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LA-7372

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A Critical Review of Analytical Techniques for Safeguarding the Thorium-Uranium Fuel Cycle

University of California

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Post Office Box 1663 Los Alamos, New Mexico 87545

LA-7372
UC-15 and UC-83

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Issued: October 1978

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A CRITICAL REVIEW OF ANALYTICAL TECHNIQUES FOR SAFEGUARDING THE THORIUM-URANIUM FUEL CYCLE

by

E. A. Hakkila

EXECUTIVE SUMMARY

Nuclear safeguards is becoming increasingly important in the public acceptance of nuclear energy. This holds true for the thorium-uranium fuel cycle as well as for the uranium-plutonium fuel cycle. Any materials measurement scheme must rely heavily on analytical chemistry both for primary accountability measurements and for calibration of NDA instruments.

The safeguards analytical chemistry needs in a plant designed to reprocess thorium-uranium fuels require highly precise and accurate measurements of uranium as well as plutonium. The ^{233}U (and ^{235}U for first-generation reactor fuel) must be measured with the same care given to plutonium. For fuels diluted with ^{238}U, significant quantities of weapons-grade plutonium will be produced and must be measured accurately.

The approach to reprocessing thorium-uranium fuels will depend on fuel design and utilization philosophy. Fuel can be reprocessed in two separate recovery operations, a Purex plant for first-generation ^{235}U fuel and a Thorex plant for second-generation ^{233}U and blanket fuels, or a single plant can be used for all fuel types. In either case, accountability measurements will be required for uranium and plutonium product as well as feed and waste streams. This is in contrast to conventional LWR fuel reprocessing where stringent safeguards accountability is required only for the plutonium product stream.

In this report it is assumed that fuels were cooled 180 days before reprocessing. For short-cooled fuel another dimension in safeguards measurements would be the accountability of protactinium which would decay to high-purity ^{233}U.

The sample selected for analysis *must* be representative of the bulk material being sampled. In Thorex or Purex reprocessing systems, several effects can alter the sample sufficiently to negate the most carefully conceived and administered analytical plans. In addition to the problems thorium-uranium samples share with plutonium, the high gamma fluxes associated with

reprocessed thorium and ^{233}U product streams will require that all analytical manipulations be performed remotely in shielded facilities. Complex analytical operations performed with manipulators in shielded caves could seriously affect measurement precision and accuracy.

Analytical problems associated with sample heat, radiolytic decomposition of reagents, polymerization, and radioactive sample decay must be considered in both the Purex and Thorex systems. Many of these problems arise from the high radiation fields in the samples, particularly at the dissolver end of the streams where high beta-gamma fluxes are present and at the product end where high alpha-radiation levels characterize the concentrated product solutions. The situation is further complicated by the high gamma-radiation levels resulting from decay daughters in the case of reprocessed ^{233}U and reprocessed thorium. Reagent stability must be considered in all analytical methods applied in high radiation fields. Isotopic decay results in loss of plutonium in storage tanks and formation of impurities that may affect analytical results. Polymeric plutonium formed during reprocessing operations behaves erratically in analytical schemes. Problems in sampling and sample storage associated with high gamma fluxes will persist through the thorium and uranium storage areas for Thorex reprocessing because of the radiation from decay products.

Isotope-dilution mass spectrometry will continue to be a key accountability measurement for both uranium and plutonium in dissolver solutions, not only because of its potential for high precision and accuracy but because isotopic analyses can be correlated with reactor data. Thorium also can be measured using a ^{230}Th spike. Microsampling using a resin bead may permit independent off-site verification of isotopic composition. Electrometric methods for uranium and plutonium measurement will be required for calibration checks of NDA instruments. Plutonium product also can be measured by electrometric titrations. In-line alpha monitors for plutonium and in-line polarography for uranium may be developed for waste-stream measurements but

will be supplemented by spectrophotometric and fluorimetric methods for calibration checks.

Thorium, though not a fissile material, must be measured for accountability checks and to meet NRC and IAEA requirements. Gravimetry and EDTA titrations probably will be the methods of choice. Thorium standard reference materials, certified by the National Bureau of Standards (NBS), are required for an effective accountability program and are being developed.

Automation of instrumentation for remote operation will be necessary for many routine analyses because of the high radiation levels associated with the Thorex uranium and thorium product streams. Much work already has been done in this direction, including the automation of the spectrophotometric determination of uranium and plutonium, potentiometric determination of uranium, controlled potentiometric determination of uranium and plutonium, mass-spectrometric determination of uranium and plutonium, and x-ray fluorescence analysis of all three elements. Remote-sampling techniques and small-sample methods will be important to minimize personnel exposure. In-line methods will be required not only for near-real-time accounting but also for minimizing exposure to personnel.

Most analytical methods for thorium and uranium have been developed and evaluated using the natural elements and for plutonium using weapons-grade material. Additional work is required to ensure that methods are applicable to reprocessed materials without significant loss of precision and accuracy under the radiation and remote operating constraints imposed by the thorium-uranium fuel cycle.

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GLOSSARY

CPC	Controlled potential coulometry
DME	Dropping-mercury electrode
DNNS	Dionyl-naphthalene sulfonic acid
DOE	Department of Energy
EDTA	(Ethylenedinitrilo)-tetraacetic acid
HTGR	High-temperature gas-cooled reactor
IAEA	International Atomic Energy Agency
LWBR	Light water breeder reactor
LWR	Light water reactor
MIBK	Methyl isobutyl ketone
NDA	Nondestructive assay
NBL	New Brunswick Laboratory
NBS	National Bureau of Standards
NRC	Nuclear Regulatory Commission
ORNL	Oak Ridge National Laboratory
PADAP	2-(2-pyridylazo)-5-diethylaminophenol
PWR	Pressurized water reactor
SNM	Special nuclear material
SRM	Standard reference material
TBP	Tributyl phosphate
TOPO	Tri-*n*-octyl phosphine oxide
TTA	Thenoyltrifluoroacetone

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ABSTRACT

Conventional analytical methods applicable to the determination of thorium, uranium, and plutonium in feed, product, and waste streams from reprocessing thorium-based nuclear reactor fuels are reviewed. Separations methods of interest for these analyses are discussed. Recommendations concerning the applicability of various techniques to reprocessing samples are included.

I. INTRODUCTION

Various analytical techniques have been developed for measuring thorium, uranium, and plutonium in ores, weapons-type materials, and/or reprocessing streams. With suitable precautions and modifications these methods are applicable to reprocessed materials from thorium-uranium fuels. The effectiveness of the techniques depends on factors such as sample type, sampling techniques, standards, and the skills of the chemists performing the work. Some of these factors will be discussed in detail.

Thorium-uranium fueled reactors convert fertile ^{232}Th to ^{233}U while generating electricity by burning fissile fuel that can contain ^{233}U, ^{235}U, or ^{239}Pu. Thus, both fissile and fertile fuels are required. Both may be present in the same fuel rods or the fertile material may be present as a thorium blanket surrounding a fissile uranium core.

The fissile fuel consists of UO_2 fuel elements similar to pressurized water reactor (PWR) fuel elements for conventional light water reactors (LWRs). Cladding may be Zircaloy or stainless steel. In the initial loading of the reactor core (referred to as the prebreeder), the fissile material is ^{235}U enriched up to 93%. In addition to the 93% enrichment (high enriched), enrichments of 20-30% (medium enriched) and <20% (low enriched) are being considered. The thorium/uranium ratio is nominally between 5 and 10, depending on reactor design. The fuel from the initial loading still contains significant amounts of ^{235}U at discharge, and recovery of the ^{235}U value is desirable. However, during burnup, significant amounts of ^{236}U, a neutron poison, are produced; hence, it may be desirable to reprocess the uranium only once and to discard the second discharge without reprocessing. Subsequent refueling will be done with the ^{233}U recovered from the fertile ThO_2 (referred to as the breeder or converter). The ^{233}U may be mixed with ThO_2 to form the breeder or converter fuel.

Also produced in the initial fissile loading is some plutonium from neutron absorption by ^{238}U as well as buildup from ^{236}U. The U/Pu ratio will depend on the ^{235}U enrichment of the fuel. The plutonium produced can be coprocessed with the recovered uranium and used to increase the fissile content of the fuel or it can be discarded to high-level liquid waste with the fission products.

The reprocessing of thorium-uranium fuels differs significantly from reprocessing in the uranium-plutonium cycle. The head end for oxide fuel elements is similar to that for LWR fuels, consisting of a chop-leach process. However, for ThO_2-UO_2 fuels, traces of HF are required to effect dissolution, and the presence of fluoride must be considered in subsequent analytical schemes.

Two separate solvent-extraction systems are required to process the fissile and fertile fuels. A Thorex (thorium recovery by extraction) process for recovering ^{233}U in the fertile fuel

is the more important from a safeguards viewpoint. A conventional Purex (plutonium-uranium recovery by extraction) process for recovering uranium from fissile fuel can also recover plutonium but the characteristics of the uranium and plutonium are not necessarily similar to LWR fuel.

For the Thorex process the fertile particles are dissolved in a solvent 11-13M in HNO_3, 0.05M in HF, and 0.1M in $Al(NO_3)_3$ (Thorex solution). Alternatively, zirconium from the Zircaloy cladding could serve as the fluoride complexant. The solution is centrifuged to remove solids which presumably consist primarily of Zircaloy fines and metallic fission-product ingots. The metallic ingots could contain some ^{233}U.

The clarified solution containing uranium, thorium, and fission products is heated and steam-stripped to adjust the solution to an acid-deficient condition and to remove most of the HNO_3 and HF, and the HNO_3 is adjusted to 1M. The uranium and thorium are purified by a three-cycle solvent-extraction system. In the first cycle--the high-acid extraction--uranium and thorium are removed from most of the fission products into a solution of 30% tributyl phosphate (TBP) in n-dodecane. The feed to the first cycle contains 200-250 g/L of thorium and 5-15 g/L of uranium. The uranium and thorium (and any plutonium and neptunium) are stripped into 0.1M HNO_3 and concentrated to ∿250 g/L of thorium. In the second cycle--the low-acid extraction, the HNO_3 is adjusted to 0.1M and uranium and thorium are again extracted into 30% TBP in n-dodecane for further purification from fission products. An acid-strip column then removes most of the thorium, after which the uranium is stripped in a third column into 0.01M HNO_3. This solution is concentrated to ∿10 g/L of uranium, sulfamic acid is added, the HNO_3 is adjusted to 3.6M, and uranium is extracted in 5% TBP in n-dodecane (the third extraction of uranium). The uranium is stripped into 0.01M HNO_3 and becomes the uranium product from the Thorex process.

For prebreeder fuel the UO_2 is dissolved in HNO_3, and after centrifuge clarification the solution is treated by a conventional Purex process.

II. CHARACTERISTICS OF PROCESS STREAMS

Three primary product streams result from the reprocessing of thorium-uranium fuels:

(1) Unreacted thorium from the Thorex process,

(2) ^{233}U from the Thorex process, and

(3) ^{235}U from the Purex process.

For low-enriched fuels (<20% ^{235}U or <12% ^{233}U) the uranium product streams may contain co-processed plutonium, or plutonium may be recovered separately. The uranium and plutonium isotopic compositions differ significantly from LWR fuel reprocessing products and vary with initial fuel characteristics. For high-enriched fuels (90% ^{235}U or ^{233}U) the plutonium produced will be primarily ^{238}Pu. As the fuel is diluted with ^{238}U, the total plutonium concentration, especially the ^{239}Pu and higher plutonium isotopes, will increase. Likewise, the ^{233}U concentration in fissile fuel will depend on the dilution and number of passes through the reactor. The isotopic compositions of fresh and equilibrium recycle fuels are shown in Table I; the actinide compositions are summarized in Table II.

