Assessment of Thorium in the Environment (A Review)

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Summary: Thorium, the radioactive metal, present in natural sediments produced in the form of detritus minerals such as monazite, rutile, granitic complexes, syenitic complexes, thorite, thorianite and progenitor of U, Th and Ac series. It is used in variety of industrial purposes, medical applications and proposed as fissile material for nuclear energy via production of ^{233}U from ^{232}Th. Anthropogenic process including modern trends in agriculture causes environmental pollution and also affect the biochemical cycle. However, changes in pH or different redox conditions of rocks enable a fraction of thorium to be released in the environment eventually. This review focuses on the radiochemical techniques, such as alpha, gamma spectroscopy as well as inductively coupled plasma mass spectrometry (ICP-MS) that are used for the measurement of thorium. A survey of current research activities intend to control the incorporation of thorium in order to minimize internal doses has been performed.

Keywords: Radionuclides, Anthropogenic, Magmatic, Complexion, Chromatography, Gamma spectrometry.

Introduction

Thorium is a natural radioactive metal discovered in 1828 by the Swedish chemist J. J. Berzelius, who named it after Thor, the Norse God of Thunder. Thorium occurs in minerals, predominantly in thorium-phosphate and monazite, which contains 12% thorium oxide [1]. Earth's crust (limestone and granite) contains harsh, dangerous and long-lived isotopes of uranium and thorium. Granite, a hard igneous rock which consists of quartz, feldspar and mica, the most durable stone available for exterior use and also lends itself as an excellent flooring material due to anti-slip paving in finished texture [2]. Thorium-232, the progenitor of the (4n) decays to produce other isotopes, which occur in thorium and uranium's decay chains and its other important isotopes ^{234}Th, ^{230}Th, ^{231}Th, ^{227}Th and ^{228}Th exist as members of the ($4n^{1+}$), ($4n^{2+}$) and ($4n^{3+}$) decay series [3]. Thorium has a variety of applications, it is a silvery white metal, retains its lustre for several months, slowly tarnishes in air becomes grey and finally black. Thorium oxide has a melting point of 3300°C, the highest of all known oxides. Uranium and thorium are lithophile elements, mostly concentrated in crystal rocks with an average Th/U ratio of 3.5 and are enriched especially in acidic igneous rocks such as granites, pegmatites as compared to basic and ultra basic intermediate [4-6].

Thorium is ubiquitous, its release in environment occurs both from natural and anthropogenic sources that elevate its level over the background. Wind blown terrestrial dust and volcanic eruptions are two important natural sources of thorium in the air [7-8], while mining, milling, tin processing, phosphate rock processing, phosphate fertilizer production, coal fired utilities and industrial boilers are the anthropogenic sources of thorium in the atmosphere [9-12].

The presence of Th In aquatic lower level animal is significant but the bioconcentration further decreases as the trophic level decreases [13-14]. The fate and mobility of thorium in soil is governed by the same principles as in water, but it remains strongly sorbed to soil and its mobility is very slow [15]. However, leaching into groundwater is possible in some soils with low sorption capacity and the ability to form soluble complexes. The soil/plant transfer ratio for thorium is less than 0.01, indicating that it is not bio-concentrate in plants from soil [16]. The plants grown at the edge of impoundments of uranium tailings contain elevated level of thorium and the soil/plant concentration ratio was found to be about 3 [17].

The average thorium concentration in atmosphere is reported 0.3 ng/m^3 in air samples collected from different sites [18]. Different trials in this respect were performed and the values of different isotopes have been cited for air, surface water and ground water [19-20]. The maximum concentration of ^{232}Th in several fruits, vegetables and other foods is reported to be less than 0.01 pCi/g and the daily intakes of ^{230}Th and ^{232}Th for residents has been estimated to be 0.17 and 0.11 pCi respectively. People who consume foods grown in high background areas, reside in homes having high thorium background levels or near radioactive waste

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disposal sites are exposed to higher than normal background levels of thorium in mBq i.e ^{230}Th-5.860 ± 0.38, ^{232}Th-3.38 ± 0.29 and ^{228}Th-11.8 ± 1.21. Annual effective doses for the worker related to uranium, thorium, tin, phosphate mining, milling and processing industries as well as gas mantle manufacturing units are reported which are higher than normal background levels of thorium [12-26].

