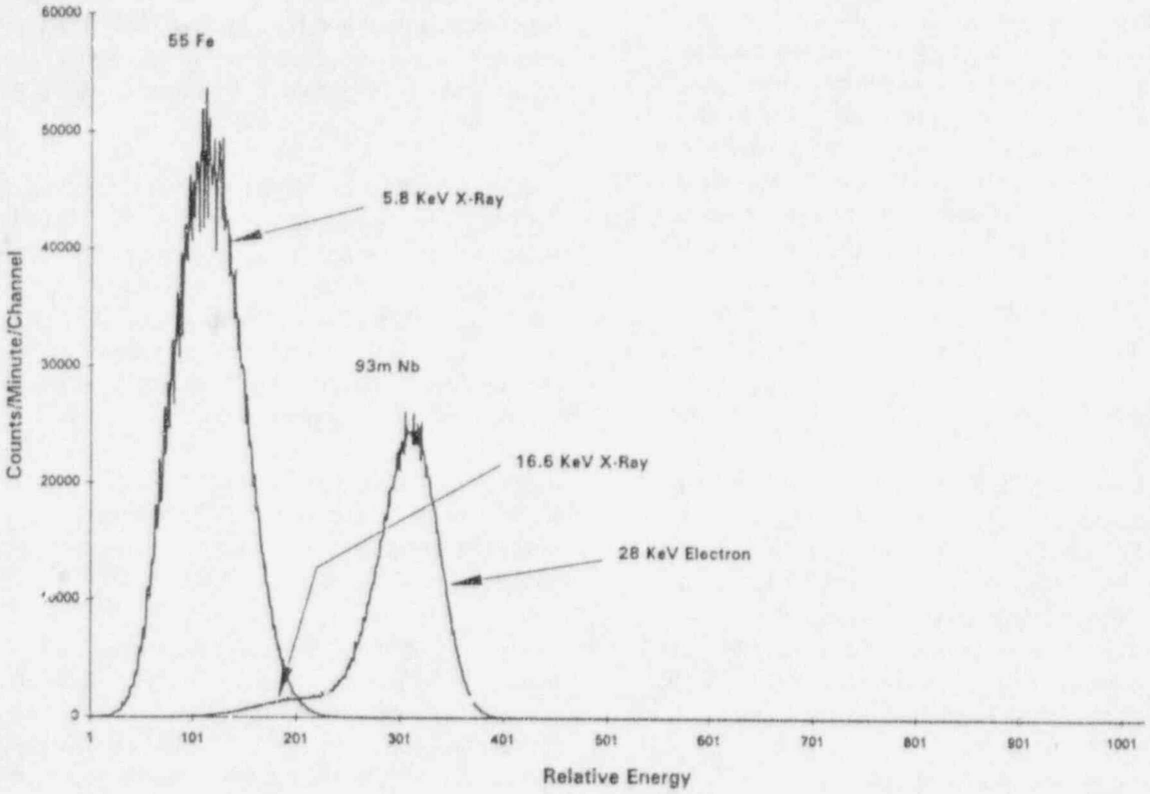

Figure 2.2. Composite Liquid Scintillation Spectrum Showing 5.8 keV x-ray from ^{55}Fe and 28 keV Electron from ^{93m}Nb

3 Recent Chemical and Radiochemical Procedures Potentially Applicable for Reactor Waste Analysis

In nearly all the references cited for possible use in updating currently used chemical separations methods, sample matrices discussed were different from those associated with nuclear power station radioactive wastes. A referenced procedure was chosen for inclusion in this section of the review if the procedure showed merit in separating certain radioactive isotopes or in separating certain stable elements. Also, procedures were cited if they showed a very high selectivity, as measured by their distribution coefficients, or large decontamination factors. These promising improvements should be investigated and tested for application to, and improvement of, current procedures for nuclear power station waste analyses. Additional procedures that may be adaptable to the analysis of reactor wastes are cited in Appendix B.

3.1 Aluminum

Kohl and Nishiizumi (1992) separated aluminum from purified quartz samples by first removing iron and titanium from 10 M HCl using Dowex-1™ anion exchange resin. Aluminum was then extracted into CCl_4 from a pH 6 solution containing acetylacetone and then back extracted into HCl. Aluminum was separated from beryllium using type AG-50 cation resin. Aluminum-26 was measured using an accelerator mass spectrometer.

3.2 Americium-Curium

Bochkarev et al. (1988) extracted americium and curium with butyric acid in the presence of sulfosalicylic acid from a sample of pH 1-2 that contained large amounts of Al, Fe, Mg, Ca, Ba, Ti, K, and Cr. Plutonium, U, Th, and Np were removed using anion exchange elution techniques.