During the irradiation some ^{232}U is formed from a series of reactions starting either from neutron absorption by ^{230}Th or an (n,2n) reaction in ^{232}Th. The (n,2n) reaction threshold requires a neutron energy >6.37 MeV, and for well-thermalized reactors ^{230}Th is the main source of ^{232}U. The source of ^{230}Th in thorium ores is the decay of ^{238}U and is therefore a function of ore type. Thorium ores obtained as a by-product of phosphate manufacturing typically have a ^{230}Th concentration of $\sim$10 ppm, whereas ores from uranium-bearing regions may contain up to 100 ppm ^{230}Th.[4] The production and decay chains for ^{232}U are summarized in Fig. 1. The ^{232}U is an alpha emitter with a half-life of 74 yr and poses no severe

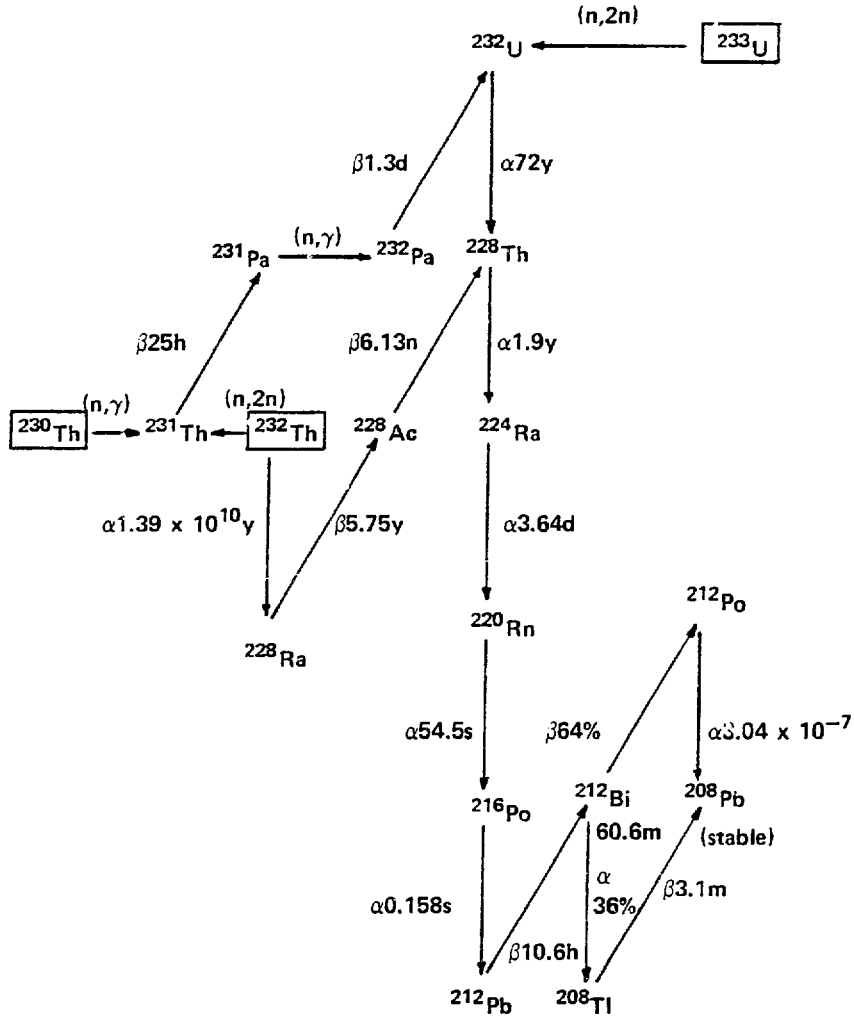

Fig. 1. Production and decay chains for ^{232}U (Ref. 1).

TABLE I

ISOTOPIC URANIUM AND PLUTONIUM COMPOSITIONS OF THORIUM-URANIUM FUELS

Isotope	First Cycle, Th Blanket[a] (%)	Enriched, Equilibrium[b] (%)	Denatured, Equilibrium[c] (%)
^{232}U	0.01-0.1	0.01	0.04
^{233}U	92	18.5	7.3
^{234}U	7.3	42.8	2.5
^{235}U	0.6	24.7	1.0
^{236}U	0.02	12.5	0.3
^{238}U	--	1.5	88.8
^{238}Pu	75	83.4	0.8
^{239}Pu	12	13.2	62.2
^{240}Pu	6	2.5	23.7
^{241}Pu	4	0.7	10.3
^{242}Pu	3	0.1	3.0

[a] Ref. 1.

[b] Ref. 2, p. B-28; steady state composite of mixture of fully enriched ^{235}U and recycled uranium product.

[c] Ref. 2, p. B-44; product from Th-^{233}U breeder.

problems, but all subsequent decay products are relatively short-lived and reach transient equilibrium rapidly. The ^{208}Tl daughter in the decay chain is an intense (3-min, 2.6-MeV) gamma emitter, and all manipulations of materials more than a few weeks old, including fuel fabrication and analytical chemistry, must be performed in shielded caves.

The thorium product stream from the Thorex process does not present a safeguards problem. Second-cycle ^{235}U fuel will be

TABLE II

PERCENTAGES OF HEAVY METALS IN SPENT FUEL
(Relative to Total Heavy Metals)

Element	Fuel Type		
	Th ^{235}U, Th Blanket[a]	Enriched, Equilibrium[b]	Denatured, Equilibrium[c]
Thorium	95	91.5	73.3
Uranium	5	8.4	26.3
Plutonium	0.04	0.026	0.3
Other actinides	0.1	0.1	0.01

[a] Calculated from data in Ref. 3.

[b] Ref. 2, p. B-28.

[c] Ref. 2, p. B-44.

discharged to high-level waste without processing and, because of the high radiation levels from the fission products, it too poses a minimal safeguards threat at present. However, accountability of the waste must be enforced because the waste might be reprocessed for plutonium content after a suitable cooling period of 50-100 yr.

The primary safeguards concerns will be the product streams containing ^{233}U, ^{235}U, and plutonium, with ^{238}U and thorium of secondary concern.

A. Characteristics of Product Streams

Two types of reactor cores will require reprocessing in a light water breeder reactor (LWBR) fuel cycle. These are the prebreeder and breeder cores. The prebreeder core consists of modules of enriched uranium-dioxide ($^{235}UO_2$ in $^{238}UO_2$) rods and thoria (ThO_2) rods. The breeder-core concept consists of rods

containing a binary mixture of $^{233}UO_2$ and ThO_2, with the $^{233}UO_2$ concentration varying in different regions.

Chopped fuels containing UO_2 or $(U\text{-}Pu)O_2$ can be leached with HNO_3 alone, but those containing ThO_2 or $(Th\text{-}^{233}U)O_2$ will require an HNO_3 leachant containing a trace of HF and perhaps some complexing agent to reduce HF activity and concomitant corrosion.

The postdissolution separation requires two separate cycles: a Thorex cycle to separate uranium and thorium in the postbreeder feed and a Purex cycle to recover uranium from prebreeder fuel. The plutonium content of the fuel is lower than in LWR fuels, and plutonium can be recovered separately, coprocessed with the uranium, or discarded to high-level waste with the fission products.

The approximate makeups of process solutions to the Thorex and Purex processes are summarized in Table III.[5] These data are representative of high-temperature gas-cooled reactor (HTGR) fuels, but similar compositions can be expected for LWR or LWBR fuels.

B. Characteristics of Waste Streams

The variability in product streams for reprocessing thorium-uranium fuels results in waste streams that are more complex than those from LWR fuel reprocessing. Considerably more solid wastes may be generated, primarily from the head end. Additives such as $Al(NO_3)_3$ will be required to complex HF from LWR or LWBR fuels.

1. Solid Wastes. Solid wastes consist of

- o Zircaloy hulls,
- o Centrifuge sludge, and
- o Second-cycle ^{235}U fuels.

a. Zircaloy Hulls. The Zircaloy hulls for LWR fuels are expected to contain 0.1% of the uranium fuel,[6] and prebreeder fuel is expected to be similar. There has been no experience with the dissolving of Zircaloy-clad ThO_2-UO_2 fuels, but because they are more refractory, higher proportions of undissolved fuel may be encountered.

TABLE III

COMPOSITION OF FEED SOLUTIONS FOR HTGR FUEL REPROCESSING

	Thorex Leacher Product	Purex Leacher Product
Average liquid flow (L/day)[a]	1479.6	1132.2
Heat load (W/L)[b]	5.1	5.0
Activity (Ci/L)	1351.9	1145.6
Carbon (g/L)	0.3	0.2
Uranium (g/L)	7.3	8.0
Thorium (g/L)	224.2	Negligible
Plutonium (g/L)	Negligible	0.4
Fission products (g/L)	7.3	15.5
Boron (g/L)	--	0.4
HNO_3 (M)	8.4	2.0
F^- (M)	0.05	--
Al^{+++} (M)	0.1	--
Cd^{++} (M)	0.075	0.075
Total NO_3^- (M)	13.0	2.5

[a] Exclusive of rework material.

[b] Decay heat only.

b. Centrifuge Sludge. The centrifuge sludge contains undissolved Zircaloy fines and metallic ingots of noble-metal fission products. Studies on LWR oxide fuels have shown that some of the noble-metal ingots can contain as much as 25% uranium and 13% plutonium.[7] The Zircaloy fines also may contain alloyed uranium and plutonium. In HTGR fuels, as much as 0.6% of the uranium may remain undissolved in the centrifuge solids.[8]

If that is also the case for LWBR fuels, either an accountability measurement must be made or an additional reprocessing step must be added to recover the uranium.

c. Second-Cycle ^{235}U Fuels. The fully enriched equilibrium fuel will contain appreciable amounts of the uranium as ^{235}U. However, if the fuel is not diluted with ^{233}U, the buildup of ^{236}U content may render it unusable for further recycling. For disposal, the fuel can be dissolved, and uranium and plutonium can be discharged to high-level waste with the fission products. Alternatively, the fuel can be stored as solids in high-level waste. The latter may have some advantage because a divertor would have to declad and dissolve the fuel before recovering the plutonium. In either case, accountability measurements are required.

2. High-Level Liquid Waste. The high-level liquid waste consists of the aqueous waste streams from the Thorex and Purex process streams and contains the bulk of the fission products, as well as an estimated 0.5% of the actinides. Some fluoride also will be present from the Thorex dissolution process.

III. STANDARDS

All procedures and instruments used for nuclear safeguards accounting should be calibrated against approved standard reference materials. All weight and volume measurements should be traceable to National Bureau of Standards (NBS)-certified weight standards. NBS-certified Class S weights are used as reference standards for laboratory measurements. Volume calibration is made by appropriate NBS-certified weights as reference standards.

Analytical standards are defined by the Subcommittee of the Analytical Chemistry Section of the International Union of Pure and Applied Chemistry[9] as follows:

- Reference or atomic weight.
- Ultimate standard: a substance that can be purified to virtually an atomic-weight standard.

- Primary standard: a commercially available substance with a purity of 100 ± 0.02 wt%.
- Working standard: a substance of lower purity that can be standardized against a primary standard.

The NBS distributes many materials for use as standards. These are referred to as "Standard Reference Materials" (SRMs) and may be a primary standard or one of lesser purity.

The primary standards available for use as oxidation-reduction standards in the nuclear safeguards accountability program are:

- SRM 136c: potassium dichromate
- SRM 83c: arsenic trioxide
- SRM 40b: sodium oxalate.

SRMs available for uranium and plutonium analyses are shown in Ref. 10, p. 42. The uranium isotopic standards are well suited for the analysis of thorium-uranium fissile fuels. However, for fertile fuels secondary standards must be prepared because primary standards containing ^{233}U are not available. In addition to the NBS standards, standards for the spectrographic determination of impurities in uranium are obtainable from the New Brunswick Laboratory (NBL) and the Oak Ridge National Laboratory (ORNL).[11]

Thorium primary standards presently are not available through the NBS, but reference materials can be obtained from the NBL, and the NBS has initiated a program to develop a primary thorium standard.

Secondary or bench standards may be working standards obtained from a source such as NBS, from various Department of Energy (DOE) contractors, or from international sources.[12] They also can be prepared from process solutions by characterization against NBS SRMs. The preparation and evaluation of secondary plutonium-nitrate standards have been described[13] and should be incorporated into the analytical laboratory standard operating procedure. The same techniques are applicable to preparation of uranium working standards from plant uranium materials. These standards should be analyzed daily or by each

shift to ensure that the method is under control. Process samples should not be analyzed until satisfactory values are obtained on bench standards.

IV. SAMPLING AND SAMPLE PREPARATION

Measurements of process product and waste streams will require the analysis of solids as well as solutions. Because of the high radiation levels associated with most process materials, remote sampling techniques will be required. The critical analytical points will be the accountability and product tanks for the Thorex and Purex processes. The waste streams will be of lesser importance but must be monitored, not only to measure the amounts of thorium, uranium, and plutonium going to waste, but to ensure that uranium and plutonium are not returned to process vessels for subsequent diversion.

The air-lift sampling system should be designed to permit extensive recirculation of solutions through the sample lines and the sample bottle. Vessel sparging, mixing time, and sample-circulation time should be considered in establishing proper sampling procedures for replicate samples. Any solids must be dissolved after sampling and be included in the total analysis. For highly radioactive samples the possibility of bubble formation must be considered in volume measurements, and temperature corrections should be applied.

The main sources of sampling error for solutions are expected to be (1) concentration or dilution of the sample by the air-lift system, (2) incomplete mixing of the solution in the tank, (3) contamination of the sample in the sample lines, and (4) sample heterogeneity caused by suspended solids. Where analytical precision better than 0.5% is required, all sampling should be done on a weight basis rather than a volume basis. Remote volume samplers seldom can provide routine precision better than 0.5%, and even normal volumetric measurements are no better than 0.2% on a routine basis.