Contamination of Thorium

Air

Combustion of coal, containing radio-nuclides of the uranium and thorium series as well as ^{40}K form a source of radioactive contamination in the vicinity of power stations. Coal contains 0.5-7.3 µg/g thorium produces thorium in the fly ash that depends upon the nature of the coal burnt and emission control devices of plant [7-8, 11, 27-31]. However, the concentration of all natural radioactive isotopes in the stack effluents produced by coal fired power plants are usually much lower than the natural background concentrations of these radionuclides. Fly ash from oil and peat fired power plants are also atmospheric sources of thorium [11, 12, 32, 33]. The intake of ^{232}Th and ^{228}Th was mainly due to the vegetables, potatoes, milk and flour [34]. Elevated levels of ^{220}Rn, ^{212}Bi and ^{216}Po are present at the rare earth extraction site, although the concentrations of thorium in air particulate samples are not significant [10, 23, 35-37]. The Environmental Protection Agency (EPA) estimated that about 0.2 Ci of ^{230}Th is annually emitted into the air from uranium mill facilities coal-fired utilities, by industrial boilers, phosphate rock processing, fertilizer production facilities, and other mineral extraction and processing facilities. About 0.084 Ci of ^{234}Th from uranium fuel cycle facilities and 0.0003 Ci of ^{232}Th from underground uranium mines are emitted into the atmosphere annually [38]. The background concentration of thorium in various environmental samples is given in Table-1.

Water

The acidic leaching of uranium tailing piles in certain areas is a source of ^{230}Th in surface water and groundwater [39, 40]. The contamination of surface waters and benthic zone by ^{230}Th from uranium mining, milling operations and from radium and uranium recovery plants has been reported [41, 42]. Other industrial processes that are expected to be sources of thorium contamination into water are phosphorus and phosphate fertilizer production as well as processing of some tin ores. Since both phosphate rocks and the tailings from tin ore processing contain mainly thorium as ^{230}Th and ^{232}Th, respectively, discharges of processed or unprocessed effluents and leaching from tailing piles are also the sources of thorium in water. Leaching from landfill sites contains uranium and thorium results in the contamination of surface water and groundwater with thorium [34, 43, 44].

The major industrial releases of thorium to surface waters are effluent discharges from anthropogenic sources [39, 41, 42, 45]. The rate of deposition in atmosphere depends on the meteorological conditions, the particle size, density as well as chemical form of thorium particles. Thorium particles with small aerodynamic diameters (<10 micron) travel long distances from their sources of emission. In water, thorium is present as suspended matter, suspension and mixing control the transport of particle-sorbed in water. The concentration of dissolved thorium in water increases due to formation of soluble complexes with carbonate, humic materials, or other ligand [45, 46].

Soil

Thorium occurs naturally in the earth's crust at an average lithospheric concentration of 8-12 µg/g. The typical concentration range of naturally occurring thorium in soil is 2-12 µg/g, with an average value 6 µg/g [10, 12, 37, 47-49]. The processes that contaminate soil due to industrial activities are precipitation of airborne dusts and land disposal of uranium or thorium containing wastes. According to Environmental Protection Agency (EPA) the primary sources of thorium at the Superfund sites are processing and extraction of thorium, uranium and radium from ores or ore concentrates. Disposal of incandescent lights and lanterns containing ^{232}Th are the additional source of thorium at waste disposal sites [50, 51].

Table-1: showing the background concentration of various matrices.