Grigor'eva and Kravtsova (1990) separated americium and curium using cation exchange resin from a 2 M HNO_3 salt-free solution. Americium-curium were eluted with 5 M HNO_3. By combining the foregoing with anion exchange, the researchers were able to isolate Am-Cm from soil and environmental samples with decontamination coefficients of 1500 from Fe, 2000 from Ca, 10 from nonferrous metals, 1×10^6 from U-Pu-Np-Ra, 1×10^5 from Th, and 1000 from Po.

3.3 Beryllium

Itoh (1986) separated beryllium from seawater and sediments by extracting the Be into methylisobutylketone with acetylacetone from a buffered solution of EDTA and ammonium acetate. The extraction was carried out in the presence of EDTA to prevent iron and aluminum from extracting.

Kohl and Nishiizumi (1992) separated beryllium from purified quartz by first removing iron and titanium from 10 M HCl with Dowex-1 anion exchange resin, then extracting from a pH 6 solution containing acetylacetone into CCl_4, and then back extracting into HCl. Beryllium was separated from aluminum using type AG-50 cation exchange resin. Beryllium-10 was measured using an accelerator mass spectrometer.

Rigin (1984) separated beryllium from coal, ash, air, and water samples by extracting the Be into trifluoroacetylacetone in benzene from an acetate buffer solution containing 0.02 M EDTA.

Vin and Khopkar (1988) quantitatively extracted beryllium from 0.01 M hydrochloric acid on a silica gel column impregnated with bis(2-ethylhexyl)phosphoric acid. Strontium, Ba, Co, Ni, Cu, Al, and Mo were not retained on the column. Beryllium was stripped from the column with 1 M hydrochloric acid.

3.4 Cadmium

Aznarez et al. (1987) extracted cadmium with diethyldithiocarbamate into chloroform from pH 11-12 aqueous media containing potassium cyanide and potassium phosphate.

Lesny et al. (1988) extracted cadmium with diphenyl thiocarbazone at pH 9 into $CHCl_3$. Cadmium was back extracted into a buffered pH 2 solution, leaving cobalt in the organic phase.

3.5 Carbon-14

Braun et al. (1980) showed that, for design of analytical procedures for the analysis of samples from reactor waste, the chemical form of the carbon in the waste is an important consideration. The researchers found that in boiling

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™ Registered trademark of The Dow Chemical Co., Midland, Michigan water reactors (BWRs) more than 95% of the ^{14}C is emitted as $^{14}CO_2$, while in pressurized water reactors (PWRs) greater than 90% of the ^{14}C is released as $^{14}CH_4$ and $^{14}C_2H_6$.

Kilius,[1] of ISOTRACE Laboratory, measured ^{14}C in CO_2, water, and organics using an accelerator mass spectrometer.

Knowles (1979) distilled ^{14}C as CO_2 from both inorganic and organic dissolved compounds from reactor primary coolant water by using persulfate at neutral pH catalyzed with silver ion. The CO_2 was precipitated as calcium carbonate, dried, weighed, and slurried in Insta-Gel™ scintillation cocktail and the ^{14}C was beta counted in a liquid scintillation spectrometer. This study showed most of the ^{14}C was associated with organic compounds.

Kunz (1985) found, at two PWRs, that the majority of the ^{14}C found was in the form of organic hydrocarbon gases. Ion exchange resins removed very little of the organically bound ^{14}C. However, at a BWR, >90% of the ^{14}C was inorganically bound. The organic-bound ^{14}C wash was separated by a gas chromatograph, and the ^{14}C was determined on each fractional cut.

Saas (1991) compared three methods for ^{14}C measurements on resin samples using 1) pyrolysis techniques with constant oxygen flow, 2) acid digestion with H_2SO_4-$HClO_4$, and 3) combustion with oxygen in a closed system. The third method was considered the best technique and required only a few minutes for analysis.

3.6 Chlorine-36

Kramer and Joseph (1984) separated ^{36}Cl from raw urine by scavenging the sample with $Fe(OH)_3$ precipitation and barium sulfate precipitation. The sample was acidified and ^{36}Cl was removed as AgCl. Chlorine-36 was measured using a gas proportional beta counter.

Beasley, et al. (1992, 1993) have reviewed accelerator mass spectrometric (AMS) methods for determining ^{36}Cl in natural waters and have measured ^{36}Cl in groundwaters near the Savannah River Site, and the Idaho National Engineering Laboratory. The ^{36}Cl is purified by AgCl precipitations prior to quantification by AMS.

3.7 Iodine-129

Brauer (1989) compared four methods for measuring ^{129}I in various types of samples: 1) direct gamma counting, 2) neutron activation analysis (NAA), 3) thermal emission negative ion mass spectrometry (TEMS), and 4) accelerator mass spectrometry (AMS). These last three methods (NAA, TEMS, and AMS) are at least a factor of 10^6 times more sensitive than beta, gamma, or x-ray counting methods; the AMS method is the most sensitive.