A sampling apparatus capable of providing pipetting accuracy of 0.1% under hot-cell conditions has been described.[14]

All steps, including pipet rinsing, are performed remotely, and the Teflon piston surface does not touch the solution being pipetted.

V. SEPARATION METHODS

Before chemical analysis the actinides often must be separated from each other or from other potentially interfering elements. For reprocessing solutions, the separation of fission products and other actinides, including protactinium, neptunium, and americium, must be considered. Unlike uranium and plutonium, thorium exists in solution only in the tetravalent state; hence, separations of thorium from other actinides rely on manipulating the valence of the uranium or plutonium. Fortunately, uranium commonly exists in solution as UO_2^{2+} and can be separated readily from thorium. Separation of thorium from plutonium generally is effected by oxidizing plutonium to PuO_2^{2+}. Separations of plutonium from uranium rely on reducing plutonium to Pu^{3+} or Pu^{4+}.

Some of the more common precipitation, ion-exchange, and solvent-extraction methods that might be useful for isolating thorium, uranium, and plutonium for safeguards applications will be discussed.

A. Precipitation

1. Thorium. The precipitation chemistry of thorium is reviewed in Ref. 15. The precipitating reagents commonly used for thorium are listed in Table IV. Many elements, including uranium and plutonium, interfere with the ammonium hydroxide and H_2O_2 precipitation but these techniques can be used for a rough separation of thorium from the rare earth fission products. Several reagents will effectively separate thorium from uranium, which is present as the UO_2^{2+} ion. However, most precipitation methods for thorium are also efficient methods for precipitation of plutonium as Pu^{3+} or Pu^{4+}. Reducing reagents such as H_2O_2 and oxalic acid will reduce PuO_2^{2+} to Pu^{4+}. The most common method for separating thorium from plutonium is fluoride precipitation following a perchloric-acid fuming to

TABLE IV

PRECIPITATION METHODS FOR THORIUM SEPARATION

Reagent	Comments
NH_4OH	Many interferences including U, Pu
$H_2C_2O_4$	Separates from U; Pu lanthanides interfere
H_2O_2	U, Pu, lanthanides precipitate
HF	Best for separating Th from Pu
IO_3	Separates Th from lanthanides, U
Benzoic acid	Separate Th from lanthanides, U

oxidize plutonium to PuO_2^{2+}. The precipitation must be carried out soon after the oxidation so that PuO_2^{2+} is not re-reduced to Pu^{4+}, particularly in the presence of high beta-gamma radiation fields.

Some of the organic precipitants such as m-nitrobenzoic acid and p-aminosalicylic acid are of interest because they can be adapted to the titrimetric determination of thorium.[15] Organic precipitants and precipitation conditions for thorium are listed in Ref. 15, p. 163. These can be applied more readily to hot cell measurements than can normal gravimetric methods.

2. Uranium. Precipitation methods for separating uranium are reviewed in Refs. 16 and 17. Precipitation is used infrequently to separate uranium in fuel reprocessing analysis, largely because of poor selectivity and the fact that ion exchange and solvent extraction are easier to apply under glovebox and hot-cell conditions. Ammonia can be used to precipitate uranium quantitatively, but thorium, plutonium, and lanthanide fission products are also precipitated. If CO_2 has been absorbed from the atmosphere by the NH_4OH, some uranium can be lost by the formation of soluble carbonate complexes, hence, pyridine or hexamethylenetetramine is more commonly used.

The solubility of UO_2^{2+} carbonate complexes has been exploited to mask uranium in the separation of numerous ions from uranium by hydroxide precipitation.

3. Plutonium. The separation chemistry of plutonium is reviewed in Refs. 16, 18 and 19. Because of its multiple valences, plutonium affords more versatility in separation chemistry than does thorium or uranium. Tri- and tetravalent plutonium are precipitated essentially quantitatively as the peroxides, oxalates, fluorides, and phosphates; tetravalent plutonium as the iodate; and all three common valences as the hydroxides. All of these reagents are useful in plutonium analytical chemistry. PuF_4 is the most insoluble of the plutonium precipitates and is useful in separating plutonium from uranium. Phosphate precipitation in which bismuth is used as a carrier will separate plutonium (and rare-earth fission products) from uranium. Plutonium can be separated from the rare earths by first oxidizing to Pu^{6+} with Ce^{4+}--the earliest process used to recover plutonium from nuclear fuel.

For separating trace amounts of plutonium, coprecipitation techniques are used (Ref. 18, pp. 383-386). The main criterion for carrier selection is that the carrier must not interfere with the subsequent measurement of plutonium.

B. Ion Exchange

Cation and anion formation for the actinides is a complex function of many variables, including valence, acid type, and acid concentration. Ion-exchange methods for separating the actinides usually involve oxidation-reduction manipulations that enable selective adsorption on or elution from cation or anion exchangers. The ion-exchange chemistry of the actinides is reviewed in Ref. 20.

The trivalent actinides show little or no adsorption on anion exchangers at all acid concentrations in HNO_3 and HCl. The tetravalent actinides exhibit little or no anion adsorption at low HCl or HNO_3 concentrations, but anion adsorption increases with increasing acidity. Anion formation is greater in HNO_3 than in HCl. Thorium is adsorbed on cation exchangers at

HNO_3 and HCl concentrations to 4N. Reprocessing solutions generally contain HNO_3, and analytical separations from this medium are of primary interest. Anion-exchange separations for actinides in HNO_3 are reviewed in Ref. 21.

Because of the similarities in chemical properties of the actinides and the fission-product lanthanides, media other than HNO_3 will be required for effective analytical separations. The separation possibilities often can be expanded by diluting the HNO_3 (or HCl) with organic reagents.[22] Thus, thorium is not adsorbed onto anion exchangers from aqueous HCl at any concentration, but strong adsorption is observed from HCl solutions containing long-chain aliphatic alcohols such as butanol[23] or other organic solvents such as acetone.[24] Use of reducing acids such as HBr or HI also can affect adsorption characteristics.[25] For example, in HI solution plutonium should be reduced to Pu^{3+}. Additional separation possibilities may be realized in neutral or carbonate solutions, particularly for uranium, which forms strong carbonate complexes.[26]

For ion-exchange separations of highly radioactive samples such as dissolver solutions, inorganic exchangers may be preferable to the normal organic exchangers because of their higher resistance to radiation degradation. The various types of available inorganic exchangers, and their applications, are reviewed in Refs. 27-29. Methods have been described for separating plutonium from uranium and fission products by using zirconium phosphate,[30] and for separating uranium and plutonium from fission products using silica gel.[31]

1. Thorium. Thorium is strongly adsorbed on cation exchangers from HCl, HNO_3, and H_2SO_4 below ∿1N. Thorium is not adsorbed on anion exchangers from HCl at any concentration, but is adsorbed from ∿0.1N H_2SO_4 and >2N HNO_3. Although cation exchange can be used to separate thorium from uranium and plutonium, distribution coefficients are better on anion exchangers and these are preferred. Both UO_2^{2+} and PuO_2^{2+} are adsorbed on strong anion-exchange resins from >6N HCl. Thorium is not adsorbed and is effectively separated.

Representative methods for separating thorium from uranium, plutonium, or fission products are summarized in Table V.

2. Uranium. Essentially all ion-exchange work has been performed using the U^{6+} valence, and only hexavalent uranium is considered here. Uranyl ions can be adsorbed on cation exchangers from dilute H_2SO_4 (<0.5N). However, most analytical separations on cation exchangers are performed under conditions

TABLE V

ION-EXCHANGE METHODS FOR THORIUM SEPARATION

Exchanger	Solvent	Application[a]	Ref. No.
	Cation Method		
Dowex 50-X8	0.6N HCl 90% alcohol	Uranyl chloride	32
Dowex 50-X8	0.1N HNO_3	Trace Th from U	33
Dowex 50	80% methanol- 20% 1N HNO_3	U	34
	Anion Method		
Dowex 1-X4	9.6N HCl	Uranyl nitrate	35
Dowex 1-X8	5-8N HCl	R.E. fp's	36
Dowex 1-X8	55% acetone 35% H_2O- 10% 6N HNO_3	R.E. fp's	37
Dowex 1-X8	6N HNO_3	R.E. fp's, U	38
Bio-Rad AG-1-X8	0.7N H_2SO_4	U	39
Dowex 1-X8	90% acetone - 1N HNO_3	U	24

[a]R.E. = rare earth; fp = fission product.

conducive to anion formation for uranium, so that the impurity elements are adsorbed. Anion formation for the uranyl ion is enhanced by using complexing agents such as acetate, chloride, fluoride, nitrate, sulfate, or carbonate. Adsorption is strongest from dilute (<0.1N) H_2SO_4 or strong (6N) HCl. Because thorium is not adsorbed from HCl at any concentration, separation of uranium from thorium is readily achieved. Tetravalent actinides are more strongly adsorbed on anion exchangers from 6N HNO_3 than is uranium, and separations can be effected in that way.

Representative methods for separating uranium from thorium, plutonium, or fission products are summarized in Table VI.

3. Plutonium. Again, the multiplicity of valence states allows more versatility in separation schemes for plutonium than for thorium and uranium. Generally, adsorption proceeds in the order $Pu^{4+} > Pu^{6+} > Pu^{3+}$ for anion exchangers, and $Pu^{4+} > Pu^{3+} > Pu^{6+}$ for cation exchangers (Ref. 18, pp. 277-279). Adsorption of Pu^{3+} and Pu^{4+} on cation exchangers is observed only at low concentrations (<1N) of H_2SO_4, HCl, and HNO_3. Little, if any, adsorption on anion exchangers from HCl or HNO_3 at any concentration is observed for trivalent plutonium. The Pu^{4+} and Pu^{6+} ions are strongly adsorbed from >6N HCl and >2N HNO_3. Separation of plutonium from thorium and uranium can be effected by reducing to Pu^{3+} with HI and adsorbing thorium and uranium on anion exchangers. Separation from the rare-earth fission products is effected by oxidizing to Pu^{6+} and adsorbing the rare earths as cations or adsorbing plutonium on anion exchangers.

Representative methods for separating plutonium from thorium, uranium, or fission products are summarized in Table VII.

C. Solvent Extraction

Solvent extraction schemes exploit the solubility differences in the elements that are to be separated in two mutually immiscible solvents. Either the element to be analyzed is extracted into an organic phase, leaving the impurities in the aqueous phase, or the impurities are extracted into the organic

TABLE VI

ION-EXCHANGE METHODS FOR URANIUM SEPARATION

Exchanger	Solvent	Application[a]	Ref. No.
		Cation Method	
Dowex Ag-50W-X8	1N H_2SO_4	R.E. fp's, Th	40
Dowex 50-X8	90% tetrahydrofuran-10% 6N HNO_3	R.E. fp's, Th, Mo, Zr	41
Dowex 50	1.5N HNO_3	Pu^{3+}	42
Liquid cation exchange	0.5N HCl	R.E. fp's, Th	43
Silica gel	Triethylenetetraaminehexaacetic acid at pH=5-6	Trace U from Th	44
Dowex 50		Th	34
		Anion Method	
Dowex 1-X8	80% methanol-20% 6N HCl + ascorbic acid	Th, Pu	45
Dowex 1	90% ethanol-10% 5N HNO_3	Th	46
Dowex 1-X8	90% methanol-10% 6N HCl	Th	23
Dowex 1	10N HCl	Th	47
Dowex 1-X8	6N HCl	Th	24
De-Acidite FF	10-11N HCl + HI	Pu	48
Dowex 1	12N HCl	R.E. fp's, Th	49
Dowex 1-X8	80% methanol-20% 5N HNO_3	Th	50
Dowex 1-X8	90% dioxane-10% 6N HNO_3	Th	51
Dowex 1-X8	1N HNO_3	R.E. fp's, Th	52

[a] R.E. = rare earth; fp = fission product.

TABLE VII

ION-EXCHANGE METHODS FOR PLUTONIUM SEPARATION

Exchanger	Solvent	Application[a]	Ref. No.
		Cation Method	
$Zr_3(PO_4)_4$	0.5N HNO_3 0.02N $NaNO_2$	U, fp's	30
Silica gel	4.5N HNO_3	U, fp's	31,53
Dowex 50	0.25N HNO_3 0.025N hydroxylamine	U, fp's	54
		Anion Method	
Dowex 1	9N HCl + SO_2	U(VI), NP(IV)	55
Dowex 1-X8	7N HNO_3	U, fp's	56
Dowex 1	12N HCl	Th	57
Dowex 1-X2	7.2N HNO_3	U and many others	58

[a] fp = fission product.

phase. The distribution coefficient K_d is the ratio of the relative concentrations of an element in the organic and the aqueous phases. A value of 1 for K_d indicates equal solubility in the two phases; a value of $K_d > 1$ indicates preferential solubility in the organic phase.