S No	Source	Concentration	References
1	Air	0.2 Ci	27
2	Coal	0.5-7.3 µg/g	27
3	Uranium fuel cycle	0.084 Ci	38
4	Underground uranium mines	0.0003 Ci	38
5	Water for Th-232	.0007-0.0326mBq L^{-1}	52
6	Water for Th-230	0.0008-0.0258 mBq L^{-1}	52
7	Water for Th-228	0.0014-1.32 mBq L^{-1}	52
8	lithosphere	8-12 µg/g	47
9	Soil	6 µg/g (general)	47
10	Soil for Th-233	30.2-48.6 Bq kg^{-1}	52
11	Soil for Th-230	32.5-60.5 Bq kg^{-1}	52
12	Soil for Th-228	31.0-53.0 Bq kg^{-1}	52

Environmental Fate

To assess the environmental fate of thorium, the isotopes of thorium with the exception of ^{234}Th, which has short half-life, 24.1 days, are considered. The presence of ^{238}U and ^{232}Th concentrations in phosphate fertilizers are of critical importance due to the concerns that via several pathways these radionuclides reach and potentially affect the human. These radionuclides are introduced in the environment via phosphate fertilizers and phosphor-gypsum that contain natural radionuclides in relatively large quantities and enter into agricultural land during cultivation. The distribution of these isotopes depend on the distribution of the rocks from which they originate and the process which concentrate them [53, 54]. The chain decay of these radioactive elements emits constantly nuclear radiations α, β and γ, in the environment. Several studies of patients treated with thorotrast, a colloidal suspension of thorium dioxide, for radio diagnostic purposes showed an excess incidence of cancer, primarily tumours and leukaemia, among other medical conditions [55, 56]. Bones are excellent candidates for the *in vivo* monitoring of thorium intake since it return on the bone surface for long time. The most important pathway is through direct inhalation of dusts resulting in radiation doses received mainly by farmers in the farming land [57-60].

Transport and Partitioning

Thorium release in to the atmosphere from mining, milling, processing operations of thorium and the air blown dust from uranium tailing piles as particulate aerosol. The aerodynamic diameters of both ^{230}Th and ^{232}Th in atmospheric aerosols are greater than 2.5 μm. The aerodynamic diameter of ^{228}Th, however, is less than 1.6 pm and can travel longer distances than both ^{230}Th and ^{232}Th [61]. Like other particulate matter in the atmosphere, thorium is transported from the atmosphere to soil and water by wet and dry deposition. The deposition of thorium through snow, rain water, dry deposition through impaction and gravitational settling has also been observed [62, 63]. The atmospheric residence time of thorium depends on the aerodynamic diameter of the particles. Those with small diameters are likely to be transported through longer distances, e.g., high ^{228}Th/^{232}Th activity ratios observed in surface air are thought to be due to transport of small particles of ^{282}Th through long distance [49,61]. The dry deposition velocity of ^{212}Pb, a thoron (thoron or ^{220}Rn itself originating from ^{232}Th) decay product has also been reported to be in the range 0.03-0.6 cm/se [64,m 65]. Thorium discharge in to water as ThO_2 which form sediments due to low solubility while soluble thorium ions hydrolyze at pH above 5 forming Th(OH)4 precipitate as hydroxy complexes, e.g., $Th(OH)_2^{2+}$,$Th2(OH)_2^{6+}$, $Th3(OH)_5^{7+}$. The concentration of soluble thorium in water is low since its hydroxy complexes are adsorbed by particulate matter in water, get suspended as sediment, and the concentration of soluble thorium in water is low [66-68]. The removal from aqueous phase is expected to be higher for finer grained particles [69, 70]. The residence time for thorium with respect to its removal by adsorption onto particles is shorter in near shore waters than in deeper waters, probably because of the availability of more adsorbents (particulate matter). The residence time vary from 1 to 70 days and the scavenging rates varied seasonally and are inversely related to the sediment re-suspension rate. Therefore, the removal rate was found to be dependent on both sediment re-suspension rate and the concentration of iron and manganese compounds, which have good adsorption properties in water .The transport of thorium in water is principally controlled by the flux of particles in the water, i.e., most of the thorium is carried in the particle-sorbed state .The sediment re-suspension and mixing control the transport of particle-sorbed in water [70, 72, 73]. Although the concentration of dissolved thorium is low in most of the waters, but concentration of dissolved thorium in an alkaline lake is up to 2.21 pCi/L as compared to sea water having the concentration about O.59 x 10-5 pCi/L [46]. The dissolved thorium concentration can be increased with the formation of soluble complexes. The anions or ligands likely to form complexes with thorium in natural water were CO_3^{2-} and humic materials, although some of the thorium-citrate complexes are stable at pH above 5 [45, 46, 74-76].