Kuleff, Zotschev, and Stefanov (1986) measured ^{129}I in 1 L of primary coolant by extraction into CCl_4 followed by back extraction into water containing Li_2SO_3, precipitation of PbI_2, irradiation in a nuclear reactor, and measurement of the ^{130}I produced from the neutron activation of ^{129}I.

Mann and Beasley (1994) measured ^{129}I in groundwaters from the Snake River Plain Aquifer and near the Idaho National Engineering Laboratory using accelerator mass spectrometry and prior radiochemical purification by AgCl precipitation. This technique could be readily modified for analysis of reactor low-level wastes.

3.8 Molybdenum; Mo-93

Ejaz and Mamoon (1987) separated molybdenum from fission products using a 0.1 M solution of 4-(5-onyl)pyridine in benzene. The fission product solution was made 0.1 M H_2SO_4 in 0.1 to 1.0 M potassium thiocyanate. Molybdenum extraction coefficients of $>10^3$ were attained. Molybdenum was back extracted into 1.0 M nitric acid.

Kapauan and Zuleta (1975) concentrated and separated molybdenum from large amounts of iron in steel samples using methylisobutylketone-8-hydroxyquinoline mixture from an H_2SO_4 solution of pH 1.5. Yields varied from 93 to 102 %.

Mok and Wai (1984) separated molybdenum from a solution of seawater, at a pH of 1.4, using a 2:1 mixture of ammonium pyrrolidinedithiocarbamate (APDC) and

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[1] L. R., Kilius, ISOTRACE Laboratory, private communication, October 1991.

™Insta-Gel is a Registered Trademark of Packard Instrument Co., Meriden, Connecticut.

sodium diethyldithiocarbamate (NaDDC) containing chloroform. Evaluation of the procedure with seawater spiked with molybdenum, natural seawater, and NBS[1] Standard River Water showed the extraction was quantitative.

Samudralwar, Lanjewar, and Garg (1987) extracted $^{99}Mo^{+6}$ with tri-n-butyl phosphate (TBP) from 5 M HCl after ^{99}Tc was removed using ethyl methyl ketone from a 5 M NaOH solution.

3.9 Nickel; Ni-63

Danesi et al. (1984) extracted cobalt from nickel using di(2,4,4tri methylpentyl) phosphinic acid [H(DTMPP)] or CYANEX 272. The high selectivity of H(DTMPP) for cobalt over nickel gave a separation factor of $>10^3$.

Kramer (1984) measured ^{63}Ni in urine by precipitating with dimethylglyoxime in the presence of tartaric acid after removal of phosphate interference as iron phosphate. The tartaric acid removed any interference from the relatively large amounts of Mn, Cu, and Co in the sample. Kramer observed a considerable loss of Ni when the Ni-DMG was wet ashed with nitric acid and allowed to go to dryness.

Strebin (1993a) measured ^{59}Ni and ^{63}Ni in Hanford tank samples by complexing iron with ammonium citrate-ammonium hydroxide and passing this solution through a column consisting of 50-mesh polyethane powder impregnated with dimethylglyoxime. After washing the column with ammonium citrate solution, the nickel is eluted with 3 M HNO_3. Nickel is precipitated as the dimethylglyoxime, filtered, washed, dried, and weighed. The filter is counted in a low-energy photon counter for ^{59}Ni. The filter is muffled, the resulting NiO is dissolved, and the solution is counted in a liquid scintillation counter for ^{63}Ni. Yields are determined gravimetrically.

3.10 Plutonium

Chen et al. (1991) significantly increased the recovery of plutonium from large amounts of seawater by controlling valence during the standard anion exchange chromatographic separation for transuranics. These researchers used gram quantities of sodium sulfite and sodium nitrite throughout the procedure to ensure that plutonium was in the proper valence state, and also equilibrated the columns with either a reducing or an oxidizing agent present.

Horwitz et al. (1990) separated plutonium from urine using ^{242}Pu as radiochemical tracer, and coprecipitating the plutonium with calcium phosphate. The precipitate was ashed, dissolved in 10 mL 0.5 M $Al(NO_3)_3$ in 2 M nitric acid and passed through a column of octyl(phenyl)-N,N-diisobuytlcarbamoylmethylphosphine oxide (CMPO) dissolved in TBP supported on an inert substrate (Amberlite XAD-7) that absorbs the plutonium. Plutonium is stripped from the column with 0.01 M ammonium hydrogenoxalate, electrodeposited on a stainless steel disc, and counted on an alpha energy spectrometer.

Joshi (1986) measured Pu in sediment samples by leaching 100-g samples with 8 M HNO_3 containing sodium nitrite. The leachate was passed through an anion column, the column was washed with 8 M HNO_3, and then 10 M HCl, and then Pu was eluted from the column with 4 M HCl. This reduced the uranium contamination. Pu was then coprecipitated with LaF_3 and mounted for alpha energy analysis.

