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Actinide Analysis in Biological Materials

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In response to an emergency radiological incident there is always a need for fast, reliable methods for the determination of actinides on bioassay samples. This is one of the utmost important for dose evaluation as well as for proper medication for the exposed one. Due to the complexities lying in the biological sample matrix, it is very important to have a proper analytical methodology for estimation of actinides. This paper summaries the basic procedures needed for the accurate and fast measurement of different actinide elements like U, Th, Pu and Am in biological matrices mainly urine and fecal samples and also isotopic ratios. For actinide analysis in biological material the most important steps involved are sample digestion, radiochemical separation, source preparation followed by detection. Depending upon the type of actinide, its concentration, sample size availability careful selection of proper procedure is needed for each step for accurate and reliable measurement. This also briefly describes the improved and modified methodologies for estimation of different actinides in biological matrices at low level by different researchers.

1. Introduction

Use of nuclear technology, for power generation, medicine, agriculture, nuclear weapons manufacturing and testing as well as nuclear power plant accidents such as Three Mile Island, Chernobyl and Fukushima have led to global spread of both natural and artificial actinides into the biosphere at ultra-trace levels. Workers in nuclear facilities, the general population, and environment have been contaminated from the released actinide[1-11]. These radionuclides could be deposited internally in the human body by inhalation, ingestion, penetration through wounds, and adsorption to skin[2, 7, 9, 12].

Actinides are considered most hazardous radionuclides due to their high radiological and chemical toxicities, and long radioactive half-live[5, 6, 11]. The determination of the nature and activity of internal contamination present in a person is necessary to assess radiation exposure for the purpose of radiation protection by both direct and indirect measurement[3, 4, 7]. Indirect bioassay is the measurement of the amount of radioactive materials in the excreta or in other biological materials removed from the body, such as urine, feces, tissue, biopsy specimens, blood, finger nails, hair, teeth, saliva, sweat, and breath[1-21].

The determination of actinide levels in human urine can be used to measure potential exposure to radioactive material of nuclear facility or other industry workers, who are generally subjected to routine occupational monitoring[3, 11]. Bioassays has also been used to evaluate exposures following unintended environmental releases and to monitor and assess potential exposure.

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Rapid, accurate and sensitive determination of trace actinides (Major actinide: U, Th, Pu and minor actinide: Am, Cm, Np, etc.) in biological materials represents a significant challenge due to their extremely low concentrations and the diverse matrix chemistry of these samples[1, 13, 14]. The actinides determination procedure in bioassays should be made at low level of detection limit, rapid turnaround time, high sample throughput, minimal sample preparation, reduced analysis costs, wide variety of matrices and also not generate any appreciable amount of mixed or hazardous waste[2, 6, 13]. Therefore, both the detection techniques and the chemical process such as sample decomposition and chemical separation are significant to enable the radionuclide or actinide analysis in biological materials to be more sensitive, accurate, rapid, and economical.

2. Radiochemical Procedure

A variety of radiochemical techniques are employed in the determination of actinides present in biological materials at low level including sample decomposition, co-precipitation, and chemical separation by using ion-exchange, extraction chromatography, or solvent extraction[2, 13].

Sample breakdown and radionuclide solubilization is accomplished by wet or dry ashing in a muffle furnace, microwave acid digestion or fusion decomposition, depending on the volatility of the radionuclides of interest. Due to very low concentration, radiochemical separation of actinides is generally carried out. Each sample is spiked with the appropriate carriers and yield tracers prior to radiochemical analysis. Following separation and purification, each radionuclide fraction is converted to a suitable form using precipitation or electrodeposition depending upon the instrument to be used. Generally activity measurement is carried out using alpha, beta or gamma counting systems with ionization chambers, magnetic spectrometers, scintillation detectors or semiconductor detectors[13].

Sample decomposition

The purpose of the decomposition process is to destroy organic matter and dissolve inorganic precipitates contained in a sample. Selection of the appropriate sample decomposition method is very important in accurate determination of actinide concentration and is dependent on the sample matrix, the chemical state of the actinide, and the chosen method of actinide determination[13].