Extraction is effected by preferential solubility of an inorganic salt or associated complex of the element of interest in the organic solvent (ion-association extraction) or by addition of a chelating agent to the organic phase to form an extractable complex of the element of interest (chelate extraction). Extractability can be modified if the reaction equilibrium is driven in the desired direction by varying temperature,

acid concentration, anion concentration, total ionic strength (salting-out), or by complex formation. As an example of the latter, fluoride will complex tri- or tetravalent plutonium; carbonate in near-neutral solutions will complex UO_2^{2+} and PuO_2^{2+}, and (ethylenedinitrilo)-tetraaceticacid (EDTA) will complex many cations.

Actinide elements of the same valence often have similar extraction properties, and solvent-extraction separations of the actinides take advantage of the differences in the extraction coefficients of different valence states. For separations of several actinides, more than one extraction may be required. For example, the tetravalent thorium and plutonium ions can be separated from hexavalent uranium by several methods, and thorium and plutonium can then be separated from each other either by reducing plutonium to Pu^{3+} or by oxidizing it to PuO_2^{2+}.

Several solvent systems have been examined extensively as group extractants for the actinides and as solvents for individual actinides. Probably the most thoroughly studied system involves TBP in both HNO_3 and HCl solutions. Because of the high viscosity and density of pure TBP it must be diluted in some organic solvent, and aliphatic hydrocarbons such as kerosene are commonly used. The tetra- and hexavalent actinides are extracted by TBP. The extraction coefficients generally increase with increasing acid and ion concentrations because of salting-out effects. The tri- and pentavalent species show little solubility under any conditions.

Methyl-isobutyl ketone (MIBK or hexone) also is used as an extractant for nitrates of hexavalent actinides. Tetravalent species are extracted to a lesser extent, and tri- and pentavalent actinides remain almost quantitatively in the aqueous phase. Hexone can react explosively with strong HNO_3, and extractions should be performed from $<\sim 0.5\underline{N}$ HNO_3.

One of the more common chelate-extraction systems involves thenoyltrifluoroacetone (TTA) in solvents such as benzene or xylene. As a rule, only the tetravalent species are extracted; hence, the system can be used to separate Pu^{4+} from UO_2^{2+},

or Th^{4+} from Pu^{3+} or UO_2^{2+}. The extraction coefficients for TTA are very sensitive to the presence of competing complexing agents, and best results are obtained from $HClO_4$ solutions. Although Pu^{4+} can be extracted from 1.0 N HNO_3, it is nearly quantitatively back extracted in 6N HNO_3.[59]

Other extraction systems have been studied for actinide separations, and some of the more appropriate extractants for analytical applications in thorium-uranium fuel reprocessing are summarized here. The method selected depends on the application. A coulometric or x-ray fluorescence measurement method may be tolerant of less-than-complete separation of plutonium from uranium but requires 100% recovery of the uranium. An isotope-dilution mass-spectrographic measurement requires complete removal of ^{238}U for quantitative measurement of ^{238}Pu, but does not require 100% recovery of the plutonium.

1. Thorium. The most commonly used ion-association extraction for thorium involves extraction of the chlorides or nitrates into a solution of TBP dissolved in an aliphatic hydrocarbon such as kerosene or n-dodecane. Extraction of thorium is most effective at high HNO_3 and TBP concentrations, and distribution coefficients are further increased by replacing part of the HNO_3 with nitrate salts. Extraction is hindered by fluoride, phosphate, and sulfate. Although uranium and plutonium also are extracted, separation from uranium is effected by manipulating acid concentration and from plutonium by manipulating plutonium valence. More efficient separation is achieved by extracting uranium from HCl, leaving thorium essentially quantitatively in the aqueous phase.[60,61]

Mesityl oxide is another important extractant for thorium, particularly for separation from rare earths.[62] Uranium extracts quantitatively. A disadvantage of mesityl oxide is the toxicity of its decomposition products.[63]

Thorium separation schemes that may be applicable to Thorex and Purex reprocessing analyses are summarized in Table VIII.

TABLE VIII

SOLVENT-EXTRACTION METHODS FOR THORIUM SEPARATION

Aqueous	Organic[a]	Application[a]	Ref. No.
0.1N ClO_4, pH 2	N-phenylbenzohydroxamic acid in chloroform	R.E.	64
0.1N ClO_4, pH 5-9	Oxine in hexone or chloroform	R.E., U	65
0.1N HNO_3	10% TTA in benzene	R.E., U	66
6N HCl	TOPO in xylene	R.E. fp's	67
EDTA at pH = 2.5; HNO_3	TOPO in xylene	U	68

[a] R.E. = rare earth; fp = fission product; TTA = thenoyltrifluoroacetone.

2. Uranium. Extraction with TBP is widely used for separating uranium, extraction being improved at high acid, TBP, and salt concentrations. Although a number of elements, including thorium and plutonium, also are extracted, selection of proper extraction conditions can eliminate many interferences. For example, plutonium interference is eliminated by reduction to Pu^{3+} before extraction. Efficiency of separation from thorium is improved in HCl systems.

The hexone-HNO_3 system has been widely investigated for process application, and some analytical applications have been devised.[59] The method is useful for recovering uranium and plutonium from fission products, but because multiple extractions are necessary and separation of uranium and plutonium is difficult, the method probably has limited value in the analytical laboratory if quantitative recovery of uranium is required. It has been applied to HTGR reprocessing solutions for the subsequent isotope-dilution mass-spectrometric measurement of

uranium.[69,70] Extraction with tri-n-octylphosphine oxide (TOPO) also is used extensively, both from HNO_3 and HCl media.[71]

Uranium extraction schemes that may be applicable to Thorex and Purex reprocessing analyses are summarized in Table IX.

3. Plutonium. As mentioned, plutonium in the tetravalent or hexavalent states is extracted by most systems, such as TBP and hexone, that extract Th^{4+} or UO_2^{2+}. In general, separations of plutonium from thorium and uranium rely on control of the plutonium valence. Thenoyltrifluoroacetone in organic solvents such as xylene or benzene constitutes an important chelate-extraction system for tetravalent actinides. Separation of plutonium from uranium is effected by performing the extraction from 1N HCl while retaining uranium as UO_2^{2+}. Plutonium can be separated from thorium by extracting Th^{4+} after reduction of plutonium to Pu^{3+}. Similar schemes can be devised using other extraction systems such as TBP, hexone, or TOPO.

Plutonium extraction schemes that may be applicable to Thorex and Purex reprocessing analyses are summarized in Table X.

VI. CHEMICAL METHODS OF ANALYSIS

A. Gravimetric Methods

Gravimetric methods involve separating a compound of the element to be determined and igniting it to a constant-weight stoichiometric compound. The method is applicable only to relatively pure materials; impurities must be determined by spectrographic or other procedures and the final weight corrected by difference. When clean separations from impurities can be obtained, precisions better than 0.1% often can be realized.

1. Thorium. In general, reagents used for precipitation separations of thorium also can be used for gravimetric analysis. Whether precipitated as the hydroxide, peroxide, oxalate, or one of the numerous organic compounds (Ref. 15, p. 183), the most

TABLE IX

SOLVENT-EXTRACTION METHODS FOR URANIUM SEPARATION

Aqueous	Organic	Application[a]	Ref. No.
7N HCl	50% TBP in MIBK	Th	60
2N HCl	30% TBP in CCl_4	U and Pu from fp's for x-ray floures-cence analysis	61
7N HNO_3; electrolyze	1% cupferron in ether	R.E. fp's	70
pH 4.1-6.5; EDTA	Oxine in hexone	Irradiated Th	72
pH 2-3; EDTA	2% diethyldithiocarbonate in pyridine	Th	73
0.1N ClO_4^-, pH 2	N-phenylbenzohydroxamic acid in chloroform	R.E., Th	64
Nitrate, pH 2.0-2.3	n-butyric acid	R.E., Th	74
3N HCl	0.1 M TOPO in cyclohexane	R.E., Th (Pu^{4+})	75
5N HCl	TBP	R.E. fp's, Th	76
3N HNO_3	Tetrapropylammonium in hexone	fp's	77
1N HCl	TOPO in xylene	R.E. fp's, Th	67
EDTA at pH = 2.5	TOPO in xylene	Th	63
6N HCl	Tri-iso-octylamine-2-nitropropane	From Th in HTGR dissolver solution	78
2N HNO_3 + NaF, + sulfamic acid	TOPO in cyclohexane	Pu, others	79
HNO_3 $H_2C_2O_4$+$Al(NO_3)_3$	Hexone	Mass spectrometric determination of U in HTGR dissolver solution	69

[a] R.E. = rare earth; fp = fission product.

TABLE X

SOLVENT-EXTRACTION METHODS FOR PLUTONIUM SEPARATION

Aqueous	Organic	Applications[a]	Ref. No.
0.5-1.5N HNO_3	0.5N TTA in xylene	R.E. fp's, U, Th	80
3N HNO_3	Tetrapropylammonium in hexone	Fp's	81,82
2N HCl	30% TBP in CCl_4	U and Pu from fp's products for x-ray fluorescence analysis	60
3N HNO_3	0.4N N-benzoylphenyl-hydroxylamine (BPHA) in chloroform	From U, fp's	83
6N HNO_3	0.1N TOPO in cyclohexane	Lanthanide fp's	84
11N NH_4NO_3 + 5N HNO_3	Hexone	U	59

[a] R.E. = rare earth; fp = fission product.

common weighing form after ignition at a suitable temperature is ThO_2.

Oxalate precipitation is used for the determination of thorium in nonradioactive leaching and aqueous solvent-extraction samples.[85] Precipitation is performed with 10% $H_2C_2O_4$ from 2N HCl and the precipitate is fired at 950°C. Accuracy of 0.1% is claimed.

The method has been modified for determining thorium in the organic phase from TBP solvent extraction.[86]

2. Uranium. Gravimetric methods can be used for the determination of uranium in pure product streams such as uranyl nitrate, U_3O_8 or UO_2, and UF_6. Nitrates are evaporated to dryness; UF_6 is hydrolyzed in H_2O and evaporated to dryness. Ignition is at 850-900 C to U_3O_8 and the final weighing provides an RSD of 0.02 to 0.5%.[87] Ignition at temperatures >946°C leads to formation of UO_2; temperatures <800°C yield slow decomposition reactions.[88] Presence of NO_3^-, F^-, Cl^-, or SO_4^{2-} does not interfere, but the presence of PO_4^{3-} leads to formation of uranyl pyrophosphate rather than U_3O_8.[89]

3. Plutonium. Of the plutonium precipitates, only PuO_2 is reported to form a compound suitable for gravimetric analysis (Ref. 18, pp. 297-298). Even with PuO_2 the stoichiometry of the compound depends on initial composition and ignition temperatures, and even when heated to 1200°C the final composition is variable. In addition, PuO_2 is hygroscopic, with the amount and rate of H_2O adsorption dependent upon the ignition temperature. The suitability of gravimetry for determination of plutonium is dubious.

B. Spectrophotometric Methods

Spectrophotometric methods rely on the principle that a compound or complex in solution will absorb light of a specific wavelength in a quantity proportional to the concentration of the measured species. Generally, the concentration-absorbance function is a simple proportional relationship expressed by Beer's law, but variations may result at high concentrations or when other competing reactions occur. The RSD attainable by direct spectrophotometric methods usually is 0.5% or more and is seldom better than 0.2%. However, it can be improved to 0.05% with differential techniques that compare the absorbance of the unknown to a reference that is known precisely.

Specificity in absorptiometry is a complex function of factors such as sharpness of absorption bands, specificity of reagents, other elements or compounds present, and the quality of the monochromators. Specificity often can be improved by using preliminary separations, masking agents, and pH control. Because of the nonspecificity of reagents for thorium, uranium, and plutonium in the presence of each other and because of the nuclear reaction products (americium, neptunium, fission products), time-consuming separations often are involved. These additional separations may limit the precision in major element analysis. For these reasons, spectrophotometric methods are of limited use for measuring uranium and plutonium in a fuel reprocessing plant, usually for process control and analysis of waste streams.

The sensitivity of many spectrophotometric reagents to high radiation levels necessitates several supplemental separations during analysis of dissolver or waste-stream solution, even in the absence of elemental interference.

1. Thorium. A number of dye reagents form intensely colored complexes with thorium and have been investigated for the spectrophotometric determination of thorium. Unfortunately, most reagents that react with thorium also form colored compounds with the rare earths and with uranium, plutonium, and other actinides. Separations procedures or masking agents coupled with pH control often are required to eliminate interferences.