Joshi (1985) coprecipitated plutonium as a fluoride with 100 µg of lanthanum carrier from an acidic solution. The precipitate was mounted on a 0.1- µ-pore membrane filter containing a LaF_3 substrate prepared from 100 µg of lanthanum. Coprecipitation yields were generally quantitative.

3.11 Strontium-90

Dietz et al. (1991) removed ^{90}Sr from urine samples by coprecipitating with calcium phosphate from an ammonium hydroxide solution at neutral pH. The precipitate is ashed and dissolved in 2 M HNO_3 containing 0.5 M $Al(NO_3)_3$. The solution may be passed through a column containing about 1 g of TRU-Spec™ to remove interfering elements and then through a column containing 0.7 g of Sr-Spec™ to remove strontium. Barium is removed from the Sr-Spec™ column with two 5-mL rinses of 9 M $LiNO_3$

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[1] National Bureau of Standards, now the National Institute of Standards and Technology (NIST).

™ Registered Trademark of Eichrom Industries, Inc., Darien, Illinois containing 0.4 M HNO_3. The column is then rinsed with 1.5 mL of deionized water and the strontium is eluted with 4 mL of deionized water into a plastic scintillation vial. Seventeen mL of scintillation cocktail is added to the vial, which is then counted on a Packard 2200 scintillation counter.

Ghods-esphahani et al. (1989) measured ^{90}Sr in environmental samples by directly extracting ^{90}Y from an HNO_3 solution using TBP.

Saas (1991) separated ^{90}Sr from nuclear waste solutions using crown ether, dicyclohexano 18-crown 6 (DCH 18 C6) from a 1 M HNO_3-1 M $LiNO_3$ solution. A 0.1 M solution of crown ether (DCH 18 C6) in 1,1,2,2 tetrachloroethane was used as the solvent. Extraction efficiencies of >99% were attained.

Strebin (1993c) measured ^{90}Sr in Hanford process waste samples by tracing with ^{85}Sr, converting the sample aliquot to 8 M HNO_3, and passing through a Sr-Spec™ resin column [which contains 4,4'(5')-bis(tert-butylcyclohexano)-18-crown-6]. After the column is washed with 8 M HNO_3, Sr is eluted with 0.05 M HNO_3, precipitated as the oxalate, and beta counted. Yield is determined by gamma counting the ^{85}Sr.

Tait, Wiechen, and Behrens (1989) removed ^{90}Sr from 100 mL of milk using a chelating resin (Chelite P) that contains aminomethyl-phosphonate groups, eluted ^{90}Sr from the resin with 2 M HCl, precipitated $SrCO_3$, and removed Ba by extracting with 21-crown-7 in $CHCl_3$ from pH 3-5 solution. Strontium was then extracted into a $CHCl_3$ solution of dicyclohexano-18-crown-6 and back extracted into an aqueous solution of HCl/NaCl/NH_4Cl, and finally precipitated as $SrCO_3$. The procedure gave 93.5% yield and decontamination factors of 31.2 for Ca, 15700 for Y, 32.2 for Ba, and 1.8×10^7 for Cs.

3.12 Technetium-99

Amano (1991) separated ^{99}Tc from molybdenum using a mixed solvent of acetonitrile and 0.04 M acetate buffer containing 5 vol% of 0.5 M tetra-n-butylammonium hydroxide as the mobile phase.

Martin Marrietta Energy Systems (ES&H Analytical Services 1991) extracted ^{99}Tc from a 6 M H_2SO_4 solution containing hydrofluoric acid into TBP. An aliquot of the TBP was added directly to the scintillation solution along with a small amount of stannous chloride to reduce the chemiluminescence and was beta counted in a liquid scintillation spectrometer.

Martin Marrietta Energy Systems (Beverly 1986) extracted ^{99}Tc into methyl ethyl ketone from a potassium carbonate solution containing hydrogen peroxide. The methyl ethyl ketone was evaporated to dryness and the residue was dissolved in 0.1 M HNO_3. This solution was added to a scintillator and the ^{99}Tc was beta counted in a liquid scintillation spectrometer.

3.13 Tin; Sn-121m,-126

Byrne (1977) extracted tin using a double solvent extraction method. Tin was first extracted as the tetraiodide into toluene from a 3.5 M H_2SO_4 +1 M KI solution, and then back extracted into 0.9 M H_2SO_4. The solution was made 4-5 M with acetic acid and 0.5 M HCl, and a small amount of tartaric acid was added. Tin was then extracted with N-benzoyl-N-phenylhydroxylamine in toluene. Yields of 96% were obtained for this dual extraction. ^{121m}Sn was beta counted using liquid scintillation spectroscopy.

Desai and Parthasarathy (1983) extracted tin from a 3.6 M H_2SO_4 solution containing 1 M KI into toluene. The decontamination factor for antimony was greater than 10^5.