Dry ashing normally is used for solid sample such as feces. Feces samples are dry ashed by drying in a closed muffle furnace by raising the temperature in the increments of 50°C to 450°C[2]. Wet ashing or acid digestion are performed on a hotplate at atmospheric pressure or in a closed digestion bomb at elevated pressures and temperatures in a convection or microwave oven. Actinides are soluble in HNO_3 and HCl so most procedures for the decomposition of actinide-containing samples utilize these acids. The addition of H_2O_2 in catalytic quantities aids in oxidizing organic matter[13].

Narayani P. et al. used dry ashing and/or wet ashing with a mixture of HNO_3 and H_2SO_4 or HNO_3 alone, depending on the matrix of sample, with addition of few drops of HNO_3 and H_2O_2. *Trivedi A. et al.* introduced the acid- and microwave-digestion in the sample digestion step of a fecal bioassay method to rapidly detect Pu and Am to increase efficiency and reduce turnaround time. The digestion process was completed in 1 hour. The turnaround time for the sample analysis was minimized to 6 hours.

The decomposition step may be followed by separation, purification, and conversion of actinide to a chemical form that is appropriate with the requirements of the method of determination[13].

Chemical separation

Chemical separation is essential for enhancement of the sensitive, accurate, and precise determination of actinides in biological material and to eliminate nonspecific and isobaric interferences from the intended actinides[2]. The techniques are co-precipitation, ion-exchange, adsorption, solvent extraction, extraction chromatography, or a combination of two or more of these methods[2, 13]. For example, Uranium can be co-precipitated with hydrous titanium oxide (HTiO)[4], calcium phosphate ($Ca_3(PO_4)_2$)[11] or ammonium hydroxide (NH_4OH)[16] from urine. Pacific Northwest Laboratory used lanthanum fluoride co-precipitation followed by extraction of Plutonium with thenoyltrifluoroacetone (TTA) from tissue samples[17].

There are many kinds of ion-exchange resin. Most of them are typically organic polymers onto which functional groups are attached. 90% of the polymers are polystyrenic matric. *Lee. Y. K. et al.* use anion (AG 1X4) and cation (AG50 WX8) exchange resin (Bio-Rad Lab.) for sequential isotopic determination of actinide and Sr in bioassay samples[7]. *Maxwell III S. L. et al.* introduced a new column separation method for emergency urine samples. The raw urine was acidified and passed directly through the stacked resin columns using extraction chromatography, TEVA+TRU+SR-Resins (Eichrom Inc.) to separate the actinides and ^{90}Sr from urine sample more quickly[18-20]. *Wei H. et al.* evaluated trace level actinides in a urine matrix on the chromatographic column packed with TRU resin for separation. The chromatographic system was coupled on-line to the ICP-MS for pre-concentration and separation of U, Th, Pu, Np, and Am[8].

Additionally, chemical separations pre-concentrate the analyte. Pre-concentration is especially useful for actinides because of their ultratrace concentrations in biological materials. *Qu H. et al.* have introduced pre-concentration of Pu and Am using the Actinide-CU Resin™ (Eichrom Inc.). Diphonix Resin (Eichrom inc.) is used to pre-concentrate the actinides from digested fecal samples. A rapid microwave digestion is used to remove the actinide from the resin[21].

3. Instrumental Methods

Depending upon the availability of sample size, actinide

concentration and nature of actinide of interest various detection techniques may be employed. Those include nuclear techniques, e.g., alpha spectrometry, gamma spectrometry, beta counting, liquid scintillation counting, neutron activation analysis, and fission track analysis for ^{239}Pu and ^{235}U, atomic spectrometric techniques, such as atomic emission spectrometry (AES), flame emission spectrometry (FES), and phosphorimetry and fluorometry, and mass spectrometric techniques, for example, inductively coupled plasma mass spectrometry (ICP-MS) and thermal ionization mass spectrometry (TIMS)[1-21].

Gamma spectrometry

Gamma spectrometry allows both qualitative and quantitative analysis of individual actinide nuclides based on the detection of emitted γ-rays possessing energies that are specific to nuclear transitions in actinide of interest.

Gamma spectrometry requires minimal sample preparation as compared to the chemical procedures required for the source preparation for alpha spectrometry. Gamma spectrometry has the advantage of being the only non-destructive radiometric technique but it is limited in general applicability to all the actinides due to the absence of intense γ-rays. Essentially all but a few of the naturally occurring actinides and environmental transuranic actinides can be determined by gamma spectrometry. This technique is frequently employed to measure recovery of long-live actinides by way of spiking with a short-lived, γ-rays-emitting isotope. The sensitivity of the technique is dependent primarily on the half-life of actinide and the percent γ-ray intensity[13].