Probably the most important chromogenic reagent for thorium determination is thoron, the disodium salt of 2-(2-hydroxy-3,6-disulfo-1-naphthylazo)-benzene arsonic acid. The reagent is sensitive to a few micrograms of thorium but more than a few tenths of a milligram of rare earths or uranium will interfere.[90] The method has been adapted to determination of thorium in both aqueous and organic phases from Thorex solvent extraction.[91]

Spectrophotometric methods of interest to measuring thorium in reprocessing samples are summarized in Table XI.

2. Uranium. Spectrophotometric methods for determining uranium in reprocessing streams generally are limited to measurement of trace concentrations of uranium in waste streams and possibly in the final product thorium and plutonium. Reagents of interest are listed in Table XI.

The method for determination of uranium with 2-(2-pyridylazo)-5-diethylaminophenol (PADAP) has been modified specifically for determining uranium in reprocessing-plant waste streams[99] and in plutonium nitrate and oxide products.[100] The method for determination of uranium as the tetrapropylammonium complex has been modified to increase the tolerance for thorium in Thorex processing samples.[107] The method also has been automated for determining uranium and plutonium simultaneously in scrap materials.[105]

TABLE XI

SPECTROPHOTOMETRIC METHODS FOR DETERMINATION OF THORIUM, URANIUM, AND PLUTONIUM

Element	Compound	Concentration Range or Amount/Sample	RSD (%)	Interferences; Comments[a]	Ref. No.
Th	Thoron	25-750 μg	2	U >5 mg	91
Th	Solochromate fast red	1-200 μg	1.5	R.E.'s, Fe, Zr, F^-, PO_4^{3-} others	92
Th	SPADNS	0.04-10 μg	--	Zr, PO_4^{3-}, F^-, SO_4^{2-}, $C_2O_4^{2-}$	93
Th	Arsenazo-III	1-25 μg	--	Pu^{4+}, U^{4+}	94
U	Uranyl nitrate	10-300 g/L	1-5	Temperature-sensitive	95,96
U	Dibenzoylmethane	30-750 μg	1.7	Ce, Th, W, Fe(III), Cr(IV); Pu at Pu/U >2	97
U	Peroxide	1-25 mg		Cr, Cu, Fe, Mn, Ni	88,[b]98
U	PADAP	1-100 μg	5	As^{5+}, Cr^{3+}, V^{5+}, PO_4^{3-}, SiO_4^{2-}, Pu, Pd; Pu removed by extraction	99,100
U	PAR	1-100 μg	?	R.E.'s, Th(IV), Pu(IV)?	101
U	5-Me- -PAN	10-80 μg	?	F^-; extraction removes most interfering cations	102
U	Bromo-PADAP	0.5-100 μg	2	Cr^{3+}, V^{5+}, PO_4^{3-}	103
U	Tetrapropylammonia	1-100 μg	0.2-2	Ce, Th	77,104,105
U	Arsenazo-III	1-50 μg	1-10	Th, Pu, R.E.'s, others	94,106
Pu	Tetrapropylammonia	1-30 mg	0.2-2	Cr^{6+}	82,105,108
Pu	Pu(III) nitrate	12-18 g/L	0.05	Differential spectrometry	109
Pu	Arsenazo-I	5-100 μg	2-6	U, Zr, others	110

[a] R.E. = rare earth; fp = fission product.

[b] Ref. 88, pp. 222-225.

The uranyl-nitrate method[95,96] used for in-line process control lacks the precision required for safeguards applications. Browning of the optics can be a serious problem in process streams containing fission products.

3. Plutonium. Most chromogenic reagents that react with plutonium also yield intensely colored species with thorium, uranium, and many fission products; therefore, if plutonium is to be determined in reprocessing samples, a separation is required. For low plutonium concentrations, methods such as alpha or gamma spectrometry may be preferred for measurements.

The tetrapropylammonium method[82] is of interest because uranium and plutonium can be determined sequentially in the same sample. The method has been automated.[105]

The differential spectrophotometric method of determining plutonium[109] can be used for plutonium-nitrate product with precision and accuracy equivalent to that obtainable by the best electrometric methods.

C. Electrometric Titration Methods

Both uranium and plutonium can be determined with high precision and accuracy by the use of titrations involving oxidation-reduction reactions. The only oxidation-reduction reaction for thorium involves the Th^0-Th^{4+} reaction, which has a potential above that for the H_2O couple. Therefore, thorium can be determined only indirectly by electrometric methods.

Electrometric methods are classified by the technique used to detect the titration end point, such as potentiometric, amperometric, or coulometric. All of these methods can provide RSDs of better than 0.1%; hence, for best precision work weight burets should be used in all critical volume measurements.

Potentiometric titrations are based on measurement of the change in potential of the system as a component is removed by oxidation or reduction. Because the change in potential is the critical measurement, the accuracy of potentiometric titrations is limited by the sharpness of the potential break at the equivalence point. An RSD of 0.02 to 0.5% is often attainable;

therefore, the method is used for measurement of final product such as U_3O_8, UF_6, PuO_2, or $Pu(NO_3)_4$.

Amperometric titrations involve measurement of the change in current between two electrodes that are maintained at a constant potential as titrant is added. The precision of amperometric titrations is limited by the accuracy of the inflection point measurement in the current-titration curve; hence the potential is selected such that the limiting current for reactant, titrant, or product can be measured, depending on which yields the sharpest end point.[111]

Controlled-potential and constant-current coulometry are well-established methods for determining uranium and plutonium in solutions. Both methods are based on the principle that the weight of a substance oxidized or reduced at an electrode is proportional to the quantity of electric charge passed through the electrode.[111] In controlled-potential coulometry the potential of the electrode is maintained at a constant value relative to a reference electrode to minimize the number of reactions that can take place. Interference from the reactions occurring at lower potentials can be eliminated by performing a preliminary coulometric titration at a potential such that those reactions have occurred before measurements are started. Reactions requiring higher potentials cannot occur. Both uranium and plutonium can be titrated in the same sample without separation by performing successive titrations at different potentials. In constant-current coulometry an electrogenerated reagent reacts with the substance to be determined.

Coulometric methods can provide RSDs of 0.1% without the use of chemical standards. Generally, smaller samples usually are required than for potentiometric or amperometric measurements. Coulometric methods have gained increased popularity in recent years, but the determination of plutonium is subject to the following considerations (Ref. 98, p. 250 and Ref. 112).

- The method is applicable to the determination of plutonium in nitrate product solutions and in dissolver solutions following an anion-exchange separation of fission products.
- The titration can be performed in 1N $HClO_4$, 1N HNO_3, 1N H_2SO_4, or 1N HCl electrolytes. However, any Pu^{6+}, if present, is only partially reduced to Pu^{3+} in HNO_3, HCl, or $HClO_4$; therefore, 1.0N H_2SO_4 is preferred if the sample is believed to contain appreciable Pu^{6+}. Titration in 1.0N H_2SO_4 must be performed in an oxygen-free atmosphere.
- If iron is present, it is titrated quantitatively in H_2SO_4 and a correction must be applied. Iron does not interfere in 1N $HClO_4$ if the plutonium-iron ratio is >50.
- If 1N HNO_3 is used as electrolyte, sulfamic acid must be added to reduce nitrites.
- Polymeric plutonium does not titrate in any case and must be destroyed. Fluorides, used to destroy polymeric plutonium, and organics interfere in all media and must be removed.
- Although electrical calibration can be used, for optimum accuracy the instrument should be calibrated using NBS-SRM-949d and a correction for isotopic composition of the sample should be applied.
- Replacement of the platinum electrodes with gold can result in a lower and more reproducible background and an approximately fivefold improvement in precision.[113]
- Coulometers may be subject to serious interference from nearby RF generators, such as induction heaters.

1. Thorium. As noted, electrochemical-titration methods generally are not applicable to the direct determination of thorium. Indirect methods involve replacing the electroinactive Th^{4+} with an electroactive ion during complexometric titration. One such technique, developed for determining thorium in radioactive samples and in the presence of iron, involves the titration of thorium with EDTA using Fe^{2+} as the electroactive

ion.[114] The end point is detected amperometrically. The RSD for determining thorium in the presence of uranium, zirconium, and other cations was 2%. An indirect method involving amperometric titration with diphenic acid has been reported to provide an RSD of 0.5%. Uranium and rare earths do not interfere; interference from plutonium was not tested.[115]

2. Uranium. The electrometric methods for determining uranium rely on the reaction $U^{4+} - U^{6+}$ after quantitative reduction of the uranium to the tetravalent state (Ref. 88, pp. 74-83 and 86-88; Refs. 116-119). Differences between methods result from the reductants and oxidants used. Reducing agents used to obtain U^{4+} include zinc amalgam, the Jones reductor, Ti^{3+}, the lead reductor, Fe^{2+} in phosphoric acid, and electrical reduction. The Jones reductor can generate a mixture of U^{3+} and U^{4+}, and the trivalent uranium must be air-oxidized to the tetravalent state before titration. The reduction with an excess of ferrous ion in concentrated phosphoric acid followed by titration with dichromate can be performed in the presence of Pu^{4+} without interference. Some of the standard electrometric techniques for determination of uranium are summarized in Table XII. Of these methods for determining uranium, the Davies-Gray method[116-117] is the most versatile and has been automated for rapid analysis of process samples (Ref. 88, pp. 77-83 and 86-88; Refs. 117-120).

3. Plutonium. For the electrometric determination of plutonium, the plutonium may be oxidized quantitatively to Pu^{6+}, then titrated to Pu^{4+}. This couple is preferred if uranium or iron is present. Oxidants for the first step include AgO and $HClO_4$. If AgO is used, the excess is destroyed by gentle heating. The oxidation capability of $HClO_4$ is destroyed by diluting the sample after the plutonium has been oxidized. Errors can be introduced into the plutonium measurement if conditions for the dilution are not followed properly. The reduction to Pu^{4+} usually is carried out with Fe^{2+}, and can be performed directly or, by using a potentiometric end point, can

TABLE XII

ELECTROMETRIC METHODS FOR DETERMINING URANIUM

Reductant	Oxidant	End Point	Interferences	RSD[a] (%)	Sample Size	Ref. No.
Zn amalgam	$K_2Cr_2O_7$	Colorimetric	Most removed by	0.62	200-300 mg	118, pp. 74-77
Fe^{2+} H_3PO_4	$K_2Cr_2O_7$	Potentiometric	Ag, Hg	0.07	200-300 mg	116,117
Electrolytic	Excess $K_2Cr_2O_7$ back-titrated with Fe^{2+}	Potentiometric	Cr, Fe, Mo, Ti,	0.02	1-10 g	88, pp. 77-83;
Electrolytic	Electrolytic	Coulometric	Fe, Hg, Ag, V	0.06-0.44	2-20 mg	88, pp. 86-88;118
Pb reductor	Ce^{4+}	Potentiometric	Mo	0.03	0.5-1 g	119

[a] Generally, the optimum obtainable for fuel process or product samples.

be sharpened by adding a measured excess of Fe^{2+} with the excess titrated with Ce^{4+}. Methods involving the Pu^{4+}-Pu^{6+} couple are summarized in Table XIII.

Alternatively, plutonium can be determined by quantitative reduction to Pu^{3+} and subsequent titration to Pu^{4+} (Ref. 88, pp. 268-299 and 385-388; Ref. 98, pp. 209-212; Refs. 126-132). Common reducing agents are liquid zinc amalgam, the Jones reductor, the lead reductor, Ti^{3+}, Cr^{2+}, and electrical methods. The liquid-zinc-amalgam method suffers in that an extra transfer is required to remove the amalgam before titration. Small amounts of titratable material can be leached from the Jones reductor. Fewer elements are reduced with $TiCl_3$ than with the Jones or lead reductors; therefore, there may be fewer potential interferences.[127] However, Ti^{3+} is readily destroyed by contact with air.

The oxidation titration to Pu^{4+} usually is performed electrolytically or with Ce^{4+} or $K_2Cr_2O_7$. Dichromate has the advantage of being available as a primary standard and it is more stable than Ce^{4+} over extended storage periods. Uranium and iron interfere with methods involving the Pu^{3+}-Pu^{4+} couple. An exception is the controlled-potential coulometric technique in the presence of uranium, and with this method, the two elements can be measured successively in the same sample.[128] For the controlled-potential coulometric determination of plutonium in dissolver solutions, zirconium must be removed completely to prevent fouling of the electrode through adsorption of hydrous zirconia.[112] Methods involving the electrometric determination of plutonium using the Pu^{3+}-Pu^{4+} couple are summarized in Table XIV.