Leaf (1987) measured ^{126}Sn in hydrothermal test solutions. The acidified sample was saturated with bromine and passed through a cation (AG-50W, X-8, 100 to 200 mesh, H^+ form) column to remove essentially all cations. After adjusting the column effluent to 6 M HCl, the solution was passed through an anion (AG-1, X-8, 100 to 200 mesh, Cl^- form) column to remove ^{126}Sn. Tin was eluted from the column with 1 M HNO_3 and the eluate measured for ^{126}Sn using a gamma ray spectrometer.

3.14 Transuranics

Strebin (1993b) has separated americium, curium, and plutonium from high-level waste tank samples. Aliquots are spiked with ^{242}Pu and ^{243}Am as yield tracers. The samples are acid leached and the leachate is adjusted to 2 M HNO_3. Iron and ascorbic acid are added to complex and reduce iron to Fe(II) and Np(VI) to Np(IV). A Tru-Spec™ resin column containing octyl(phenyl)-N,N-diiso-

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™ Registered Trademark of Eichrom Industries, Inc., Darien, Illinois.

butylcarbamoylmethylphosphine oxide is equilibrated with 2 M HNO_3 and the sample is passed through.

After the column is washed, americium and curium are respectively eluted with 9 M HCl and 4 M HCl. Plutonium is eluted with 4 M HCl—0.1 M hydroquinone. Small amounts of Nd carrier are added to the plutonium and americium-curium fraction and the fluorides are precipitated and counted by alpha energy analysis.

3.15 Liquid Scintillation

Bickel et al. (1992) demonstrated that pulse shaping analysis (PSA) in liquid scintillation counting, for the separation of alpha and beta pulses, could be used to monitor the alpha activity in primary coolants. The extractive scintillator used was a mixture of trioctylphosphineoxide (TOPO), 2,5-diphenyloxazole (PPO) in toluene, and naphthalene. The first extraction with 4 M HNO_3 removed uranium and plutonium isotopes from the solution. The second extraction, after adjusting to pH 1, removed the americium and curium isotopes. The organic phase was put directly into a scintillating vial and the alpha activity was measured at a PSA value of 135.

Yonezawa et al. (1983) extracted Ni-DMG into xylene for liquid scintillation counting. They reported that xylene is much superior to chloroform as an organic solvent in liquid scintillation counting because of its high emission efficiency and absence of oxygen quenching. The scintillation cocktail they used was 2,5-diphenyloxazole (DPO), which contained 1,4-cis[2-(4-methyl-5-phenyloxazole)]-benzene (DMPOPOP) as a wave shifter.

3.16 Gamma-Ray Spectroscopy

There are numerous computerized programs for handling, identifying, and calculating complex gamma-ray spectra. Individual hardware vendors and laboratories have developed programs which are specially suited to their specific needs. Each of the several technical approaches has its strengths and weaknesses, and all are adequate for their intended application. Additionally, there have been significant advances in the computer hardware used with these programs. These subjects will not be further addressed in this review.

4 New Technology Potentially Applicable for Reactor Waste Analysis

These novel, relatively new or very expensive technologies were included because, like those in Section 3, they are potentially applicable for reactor waste analysis, but because of their unique capabilities, have been separated from those in Section 3.

4.1 Novel Chromatographic Chemicals

Several efficient and selective chromatographic materials have recently been developed for liquid-liquid extraction methods that can be used to isolate various radionuclides from nuclear wastes streams. Much research has focused on the development of a workable acid-side liquid-liquid extraction process for the removal of strontium. Kimura et al. (1977), for example, utilized one of the macrocyclic polyethers (dicyclohexano-18-crown-6) to separate ^{90}Sr from milk. This crown ether was observed as ineffective in highly acid samples, a significant limitation. The extraction was further complicated by the chemistry of the strontium ion itself. Because of the large ionic radius and low charge, the energy associated with bond formation between strontium ions and the crown ether functional groups was not sufficient to completely dehydrate the cation. Thus, extraction into the organic phase resulted in transfer of a strontium complex bearing a number of molecules of water. The net result was poor extraction. Horwitz, Dietz, and Fisher (1991) recently developed a solution to this problem by combining a crown ether with an organic solvent capable of dissolving a substantial amount of water. This approach, using a solution of bis-4,4'(5')-tertbutylcyclohexano-18-crown-6 in 1-octanol, provided the basis for a new process called Sr-Spec™, which has been very successful in isolating strontium from large amounts of calcium. During this same time period, considerable work was being done to find a more suitable acid-side extractant for the transuranic elements. A satisfactory acid-side extraction of all actinides, including trivalent americium, was achieved using a solution of an organophosphorus extractant, octyl(phenyl)-N,N-diisobutylcarbamylmethylphosphine oxide (CMPO), in a paraffinic hydrocarbon containing a moderate amount of a second extractant, TBP, that prevents the formation of a third phase during extraction. This extraction system became the basis for a process called TRU-Spec™. Recently, a higher molarity of carbamylphosphine oxide has been marketed as RE·Spec™ and does retain the higher atomic weight lanthanides more efficiently than TRU-Spec™. A product called UTEVA-Spec™ composed of (diamyl)amyl phosphonate has been marketed for the removal of mainly tetravalent uranium and thorium from acid-side solutions. Also, a new material called TEVA-Spec™ has been marketed and consists of a quaternary ammonium salt of didecyloctylmethylammonium+ and it removes tetravalent plutonium, thorium, and neptunium from acid-side solutions. TEVA-Spec™ has also been used to separate ^{99}Tc from waste samples by eluting technetium from the resin with HNO_3 and measuring ^{99}Tc using an inductively coupled plasma mass spectrometer (ICP-MS). Another group used TEVA-Spec™ to remove ^{99}Tc from a waste sample, then removed the resin into a scintillation vial, added Insta-Gel™, and measured the ^{99}Tc in a scintillation spectrometer (Kimura et al. 1977; Horwitz, Dietz, and Fisher 1991; Spec News 1992-1993).