Alpha spectrometry

Conventional radioanalytical techniques for the routine determination of actinide in biological materials are alpha spectrometry or liquid scintillation radiometry. *Narayani P. S. et al.* have determined of U, Th, and Pu in biological sample including soft tissue, bone, urine, and feces using solvent extraction, electrodeposition and alpha spectrometry. The technique has been very successful for most samples, with radiochemical recoveries exceeding 70%[15]. *Maxwell III S. L. et al.* have used alpha spectrometric technique to analyze Pu and Am in feces[21], actinides in urine[18, 19], and animal tissue[20]. *Xiongin D.* has analyzed isotopic uranium in urine sample by alpha spectrometry[4]. The minimum detectable activity concentration were determined to be 0.43, 0.21, and 0.42 mBq/L for ^{238}U, ^{235}U and ^{234}U, respectively.

Alpha spectrometric techniques are based on the measurement of activities of radioisotopes and have limited sensitivity. They are often not sensitive enough for the determination of long-lived radionuclides in environmental and biological samples because such nuclides have low specific activities, and therefore, very long measurement times are required. Although some sophisticated methods, coupled with implanted passivated junction silicon detectors and special spectra deconvolution software, were proposed to improve alpha spectrometry resolution, those approaches are mainly restricted to high-activity samples, as relatively high peaks are needed to define the spectrum well enough so that the multivariate analysis techniques can be applied.

Accurate and precise alpha spectrometric analysis also requires careful chemical separation of actinide to eliminate source of alpha particles with energies similar to the analyte, correction for the recovery of the chemically separated nuclide with an isotopic spike, and preparation of thin source which are delicate and time-consuming. This means that analysis can take several days or even several weeks. An additional limitation of alpha-spectrometry for Pu analysis is that usually only the sum of ^{239}Pu and ^{240}Pu activity can be determined due to similar alpha energies (5.24 MeV and 5.25 MeV, respectively)[1].

Although the radiochemical methods are still dominantly used for the analysis of many short-lived radionuclides they are increasingly replaced by inorganic mass spectrometry for the long-lived radionuclide analysis due to its high sensitivity for long live isotope (especially ^{238}U and ^{235}U), high sample throughput, and minimal sample preparation requirements[4].

Mass spectrometry

Mass spectrometric methods have been applied for actinide isotopic measurements, such as thermal ionization mass spectrometry (TIMS)[1, 3, 9, 23], accelerator mass spectrometry (AMS)[1], resonance ionization mass spectrometry (RIMS)[1], glow discharge mass spectrometry (GDMS)[1], secondary ion mass spectrometry (SIMS)[1], inductively coupled plasma mass spectrometry (ICP-MS)[1-3, 8-9, 16], laser ablation ICPMS (LA-ICP-MS)[12], inductively coupled plasma quadrupole mass spectrometer (ICP-QMS or IC-Q-ICP-MS)[3, 12] etc. Mass spectrometry is being increasingly used for the determination of actinide[1,2] with low specific activity in biological sample, especially ICP-MS has become an important tool for actinide analysis. The advantages of mass spectrometry methods include low detection limit (ICP-MS, TIMS), simple experimental procedure, reliable and high precision of the measured isotopic ratio (multi-collector ICP-MS, TIMS), high selective and abundance sensitivity (RIMS, AMS), and possibility for a spatially resolved isotope analysis (SIMS, LA-ICP-MS)[1, 22].

Hang W. et al. have developed a novel concentration and separation method to determine trace levels of actinides in urine samples and used an inductively coupled plasma quadrupole mass spectrometer (IC-Q-ICP-MS) for detection. The detection limits for pure urine samples are 29 pg/mL of Th, 18 pg/mL of Np, 1.5 pg/mL of U, 31 pg/mL of Pu, and 0.02 pg/mL of Am. The technique can be successfully used for the validation and quantification of ultra-trace U and Am, even in the most complicated urine matrix[3].