D. Polarographic Methods

Polarography is a nontitrimetric analytical electrochemical technique. The voltage between two electrodes immersed in the solution is monitored across a range that includes a redox reaction for the element to be determined. For quiescent solutions

TABLE XIII

ELECTROMETRIC METHODS FOR PLUTONIUM DETERMINATION USING THE Pu(VI)-Pu(IV) COUPLE

Reductant	Oxidant	End Point	Interferences	RSD[a] (%)	Sample Size	Ref. No.
Fe^{2+}	AgO	Amperometric	Ce, Cr, V, Mn Ru, Au, Rh, Pt Pb, Am, Np	0.03	10-20 mg	121,122[b] 128,129
Excess Fe^{2+} Ce^{4+}	AgO	Potentiometric	Ce, Cr, V, Mn	0.1-0.19	4 mg	88, pp. 261-268
Excess Fe^{2+} $K_2Cr_2O_7$	AgO	Potentiometric	Cr, Ce, Mn, V, Ru	0.17	20-80 mg	123
Excess Fe^{2+} Ce^{4+}	$HClO_4$	Potentiometric	Cr, Au, Mn, Pt,	0.03	200-250 mg	124[c]
Electrically generated Fe^{2+}	$KMnO_4$	Coulometric	Ag, Hg, Ru, Pd, Os, Ce, Au, Sn, (U)	1	3 g to 10 mg	125
Electrical	Electrical	Coulometric		0.1	1-10 mg	112

[a] Generally, the optimum RSD obtainable for fuel process or product sample.

[b] See also Ref. 88, pp. 254-261 and Ref. 98, pp. 213-216.

[c] See also Ref. 88, pp. 274-285.

TABLE XIV

ELECTROMETRIC METHODS FOR PLUTONIUM DETERMINATION USING THE Pu(III)-Pu(IV) COUPLE

Reductant	Oxidant	End Point	Interferences	RSD (%) [a]	Sample Size	Ref. No.
Zn amalgam	Ce^{4+}	Potentiometric	Fe, Mo, Ti, W	0.02-0.02	600 mg	88, pp. 274-285
Zn amalgam	$K_2Cr_2O_7$	Potentiometric	Cr, Fe, Mo, Ti, U, V, W	0.03	250-400 mg	126[d]
Pb or Jones reductor	Ce^{4+}	Spectrophotometric	Fe, Ga, Mo, Ti, U, W, V, Cr, NO_3^-	0.07	500 mg	88, pp. 253-274
Ti^{3+}	Ce^{4+}	Potentiometric	Cu, Fe, U, W NO_3^-	0.1	25 mg	127[e]
Cr^{2+}	Ce^{4+}	Potentiometric	Fe, U, Cu, W	0.4	20-50 mg	129
Electrical	Electrical	Controlled potential coulometric	Dependent on electrolyte	0.04[b] 0.63[c]	1-10 mg	113,130-132[f]

[a] Generally, the optimum RSD obtainable for fuel process or product samples.

[b] For nitrates.

[c] For dissolver solutions.

[d] See also Ref. 88, pp. 285-292.

[e] See also Ref. 88, pp. 293-299.

[f] See also Ref. 88, pp. 385-388; Ref. 98, pp. 209-212.

the current, which is diffusion-controlled, is proportional to the concentration. For stirred solutions the relationship is more complex.

The attractiveness of polarography for in-line or at-line analysis lies in the fact that no titrant is required, and analysis can be performed by adding a suitable supporting electrolyte. However, oxygen interferes and must be removed by sparging with an inert gas such as nitrogen or helium.

Polarography has been investigated for the in-line or at-line determination of uranium in reprocessing samples, and the literature is reviewed in Ref. 16, pp. 130-135, and Ref. 133, pp. 151-155. Problems associated with uranium determination by at-line polarography using a dropping-mercury electrode (DME) are reviewed in Ref. 134.

Conventional DME polarography is a diffusion-dependent process and can be used only in a quiescent system. The process sample is circulated to the sample cell through a bypass line and is allowed to sit after addition of the supporting electrolyte and sparging. Any turbulence caused by pipe variations, sparge lines, or other system malfunctions will affect the results. Interference in uranium determination also results from elements such as molybdenum, copper, or neptunium that are reduced near the uranium reduction potential,[135] ions or molecules adsorbed on the mercury drop, or compounds such as nitrite that increase the reactivity of the mercury.[134] Nitrite can be volatilized as methyl nitrite by addition of methanol during the air sparging.[136]

Problems associated with the use of mercury can be eliminated by using a mercury-plated platinum, gold, or graphite electrode. Vibration and other turbulence effects can be eliminated by using rotating electrode techniques. Then, however, the process would no longer be diffusion dependent and empirical calibration must be used, which may be difficult for in-line or at-line analysis. Further development work in this area may be warranted.

1. Thorium. Direct polarographic methods are not applicable to thorium measurement. Indirect methods that involve electroactive complexing agents such as m-nitrobenzoic acid, m-nitrophenylarsonic acid, or 8-hydroxyquinoline can be applied to pure thorium samples,[137] but are not applicable to reprocessing samples because plutonium, tetravalent cerium, zirconium, and ruthenium interfere.

2. Uranium. Polarography has been used at Hanford[134] to measure uranium in reprocessing-plant waste streams in the concentration range ∿0.01 to 10 g/L with 7.5-min analysis times. Although the RSD for synthetic solutions was 2% (1σ), an RSD of 10% was obtained for process samples.

In France, early experience with polarography yielded low results for feed and extraction samples containing >50 g/L of uranium, but gave reasonable results for raffinates (<0.5 g/L).[138]

Polarography using a dilution method has been applied to measurement of uranium in the concentration range 100-200 g/L in extraction streams from ore processing.[139] The dilution error was 0.5% and the overall RSD was 0.5%. Analyses were obtained at 5-min intervals.

The technique also has been used in Japan to make measurements in waste streams containing 0.01 to 1 g/L of uranium,[140] and in TBP recycle streams containing 0.01 to 0.08 g/L of uranium.[141]

A cell using two synchronized DMEs as proposed by Lewis and Overton[143] was constructed at SRP[157] for measuring 10^{-4} to 10^{-5} M uranium in flowing streams. Concentrations of 10^{-2} M Fe^{3+} or nitrite, or dissolved TBP, did not interfere. The maximum period of continuous operation was 8 h. The instrument was not installed in line after the evaluation.

Polarography will be used for determination of uranium in process waste streams at the HTGR reprocessing plant at Julich.[144]

3. Plutonium. Square-wave polarography has been investigated for the determination of 10^{-5} to 10^{-6} M plutonium.[145] Iron

at concentrations five times that of the plutonium concentration interferes seriously in HNO_3 solutions. The method probably is of little value for reprocessing samples.

E. Complexometric Titration

Reagents that form stable complexes with thorium, uranium, or plutonium can be used in titrimetric analysis provided a suitable end-point indicator is available. If the reagent forms a colored complex or removes a colored compound, the formation or removal of the color can be used for end-point determination. Or the end-point indicator may be a dye that forms a colored complex with a slightly lower stability constant than the compound being titrated.

Probably the most commonly used titrant for thorium, uranium, and plutonium is EDTA. Strong complexes are formed; hence, sharp end points can be obtained. The major drawback results from the fact that EDTA complexes with most elements in the periodic chart. Nevertheless, by careful selection of pH and indicator and by selective complexing of potential interferences the method is valuable, particularly for the determination of thorium. A RSD of <0.1% often can be obtained. Tetravalent actinides also can be titrated with diethylenetriaminepentaacetic acid using xylenol orange as the indicator.[146]

1. Thorium. The complexometric determination of thorium with EDTA using various dyes as indicators has been reviewed in Ref. 147, pp. 57-65, and Ref. 15, pp. 184-186. For most of the reagents, titration must be performed at a pH <3.5, above which $Th(OH)_4$ precipitates. Sulfate, fluoride, oxalate, and phosphate interfere with most of the methods by forming complexes with thorium. Interference by a 500:1 excess of uranium is eliminated by using pyrocatechin violet as the indicator (Ref. 147, p. 60). When Alizarin Red-S is the indicator, 5-10 mg of thorium can be titrated with a RSD of 1%. Uranium as the uranyl ion in equal amounts with thorium does not interfere.[148] A similar method has been applied to the successive titration of thorium and uranium in mixed solution using xylenol orange as the indicator.[149] In this procedure the thorium is titrated,

an excess of EDTA is added, uranium is reduced to U^{4+} with formaldehyde, and the excess EDTA above that required to complex uranium is back-titrated with thorium. Thorium also can be titrated with EDTA in the presence of uranium using Arsenazo as the indicator and diethyldithiocarbamate to mask uranium.[150]

Complexometric titration is a primary method for measurement of thorium and should find applications in fuel reprocessing analyses.

2. Uranium. Complexometric titration of uranium with EDTA requires reduction of UO_2^{2+} to U^{4+}. As with the titration of thorium, anions such as sulfate, fluoride, oxalate, and phosphate interfere. The interference of fluoride can be reduced or eliminated by addition of an excess of beryllium.[151] Uranium and thorium can be titrated without separation using xylenol orange as an indicator.[149]

Complexometric titrations probably offer no advantage over electrometric methods for determining uranium and do not provide equivalent precision.

3. Plutonium. Plutonium forms stable EDTA complexes in both the tri- and tetravalent states, and both have been used for the complexometric titration of plutonium. Trivalent plutonium can be titrated in HCl media after adjustment of pH to 2.5.[153] When a mixture of Alizarin Red-S and methylene blue was used as an indicator, some interference from the blue plutonium-chloride complex was observed. The end point was sensitive to aging of the sample.

Several indicators can be used to titrate tetravalent plutonium in HNO_3 solution. With Arsenazo-I, the titration can be performed in 0.1 to 0.2N HNO_3 without serious interference from trivalent lanthanides or UO_2^{2+} (Ref. 153.). As expected, thorium interferes quantitatively.

When copper-1-(2-pyridylazo)-2-naphthol (Cu-PAN) is used as an indicator the titration can be performed in H_2SO_4 solutions after adjustment of pH to 2.5-3.0 (Ref. 154). The RSD for determining 14 mg of plutonium is 0.6%. Thorium interferes quantitatively.

An indirect titration with zinc using dithizone has been described for determining plutonium in dissolver solutions.[167] The plutonium must be extracted from the bulk of the fission products and uranium. Under carefully controlled conditions 100 μg of plutonium can be measured with a precision of 0.4% (1σ).

F. Mass-Spectrometric Methods

In most existing Purex reprocessing plants thermal-ionization mass spectrometry is used to determine the amount of each isotope of uranium and plutonium and, subsequently, to determine the effective atomic weights used in calculating the total uranium and plutonium from the chemical analysis of accountability-tank samples. Isotope-dilution mass spectrometry can be used to measure the plutonium and uranium concentrations in the tanks.

Mass spectrometry also can be used in Thorex reprocessing plants to measure thorium as well as uranium and plutonium. The major limitation for measuring thorium measurement results from the lack of suitable NBS-certified standards. For uranium measurement, ^{235}U rather than ^{233}U is proposed as the spike because ^{233}U is the major isotope to be measured.

The instrumentation for mass spectrometry is complex and expensive, consisting basically of a source, which is either a single or triple filament; a mass spectrometer; a detector, which is either a Faraday cup or an electron multiplier; and associated control and readout electronics.[156,157] Much of the instrumentation can be computer controlled.[158] Single-filament ion sources require precarburization to provide high metal ion yields, and triple filaments are preferred. The mass spectrometer should have an abundance sensitivity of 100 000 or better and a resolution, expressed as $M/\Delta M$, of 400 or greater, where ΔM is the peak width at 5% of the height above background. For the detector, the Faraday cup provides better measurement accuracy but the electron multiplier yields better sensitivity.

The methods require elaborate sample preparation (Ref. 88, pp. 353-368; Ref. 98, pp. 700-708; Refs. 159-161). A typical

mass-spectrometric procedure involves (1) dissolving and diluting the sample with HNO_3, (2) for isotope-dilution mass spectrometry, spiking part of the diluted sample with accurately known amounts of ^{233}U and ^{242}Pu or ^{244}Pu, (3) oxidizing plutonium to the hexavalent state, (4) sequentially separating the fission products, plutonium, and uranium by an anion-exchange procedure or by solvent extraction; and (5) transferring aliquots of the separated uranium and plutonium fractions to separate mass spectrometer filaments.

Because small amounts of uranium and plutonium (100 g, and generally <1 μg for plutonium) are to be analyzed, extreme care must be taken in sample preparation and filament loading to avoid contamination by environmental uranium. Determination of ^{238}Pu is particularly sensitive to the presence of ^{238}U, and for ^{238}Pu concentrations <0.7%, alpha-counting methods are preferred. For the measurement of ^{241}Pu, ^{241}Am must be completely separated. For the isotope-dilution mass-spectrometric determination of plutonium, both spiked and unspiked samples must be analyzed to correct for ^{242}Pu in the sample.