4.2 ICP-MS

Wyse (1993) prepared a general procedure to supplement the manufacturer-provided operations and instruction manuals for the operation of a Fisons PlasmaQuad (PQ) ICP-MS to analyze several radioisotopes. Controlling software is also provided by Fisons. The ICP-MS has been used to measure ^{99}Tc in aqueous, acidified samples. Samples in other physical forms or matrices were digested, fused, or leached to give acidified solutions. This procedure is applicable to the determination of ^{99}Tc at concentrations $\geq$10 ppt (170 pCi/L). Uranium isotopic concentrations were measured in acidified waste samples at concentrations of $\geq$10 ppt for each isotope (^{238}U, ^{235}U, ^{234}U, ^{233}U, and ^{236}U). Thorium-230,-232 isotopes, ^{237}Np, and ^{239,240,242,244}Pu isotopes have also been measured in acidified samples. Some of these required chemical separations before measurement. Additional isotopes which are presently being considered for application of this technique are ^{129}I, ^{241}Am, ^{243}Am, ^{247}Cm, and ^{248}Cm. Given appropriate chemical separations and aliquot sizes sufficient to give concentrations of about 10 ppt,

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the ICP-MS could also measure such isotopes in reactor hardware as ^{59}Ni, ^{79}Se, ^{93}Zr, ^{93}Mo, ^{94}Nb, ^{107}Pd, and ^{135}Cs.

4.3 Accelerator Mass Spectrometer

The literature review revealed about 50 papers that used the AMS technique for measuring several long-lived radionuclides. Only a few of these papers have been included as a brief overview. Typically, AMS improves sensitivity by several orders of magnitude compared to conventional methods. However, the technique requires extremely expensive instrumentation and has primarily been applied to measurement of the ultra-low concentrations of radionuclides found in environmental samples.

Beasley, et al (1992; 1993) and Mann and Beasley (1994) have reviewed a number of applications of accelerator mass spectrometry for determination of ^{36}Cl and ^{129}I in natural waters and other geochemical media. This technology provides more than adequate sensitivity and selectivity for measuring these radionuclides in low-level wastes from nuclear power reactors, and could be adapted for these samples by minor procedural modifications.

Bertsche et al. (1990) built a small cyclotron (the "cyclotrino"). The initial work emphasized ^{14}C, but measurements of other radionuclides, such as ^{26}Al, ^{10}Be, and ^{3}H, are also possibilities for the cyclotrino.

Davis (1991) suggested that a family of very small spectrometers optimized for tritium and/or radiocarbon could be built in the very near future for about $400K.

Fifield et al. (1991) enhanced AMS detection levels for measuring ^{36}Cl and ^{14}C isotopes through increased accelerating voltage (i.e., from 12 MV to 14 MV) which results in a substantial increase in the yield of ^{36}Cl and ^{14}C ions. In addition, they have implemented an AMS ^{129}I capability.

Fink, Middleton, and Klein (1991) routinely analyzed ^{10}Be, ^{26}Al, and ^{41}Ca in various types of environmental samples using AMS. In addition, they recently experimented with measuring ^{3}H, ^{14}C, ^{36}Cl, and ^{59}Ni by AMS and produced encouraging results.

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Appendix A

Summary of PNNL Radiochemical Procedures for 10 CFR Part 61 and Additional Long-Lived Radionuclides

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Summary of PNNL Radiochemical Procedures for 10 CFR Part 61 and Additional Long-Lived Radionuclides

A.1 Aluminum-26

Aluminum-26 in aliquots of borosilicate glass from burnable poison rods is measured by instrumental analysis. A triple coincident gamma-ray spectrometric technique is used which measures both 511-keV gamma photons from positron annihilation and the 1809-keV gamma photon.