Laser ablation inductively coupled plasma mass spectrometer (LA-ICP-MS) detection limits were generally better than the detection limits of alpha spectrometry for all radionuclides with half-lives that are longer than 1000 years[1]. *Sela H. et al.* have worked on biomonitoring of hair samples using ICP-MS and LA-ICP-MS. The lowest detection for

Table 1. Detection limit of actinides in urine sample by radioanalytical and mass spectrometric methodbin.

Radionuclide	Analytical technique	Detection limit	
^{232}Th	Alpha spectrometry	1.00E-02 Bq/L[2)]	2.46E+03 pg/mL
	IC-Q-ICP-MS	1.18E-04 Bq/L[3)]	2.90E+01 pg/mL
	NAA	1-4 E-07 Bq/L[2)]	2.46-9.86E-02pg/mL
	ICP-MS	8-80 E-05 Bq/L[2)]	
^{238}U	Alpha spectrometry	4.30E-04 Bq/L[4)]	1.97-19.7E+01pg/mL
	ICP-MS	2.49E-07 Bq[1)]	
	IC-Q-ICP-MS	1.87E-05 Bq/L[3)]	3.46E+01 pg/mL
	NAA		2.00E+01 pg
	Fission track analysis	1.24E-09 Bq[2)]	1.50E+00 pg/mL
	Laser-Induced Fluorescence	1.24-4.98E-07	
	Extraction	Bq/L[2)]	1.00E-01 pg
^{236}U	Kinetic Phosphorescence	4.98E-07 Bq/L[2)]	1.00-4.00E-02 pg/mL
^{235}U	Analyzer	7.18E-09 Bq[1)]	
	ICP-MS	2.10E-04 Bq/L[4)]	4.00E-02 pg/mL
^{234}U	Alpha spectrometry		3.00E-03 pg
	ICP-MS	4.20E-04 Bq/L[4)]	2.63E+00 pg/mL
^{239}Pu	Alpha spectrometry		
	ICP-MS	2.30-115E-05 Bq [1)]	1.82E-03 pg/mL
	Alpha spectrometry		
	ICP-MS	2.30E-06 Bq[1)]	1.00-5.00E-02 pg
	TIMS	1.22E-06 Bq/L[5)]	1.00E-03 pg
	IC-Q-ICP-MS	7.12E+01 Bq/L[3)]	5.30E-07 pg/mL
	AMS	1.01E-06 Bq[1)]	3.10E+01 pg/mL
^{241}Am	RIMS	1.01E-06 Bq for ^{244}Pu[1)]	4.40E-04 pg
	Fission track analysis		4.40E-04 pg
	Alpha spectrometry	1.90-3.00E-06Bq/L[2)]	0.82-1.31E-06 pg/mL
	ICP-MS	1.21E-03 Bq[1)]	9.50E-03 pg
	IC-Q-ICP-MS	4.69E-01 Bq[1)]	3.70E+00 pg
		2.54E+00 Bq[3)]	2.00E-02 pg/mL

uranium determination (0.2 ng/g) was observed for ICP-MS analysis of digested hair samples. The detection limits for LA-ICP-MS were one order of magnitude higher than ICP-MS. However, the analysis time and sample preparation of laser ablation techniques were shorter than the solution-based analysis[12)].

Thermal ionization mass spectrometry (TIMS) has been the technique of choice for achieving the highest accuracy and precision of isotope ratios[1)]. *Elliot N.L. et al.* have successfully determined femtogram quantities of ^{239}Pu and ^{240}Pu in bioassay samples by TIMS. The detection limit of the method was 0.53 fg (1.2 μBq) for ^{239}Pu and the instrumental detection limit was 0.1 fg. The determination of the isotopic signature of the sample with ^{239}Pu, ^{240}Pu and ^{241}Pu amount for several femptograms level is possible[5)].

Accelerator mass spectrometry (AMS) is good for the determination of low-abundant isotopes of heavy elements and it typically reaches abundance sensitivities for actinide isotopes in the range of 10^{-11} to 10^{-13}. Halmilton et al. have used ultra-high sensitivity AMS to measure the Pu isotopic ratio in marine organism tissue samples. Those data demonstrated that ^{240}Pu/^{239}Pu isotope signatures might well provide a useful investigative tool to monitor source term attribution as well as to assess the health and ecological impacts of leakage of Pu from low-level radioactive waste repositories[1)].

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