Chemical errors may arise also from the presence of high concentrations of alkali elements. Potassium, in particular, interferes with the measurement of ^{234}U and ^{236}U because of overlap of K_6 polymers. Filaments must be checked to ensure that they are free of organics. If organics are detected at ion currents greater than background, the analyses are suspect.[162]

For thermally produced ions the light isotopes are evaporated and ionized preferentially relative to the heavier isotopes of an element.[157] This effect is temperature dependent and is a function of the mass, sample size, and time. It is referred to as the filament bias and must be measured for the instrument every 6 months, and must be controlled as accurately as possible between samples and standards in a series. Temperature can be controlled by direct pyrometer measurement or by adjusting to a constant signal intensity of a filament ion.

Figure 2 shows the precision obtainable by mass spectrometry for different plutonium isotopes.[163] A similar curve

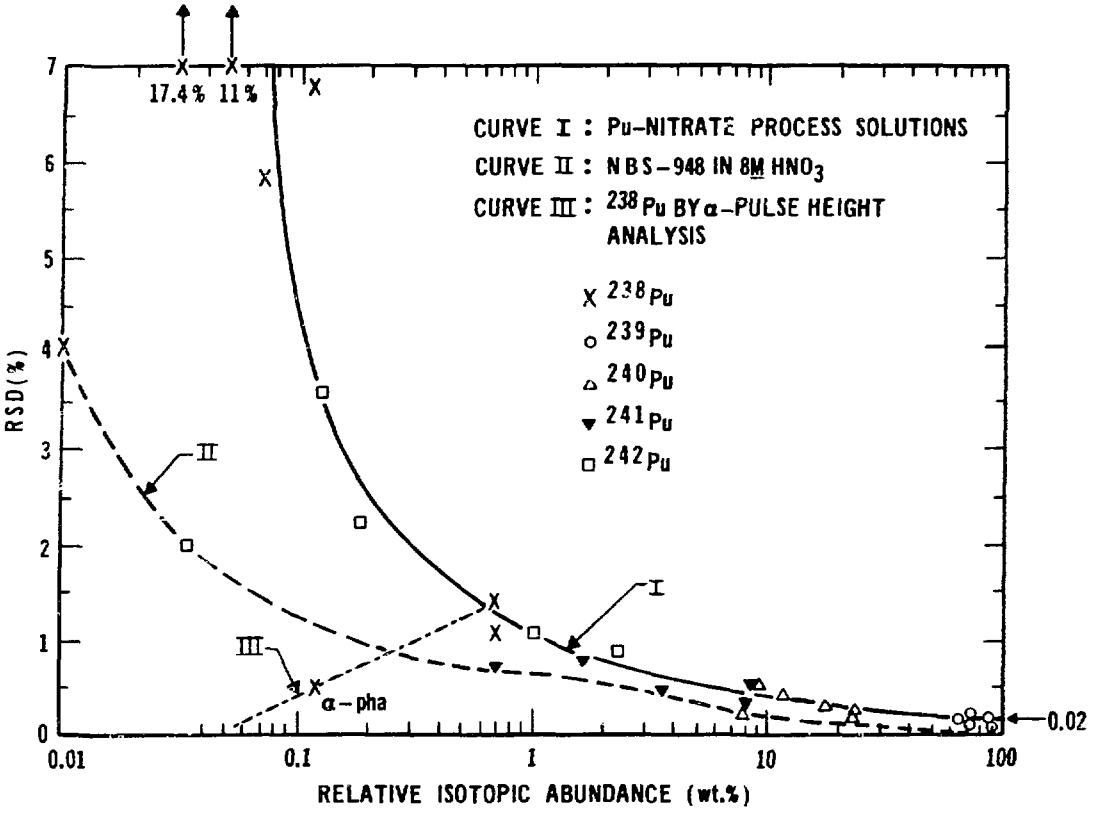

Fig 2. Precision of plutonium isotopic measurement.

applies to uranium isotopic determinations. The figure demonstrates that for major isotopes, RSDs of 0.01 to 0.02% can be attained. The precisions obtained for well-characterized material (a solution of NBS SRM) are significantly better than for the process and product solutions, particularly at isotopic concentrations >1%. The figure also shows that for measurement of ^{238}Pu concentration <0.7% alpha spectrometry is more precise than mass spectrometry. Recent studies show that improvements in precision and accuracy are obtainable if proper care is taken to minimize instrumental and operating errors. In an interlaboratory exchange program an overall RSD of 0.1% was obtained in measuring total plutonium in four samples having different isotopic compositions.[164] In terms of these data an RSD of 0.1

to 0.2% should be obtainable for measuring total plutonium in dissolver solutions if careful attention is paid to details of separation chemistry and instrument operation.

High gamma-radiation levels limit the mass-spectrometric analysis of dissolver solutions to extremely small samples or to samples that have been purified previously in shielded facilities. Microsamples of uranium and plutonium can be obtained on ion-exchange resin beads for subsequent analysis.[165] The analytical precision is <1% (RSD). Alternatively, the mass spectrometer can be modified for analysis of radioactive samples by enclosing the sparking chamber and the initial stage of the flight tube with 10 cm (4 in) of lead shielding.[166] Samples emitting up to 100 R/h of gamma activity can be analyzed in this fashion.

Mass spectrometry currently provides the most accurate isotopic analysis, even in the presence of fission products. The isotope-dilution method provides overall accuracy of 0.3-1% for the measurement of total uranium and plutonium concentrations in dissolver solutions. However, Teledyne Isotopes qualified for a uranium analysis in thorium-uranium fuels with an overall measurement error (isotopic plus total uranium) of 0.12%. This more nearly represents the state of the art.[167] The control of sample preparation is crucial to the accuracy. Even under ideal experimental conditions some 10% of the plutonium assays had to be discarded, probably because of poor sample preparation.

G. Alpha-Spectrometric Methods

Quantitative alpha-particle spectrometry is based on measurement of the alpha-radiation intensity of the sample. The alpha particles are ejected with discrete energies, and for the uranium, neptunium, plutonium, and americium isotopes found in the nuclear fuel cycle these energies range from 4 to 5.5 MeV. Alpha-particle energies are rapidly degraded by interactions with electrons, and complete attenuation is effected by ∿5 cm of air. Absorption by H_2O and self-absorption by the sample are even more rapid, and normal quantitative alpha spectrometry is limited to analysis of thin, dry films. The method has been

applied to determination of plutonium in dissolver solutions following solvent-extraction separation of the plutonium (Ref. 81; Ref. 88, pp. 392-398). The RSD for dissolver samples is in the range 3-5% (1σ). The method also is used for determining plutonium in uranium product and process waste streams.[169]

Because of the long half-lives of the major isotopes and possible interference from other alpha emitters such as neptunium, plutonium, and americium, the method probably is not applicable to thorium or uranium analysis.

Detectors used for alpha spectrometry include standard radiation instruments such as proportional counters, scintillation detectors, and solid-state devices. Special techniques have been developed for alpha-counting of Purex process streams, where the detector must be in direct contact with the alpha radiation sources.[170-174] Performance requirements are severe. The detector must operate in a flowing-liquid environment that is often of high acidity; it must be corrosion- and abrasion-resistant; it should discriminate alpha signals in the presence of high beta-gamma fluxes from fission products; and it should be insoluble in organics. Originally, ZnS(Ag) scintillation detectors were used, but were too fragile and difficult to fabricate. Organic scintillators in general cannot withstand the liquid environments. A cerium-activated Vycor glass detector has been developed[171] that will operate for months in a Purex process stream. The stopping distance for 5-MeV alpha particles in Vycor glass is estimated to be 25 μm, whereas beta particles of energies >0.5 MeV have penetration thicknesses in excess of 900 μm.[173] Thus, by reducing the cerium-activated layer to the alpha-particle penetration thickness, the alpha particles can be stopped in the active layer while most of the high-energy betas will pass through undetected. A further decrease in beta interference is attained by using thin sample cells,[175] and electronic pulse-shaping circuitry.[176]

The instruments can measure plutonium solutions in the concentration range between 10^{-4} and 1 g/L in the presence of beta-gamma fields up to 10^{8} dis/min-mL.[177] Deviations from

linearity at low plutonium concentrations ($<10^{-3}$ g/L) are caused by plating on the detector window and at high plutonium concentrations (>0.1 g/L) are caused by pulse pile up. Interference results from large variations in sample density that cause self-attenuation problems and from the presence of other alpha emitters such as neptunium, americium, or uranium. Calibration is performed empirically for each stream by chemical analysis.

The method still is being evaluated to measure its tolerance for beta and gamma emitters and to assess its applicability to in-line analysis.[178]

Diamond detectors recently were investigated as in-line alpha monitors, but data for process operation in the presence of high beta-gamma fluxes are not available.[179]

H. Fluorimetric Methods

The fluorimetric determination of low concentrations of uranium is based on the fluorescence of uranium when it is excited by ultraviolet light. The fluorescent spectrum consists of four bands in the visible region, with the most intense band at 554.6 μm. With 365-μm excitation from a high-intensity mercury lamp, few other elements will interfere by fluorescence.

Samples are evaporated and fused in a carbonate flux containing 10% NaF (Ref. 180) or NaF flux and sometimes containing LiF (Ref. 181) or some carbonate. Carbonate fluxes are easier to handle and provide better analytical precision. Fluoride fluxes provide better sensitivity but are more sensitive to variations in flux temperature and cooling conditions.

Although few elements or compounds have overlapping fluorescence spectra that interfere with the method, a number of elements interfere through quenching or enhancement. Quenching can result from absorption of the incident light, absorption of the fluorescent light, interference with the energy-transfer paths at phosphor centers, or precipitation of uranium.[17,182]

Most of the transition elements interfere to some degree through quenching. With a flux of 98% NaF-2% LiF, serious quenching is observed in the presence of small amounts of

cadmium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, lead, platinum, silicon, thorium, and zinc. Niobium and tantalum enhance the uranium fluorescence (Ref. 98, pp. 588-594). Many of the interferences can be removed by a combination of precipitation and solvent extraction of the uranium into ethyl acetate (Ref. 88, pp. 232-237) or into methyl-isobutyl ketone containing tetrapropylammonium nitrate. Alternatively, quenching interference can be minimized by comparing the measured fluorescence from a fused button of the sample and a similar button containing a known added amount of uranium (spiking).

As little as 1 ng of uranium can be detected by the fluorimetric method. The RSD for measuring uranium in simulated reprocessing-plant waste streams is reported to be 13%.[183]

I. Specific-Ion Electrodes

Specific-ion-sensitive electrodes have been studied for several years both for process control and analytical end-point detection. The applications of ion-selective electrodes to on-line analysis have been reviewed.[184] Although electrodes are not specific for thorium, uranium, and plutonium because all three are expected to behave similarly in the tetravalent state, the technique has elicited some interest, particularly for the determination of uranium.

The theory and applications of ion-sensitive electrodes have been discussed extensively.[185-188] The technique is based on the Nernstian response of an electrode pair (one electrode is sensitive to the ion measured and the second electrode is a reference) to the ion activity (or concentration) of the element determined. The measuring electrode incorporates the element to be determined in some form that is responsive to the activity or concentration in solution.

1. Thorium. Most solid ion-selective electrodes are sensitive to mono- and divalent cations. Liquid ion-exchange membranes using dinonyl-napthalenesulfonic acid (DNNS) electrodes have been developed that are sensitive to tri- and tetravalent cations, including thorium.[189] The response is near Nernstian but selectivity is poor.

2. Uranium. Several attempts have been made to form uranium-sensitive electrodes. An electrode based on a uranyl complex of an organophosphoric acid embedded in a polyvinyl chloride matrix was patented in 1975.[190] A number of organophosphorus complexes subsequently were studied for possible application as uranium-ion sensors.[191] Several sensors showed near-Nernstian response and linearity to uranium concentration in the range 10^{-1} to 10^{-4} M. The optimum pH range was 2-3.5. The membranes were poisoned by Fe^{3+}. Solid-state electrodes fabricated from uranium alloyed with titanium, molybdenum, or niobium gave a linear response proportional to uranium concentration, but sensitivity was poor.[192] Electrodes of UO_2, U_3Si_2, US_2, UC_2, and UP did not respond. Membrane electrodes also were studied, but response to uranium concentration was low and erratic.

Additional work on uranium-sensitive electrodes may be warranted for on-line or at-line measurement of low concentrations of uranium.

3. Plutonium. Plutonium-sensitive electrodes have not been studied, and probably would be of questionable value because other more sensitive methods for measuring plutonium are available.