A.2 Beryllium-10

The concentrations of ^{10}Be in aliquots of borosilicate glass from burnable poison rods and boron carbide from cruciform control rods are determined by adding beryllium carrier and ^{7}Be tracer to the aliquots, alkali fusing the samples, dissolving the residues in acid, and precipitating beryllium as the hydroxide. The precipitates are dissolved in dilute nitric acid, adjusted to pH 5, extracted with acetylacetone into chloroform, and back extracted into nitric acid. Beryllium is precipitated as the hydroxide and then as $BaBeF_4$. Beryllium-10 is measured in a beta scintillation spectrometer. Yields are determined by measuring the ^{7}Be tracer in a gamma spectrometer.

A.3 Cadmium-109,-113m

Cadmium-109,-113m are measured in the Ag-Cd-In alloy of rod cluster control assemblies (RCCAs) by treating aliquots of nitric acid dissolutions of the alloy with repeated silver chloride precipitate scavenging steps. The supernates from each aliquot are combined and evaporated to dryness. The residues are dissolved in dilute HBr-nitric acid solution and passed through anion columns. The columns are washed and the cadmium is eluted with 2 M nitric acid. The eluates are evaporated to dryness, the residues are dissolved in NH_4OH and adjusted to pH 8 with HCl/NaOH. Cadmium sulfide is precipitated with thioacetamide, filtered, and dried. Cadmium-109 is determined by gamma spectrometry and ^{113m}Cd is determined by beta absorption counting.

A.4 Carbon-14

Carbon-14, in irradiated metals, is measured by total combustion in oxygen in a LECO induction furnace within shielded hot cells. Carbon-14, in the form of CO_2, is collected in NaOH collection bubblers and measured by liquid scintillation spectrometry. Yields are determined by using suitable NIST-traceable metal standards.

Carbon-14, in ion exchange resin, is measured by total combustion with alcohol at 250°C in a Packard sample oxidizer. Carbon-14, in the form of CO_2, is dried and collected on a Carbo-sorb™ column and counted in a beta scintillation spectrometer.

A.5 Chlorine-36

Chlorine-36, in borosilicate glass from burnable poison rods, is measured by alkali fusing the sample, dissolving the residue in acid, and scavenging with a ferric hydroxide precipitation. Chlorine is precipitated as silver chloride and chlorine-36 is measured in a beta scintillation spectrometer. Yield is determined using ^{38}Cl tracer.

A.6 Iodine-129

Iodine-129 is measured in various reactor samples by absorbing iodine on an anion column from a liquid aliquot of the sample. The ^{129}I is eluted from the column by oxidizing with NaOCl. Iodine is further purified by solvent extraction using carbon tetrachloride and hydroxlyamine-hydrochloride and back extraction into a water-sulfite solution. The iodine is precipitated with palladious chloride, and iodine-129 is determined by measurement of xenon daughter x-rays using a thin-window intrinsic germanium detector. Yields are determined gravimetrically.

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A.7 Molybdenum-93

Molybdenum-93 is measured in reactor hardware samples by scavenging acid dissolution aliquots repeatedly with Fe-Co-Ni-Nb hydroxide precipitates from a weak sodium hydroxide solution containing a trace of $NaNO_2$. Molybdenum is then precipitated as lead molybdate. Molybdenum-93 is determined using a thin-window intrinsic germanium detector through measurement of the niobium daughter x-rays. Yields are determined by using ^{99}Mo tracer.

A.8 Neptunium-237

Neptunium-237 is separated from nuclear waste samples onto anion exchange resin from a strong nitric acid solution. The anion column is washed with strong HCl and neptunium is eluted using HCl-HF acid. The eluate is evaporated to dryness with nitric acid, and neptunium is subsequently electroplated from a dilute sulfuric acid solution. The separated and purified ^{237}Np is quantified using an alpha energy spectrometer. Neptunium-239 is utilized during the separation procedure as a yield tracer.

A.9 Nickel-59,-63

Nickel radionuclides are separated from reactor waste by successive steps of chelating iron with citric acid and precipitating the nickel as dimethylglyoxime. The final dimethylglyoxime precipitate is weighed and mounted for measurement of the ^{59}Ni x-rays with a low energy gamma spectrometer. The precipitate is then carefully dissolved in nitric acid and taken to dryness. The residue is dissolved in weak HCl and prepared for beta counting in a liquid scintillation spectrometer for ^{63}Ni. Yields are determined gravimetrically.

A.10 Niobium-93m,-94

Niobium-93m,-94 are measured in neutron-activated reactor hardware, after dissolution of the metal samples, by precipitation of niobic oxide in concentrated nitric acid. Both stable niobium carrier and ^{95}Nb tracer are added during the separation. Niobium-94 is measured by gamma-ray spectrometric techniques while ^{93m}Nb is determined by measuring the niobium x-rays using a thin window intrinsic germanium detector. Yields are determined by measuring the ^{95}Nb tracer by gamma-ray spectrometry.

A.11 Strontium-90

Strontium-90 is measured in aliquots of dissolved reactor samples using [illegible] as tracer. The sample aliquot is c[illegible] M HNO_3 and passed through a Sr-Spec™ resin column [contains 4,4'(5')-bis(tert-butylcyclohexano)-18-crown-6]. After washing the column with 8 M HNO_3, Sr is eluted with 0.05 M HNO_3, precipitated as the oxalate, and beta counted. Yield is determined by counting the ^{85}Sr in a gamma spectrometer.

A.12 Technetium-99

Technetium-99 is separated from aliquots of dissolved reactor samples using repeated iron hydroxide co-precipitations followed by further co-precipitation, with rhenium carrier, using tetraphenyl arsonium chloride reagent. Technetium-99 is quantified using a thin-window beta proportional counter. Absorption curves are obtained for all samples to confirm the presence of ^{99}Tc. Technetium-95 is used as a tracer for analytical yield.

A.13 Tin-121m,-126

Tin radionuclides are separated from acid dissolutions of reactor samples by extracting with toluene from a sulfuric acid-KI solution, washing with H_2SO_4-KI solutions, and then back extracting into a dilute sulfuric acid solution. Tin-117 is used as tracer for radiochemical yield determinations. Measurement of the Sb x-rays from ^{121m}Sn and the 87.6-keV gamma rays from ^{126}Sn is accomplished using a low-energy gamma spectrometer. The Sb x-rays from ^{121m}Sn are corrected for any contribution from Sb x-rays associated with the decay of ^{126}Sn.

A.14 Transuranics

Isotopes of americium, curium, and plutonium are separated from acid dissolutions of reactor samples. Aliquots are spiked with ^{242}Pu and ^{243}Am as yield tracers. The solutions are adjusted to 2 M HNO_3 and iron and ascorbic acid are added to complex and reduce iron to Fe(II). TRU-Spec™ resin columns containing octyl(phenyl)-N, N-diisobutylcarbamoylmethylphosphine oxide are equilibrated with 2 M HNO_3 and the samples are passed through the columns. After washing the columns, americium and curium are respectively eluted with 9 M HCl and 4 M HCl. Plutonium is eluted with 4 M HCl—0.1 M hydroquinone. Small amounts of Nd carrier are added to the plutonium and americium-curium fractions and the fluorides are precipitated and counted by alpha energy analysis.

A.15 Tritium

Tritium is measured in reactor waste samples of dissolved borosilicate glass, boron carbide, and ion exchange resin by multiple distillation of tritium oxide and beta measurement in a liquid scintillation spectrometer.

Total tritium is determined in Zircaloy cladding and other metals which are non-volatile at 2600°C. The method uses a LECO Impulse resistance furnace, Model EF-10. The samples are melted in a graphite crucible in the furnace for 2-3 minutes in a flowing stream of 6% hydrogen in helium. The gas stream is routed through a hot copper oxide column to convert tritium gas to water. Tritiated water is collected in a bubbler trap and the carrier gas is routed back into the cell. Tritium is measured by liquid scintillation counting.

Appendix B

References to Procedures That Might Be Further Adapted to Analyze Radioactive Wastes

Appendix B

References to Procedures That Might Be Further Adapted to Analyze Radioactive Wastes

B.1 Aluminum-26

Largarde-Simonoff, M., J. Dedieu, S. Regnier, and G. Simonoff, "Separation Chimique Simultanee des Horloges Cosmiques ^{36}Cl, ^{26}Al, ^{10}Be Fornees dans des Cibles de Fer, Titane et Calcium par Protons de Haute Energie," *Radiochemical and Radioanalytical Letters*, 47(1-2):1-10,1981.

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B.5 Carbon-14

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11. ABSTRACT *(200 words or less)*

A comprehensive literature review and assessment was conducted to identify and evaluate radioanalytical technology and procedures used for measuring 10CFR61 radionuclides and other long-lived isotopes. This review evaluated radiochemical procedures currently in use at a number of laboratories in the US, as well as identifying new advanced methods and techniques which could be adapted for routine radiochemical analyses of low-level radioactive waste. The 10CFR61 radionuclides include ^{14}C, ^{60}Co, ^{59,63}Ni, ^{90}Sr, ^{94}Nb, ^{99}Tc, ^{129}I, ^{137}Cs, and TRU Isotopes with half-lives greater than five years. The other low-level radionuclides of interest include ^{7,10}Be, ^{26}Al, ^{36}Cl, ^{93}Mo, ^{109,113m}Cd, and ^{121m,126}Sn, which may be present in various types of waste streams from nuclear power stations.

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