J. X-Ray Fluorescence Techniques

X-ray fluorescence techniques have been applied to the analysis of actinide solutions for over 25 years. They are sensitive and accurate and, with appropriate separation and sample-preparation schemes, are capable of measuring microgram quantities of material to relative accuracies of 1% or less. Typical analysis times are short (0.5 h or less). The fundamentals of x-ray fluorescence analysis have been reviewed in detail in the literature.[193-196] The analyst has considerable latitude in selecting a technique, including choices of excitation source, detector, and x-ray line.

The most commonly used excitation source is the x-ray generator because of its high flux, although the use of radioisotopes

is becoming more common because solid-state detectors are available and can detect the lower, secondary x-ray levels. X-ray tubes generally are required when wavelength-dispersive spectrometers are used (because of the low spectrometer efficiencies) and when radioactive solutions from spent fuels are measured (because the signal generated by the excitation source must be greater than that caused by the fission products). When they are applicable, radioisotopic sources[197,198] (such as ^{125}I, ^{109}Cd, and secondary targets fluoresced with ^{241}Am) offer advantages such as ease of measurement configuration, long-term stability, and lower cost.

Both wavelength- and energy-dispersive detection systems have been used to measure thorium, uranium, and plutonium in solution. Wavelength dispersion offers high resolution, but at low efficiencies. Energy dispersion is more efficient but has poorer resolution at energies <20 keV. At energies >20-25 keV, a Si(Li) energy-dispersive spectrometer provides better resolution and efficiency. The high resolution of wavelength-dispersive spectrometers is an asset in the measurement of spent fuels where there is a potential for interference from the multitude of fission products. The high efficiency of energy-dispersive, solid-state Ge(Li) detectors is often an asset in measurements of "cold" solutions when radioisotopic excitation sources are used.

1. Selection of a Line. For thorium, uranium, and plutonium measurements, lines in the K, L, or M series can be used; the more intense lines in these series are summarized in Table XV. When selecting a line to use in an x-ray fluorescence measurement, the main considerations are line intensity above background and interferences from adjacent lines.

The high energies of the K-series lines require either the use of generators and x-ray tubes capable of producing up to 150-keV x rays, or the use of gamma-ray excitation sources. Diffraction gratings or crystals that provide good dispersion in

TABLE XV

X-RAY LINES COMMONLY USED FOR URANIUM AND PLUTONIUM

Line	Energy (keV) Thorium	Uranium	Plutonium
$K\alpha$	93.350	98.440	111.303
$K\beta$	105.609	103.763	117.256
$L\alpha_1$	12.969	13.612	14.276
$L\alpha_2$	12.810	13.437	14.082
$L\ell$	11.119	11.616	12.122
$L\beta_1$	16.202	17.217	18.291
$L\beta_2$	15.624	16.428	17.255
$L\gamma_1$	18.902	20.164	21.414
$M\alpha$	2.993	3.167	3.356
$M\beta$	3.146	3.336	3.550

this energy region are not available, so energy-dispersive systems must be used. In addition, there may be significant overlap of plutonium gamma rays with the uranium and plutonium x rays. Nevertheless, K-series x rays have been applied to solution analysis.[199] Use of the M-series x rays requires either a helium or vacuum path to minimize air absorption, and use of these lines usually is limited to solids. Because of the close proximity of the thorium, uranium, and plutonium lines, wavelength-dispersive systems must be used. Even then, serious problems can result from the overlap of the $M\alpha$ and $M\beta$ lines of plutonium by the $M\beta$ and $M\gamma$ lines, respectively, of uranium and of the $M\alpha$ and $M\beta$ lines of uranium by the $M\beta$ and $M\gamma$ lines of thorium. Nevertheless, M-series lines have been used for some types of analyses.[200]

The most common choice is one or more of the L lines. They provide good intensities in an air path for analyses of solutions or solids, and can be used with any type of excitation or detection system.

2. Interferences. Three types of matrix interference are encountered in x-ray fluorescence: line overlap, absorption, and enhancement.

Line interference occurs when a matrix element has an emission line that overlaps that of the special nuclear material (SNM). In the 11- to 20-keV energy region, the elements from arsenic to molybdenum have one or more strong K lines that are close enough in energy to the commonly measured L lines of thorium, uranium, and plutonium to be a possible source of interference. Unfortunately, many of these elements appear as fission products in spent fuel.

Absorption and enhancement are essentially two manifestations of the same phenomenon. Absorption, which occurs in varying degrees in all samples, is the more serious of the two. Both the matrix and the SNM can attenuate the SNM line, causing a negative bias in the assay result. Matrix enhancement occurs if a matrix element has a strong x-ray line above the energy of the absorption edge of the SNM analyte. For example, if molybdenum is present in a uranium solution, the molybdenum $K\alpha_1$ line can excite the uranium $L\alpha$ lines and cause a positive bias in the uranium measurement. For uranium and the transuranics, self-enhancement also can occur.[201] For these elements, the $L\beta_1$ emission line is above the L_{III} absorption edge in energy and can excite the L lines commonly used for measurement. Self-enhancement is generally not noticeable unless large quantities of uranium and plutonium are present.

The internal-standard method corrects for matrix absorption-enhancement effects by adding a known standard to the solution and comparing the counts in the SNM line to the counts in the standard line. The standard line is chosen as close to the analyte line as possible, preferably with an absorption edge

above the energy of any enhancing matrix lines. Different internal standards, including strontium for aqueous solutions and bromobenzene for organic solutions, have been used in the measurement of thorium and uranium at different stages of solvent extraction.[202] Zirconium also has been suggested as an internal standard for organic uranium and thorium solutions.[203]

Thorium is the commonly used internal standard for uranium and plutonium solutions,[203-205] but yttrium also is used[206] when the possibility of thorium contamination exists in the sample, as would be the case for Thorex reprocessing samples.

Another matrix-correction technique, the scattered x-ray method, primarily corrects for matrix absorption but not, in general, for enhancement. Thus, its application is best suited to process-control situations where matrix properties are well known and nonvariable. In this method, instead of adding lines to the spectrum by adding a standard to the solution, a scattered x-ray line is used as a standard. The Compton-scattered molybdenum Kα line has been used to measure plutonium in solutions of plutonium-aluminum alloys,[207] and the incoherently scattered iodine Kα line has been used to measure uranyl nitrate solutions.[208] These authors report that the technique could extend the range of measurable concentrations up to 500 g/L of uranium.

A novel scattering technique has been reported[209] that can rapidly measure uranium concentrations of 1 to 10 g/L in the presence of high concentrations of low-Z matrix elements. Instead of measuring an SNM line, coherent (Rayleigh-scattered) radiation is measured at appropriate angles. The method is not completely matrix-compensating; the addition of 60 g/L of aluminum to an 8 g/L uranium solution increased the uranium measurement by 1 g/L. In situations where matrix concentrations are known to fluctuate by only a few per cent, McCue et al.[209] claim that accuracies of 0.7% or better are possible in short counting times.

3. Applications to Reprocessing Samples. Although x-ray fluorescence measurements of SNM solutions have had wide exposure in the literature, current safeguards applications are limited because of competition from other less complex and less matrix-dependent methods. To reduce the matrix sensitivity, samples are often evaporated as thin films. This technique reduces the scattered background compared to the sample signal, thus increasing sensitivity and reducing counting times.[210] Measurements of thin films are linear with the concentration of SNM over a small range, above which saturation effects become important.

Several systems have been developed to assay highly radioactive spent-fuel solutions. One of these systems[203,204,211] uses a wavelength-dispersive spectrometer to assay solutions having uranium-plutonium ratios of from 50:1 to 300:1 with accuracies of ∿1% (1σ) in 2-5 min. Solutions having activities of <1 Ci/mL are handled routinely by evaporating small samples onto a filter paper. Samples having low beta-gamma activities can be analyzed directly in solution after addition of an internal standard. The fission products cause no serious line interference. An automatic sample-preparation system is being developed to allow on-line analysis.

Uranium and plutonium in solution having beta-gamma activities to 1 Ci/L have been measured directly through a Plexiglas window.[206] The system used is as close to in-line analysis as one can devise. An automatic sampler removes solutions from the sample line and yttrium is added to serve as an internal standard. Solution transfers are made by pneumatic tube. A minicomputer performs data reduction, and overall precision and accuracy of better than 1% are claimed for the technique.

In another system,[212,213] hot dissolver solutions containing uranium and plutonium at ratios up to 400:1 and uranium concentrations of ∿50 g/L are measured with an x-ray tube in combination with a Si(Li) detector. Preliminary tests indicate that accuracies of 1-2% are possible with 10-min analysis times.

However, accuracies of only 3% are obtained because of problems in sample preparation. A new preparation method now being evaluated should improve measurement accuracy.

A system has been developed for automatic sampling and sample preparation of dissolver solutions from the reprocessing of thorium-uranium fuels.[203] For solutions emitting up to 2000 Ci/L, samples containing 1.0 ml of solution are automatically aliquoted and mixed with an internal standard. The aliquots are evaporated onto a filter paper, which is transferred to a shielded x-ray spectrograph. All operations are performed remotely under computer control.

Thorium and uranium have been measured directly in solution by using strontium as an internal standard.[214] The method yields a RSD of 1.5% (1σ) in the concentration range 0.1 to 10 g/L but probably cannot be applied to highly irradiated samples.

VII. PROBLEM AREAS

The sample selected for analysis *must* be representative of the bulk material being sampled. In Thorex or Purex reprocessing systems several effects can alter the sample sufficiently to negate the most carefully conceived and administered analytical plans. The high radiation fields in the samples can cause sample heating, solvent decomposition, reagent degradation, and oxidation-reduction reactions. This is particularly true at the dissolver end of the stream where high concentrations of fission products result in intense beta-gamma fields and at the plutonium product end where high alpha-radiation levels are present. The high gamma fluxes associated with reprocessed thorium and ^{233}U product streams require that all analytical manipulations be performed remotely in shielded facilities.

Analytical problems associated with sample heat, radiolytic decomposition of reagents, polymerization, and radioactive sample decay have been summarized.[215-217] Problems in sampling and sample storage associated with high gamma fluxes will persist through the thorium and uranium storage areas of Thorex

reprocessing because of the radiation from thorium and uranium decay products.

VIII. SUMMARY AND CONCLUSIONS

The analytical chemical needs in a plant designed to reprocess thorium-uranium fuels will require highly precise and accurate measurements of uranium as well as plutonium. The ^{233}U (and ^{235}U for first-generation reactor fuel) must be measured with the same care given to plutonium. For fuels diluted with ^{238}U, significant quantities of weapons-grade plutonium will be produced and must be measured accurately.

Isotope-dilution mass spectrometry will continue to be a key accountability measurement for both uranium and plutonium in dissolver solutions, not only because of its potential for high precision and accuracy but because isotopic analyses can be correlated with reactor data. Thorium also can be measured by using a ^{230}Th spike. Electrometric methods for uranium and plutonium measurement will be required for calibration checks of NDA instruments. Plutonium product also can be measured by electrometric titrations. In-line alpha monitors for plutonium and in-line polarography for uranium may be developed for waste-stream measurements but will be supplemented by spectrophotometric and fluorimetric methods for calibration checks.

Thorium, though not an SNM, must be measured for accountability checks and to meet NRC and IAEA requirements. Gravimetry and EDTA titrations probably will be the methods of choice. For thorium product measurements, analyses must be adapted to hot-cell operation. The process of radioactive decay cannot be ignored in the analytical scheme nor can the influence of thorium content on the analyses of the fissile materials.

Automation of instrumentation for remote operation will be necessary for many routine analyses because of the high radiation levels associated even with purified uranium and thorium product streams. Much work already has been done in this direction, including the automated spectrophotometer for uranium and

plutonium analyses,[105] potentiometric determination of uranium,[117] controlled-potential coulometric determination of uranium and plutonium,[218] mass-spectrometric determination of uranium and plutonium,[168] and x-ray fluorescence analysis of all three elements.[203-206,211,212] Remote-sampling techniques[203] and small-sample methods such as the resin-bead[165] will be important to minimize personnel exposure. In-line methods will be required not only for near-real-time accounting but also for minimizing exposure to personnel.

ACKNOWLEDGMENTS

The author gratefully acknowledges the helpful suggestions and criticism of R. J. Dietz, D. D. Cobb, H. A. Dayem, C. A. Ostenak, and J. P. Shipley of the Q-4 staff; J. R. Phillips of Q-1; G. R. Waterbury of CMB-1; J. A. Goleb of the Office of Safeguards and Security, DOE; C. D. Bingham of the New Brunswick Labortory; T. L. Williams of Allied-General Nuclear Services; R. S. Swingle II and E. Lukosius of the Savannah River Laboratory; W. Lawless, DOE/SRO; and L. Abraham, G. E. Benedict, H. C. Carney, N. D. Holder, E. M. Knox, J. J. Shefcik, and R. G. Wilbourn of the General Atomic Company. The manuscript was prepared by Sharon Klein.

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