The transport of thorium from water to aquatic species has also been studied. The bio concentration factor (concentration in dry organism/ concentration in water) in algae is as high as $9.75x10^4$, but the maximum value in zooplankton (calanoids and cyclopoids) is $2x10^4$. Moreover, it is suggested that sinking plankton and their debris account for the sedimentation of most of the thorium from oceanic surface waters [14]. The highest observed thorium bio concentration factor in the whole body of rainbow trout (Salmo gairdneri) is 465. The succeeding lower bio concentration factor, in higher trophic animals, indicates that thorium will not biomagnify in the aquatic environment. It was also noted that the majority of thorium body burden in fish was in the gastrointestinal tract [13, 15].

Chelating agents produced by certain micro-organisms such as *Pseudomonas aeruginosa* present in soils enhance the dissolution of thorium in soils [77]. The transport of atmospherically deposited thorium from soil to plants is low. The soil to plant transfer coefficients concentration in dry plant to concentration in dry soil were estimated to be 10^{-4} to $7x10^{-3}$ and $0.6x10^{-4}$ for ^{232}Th [16, 78]. The root systems of grasses and weeds adsorb thorium from the soil but its transportation to the upper parts of the plant is not very extensive. Almost l00 folds higher concentrations of all three isotopes ^{228}Th, ^{230}Th, and ^{232}Th were detected in the root than in the parts of the plant above ground level [79]. Ibrahim and Whicker in 1988, predicted that under certain conditions vegetation can accumulate ^{230}Th, as indicated by the plant/soil concentration ratio (dry weight) of 1.9-2.9 for mixed grasses, mixed forbs and sagebrush plants grown at the edge of uranium tailings impoundments. Higher concentration of ^{228}Th as compared to ^{232}Th was reported, furthermore, it was found that in plants from various locations in USA the concentration of ^{228}Th was higher than that of ^{232}Th by a factor three to seven. Higher intake of ^{228}Th can be explained by the in growth of this radionuclide in plants followed by the decay of ^{228}Ra and or ^{228}Ac which are taken up in addition to the direct uptake of ^{228}Th [17]. However, it is possible that the observed difference in the uptake of the three isotopes by plants is due to a difference in the chemical compounds formed by these isotopes, making one more leachable than the other under the prevailing local conditions.

Sample Preparation and Detection Methodology

The purpose of this review is to describe the analytical methods available for the detection and to monitor thorium in environmental media, the methods used for this purpose are given in Table-2. Radiometric methods, such as alpha and gamma spectrometry, neutron activation analysis (NAA), liquid scintillation spectrometry; spectrophotometric methods, such as inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), voltammetry which is electrochemical method and mass spectrometry, such as thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS) are all being routinely used for thorium analysis in monitoring activities. But mostly, thorium analysis is currently performed by alpha spectrometry, gamma spectrometry, NAA, liquid scintillation spectrometry, ICP-MS and ICP-AES [85, 86].

Table-2: showing the well established techniques for the detection and measurement of thorium and limit of its detection in various environmental samples.

S No	Thorium measurement technique	Limit	References
1	Alpha-spectrometry (water sample)	(0.070 Bq For Th-332	52
2	Alpha-spectrometry (water sample)	0.13 Bq for Th-230	52
3	Alpha-spectrometry (water sample)	0.16 Bq for Th-228	52
4	Alpha-spectrometry (Soil)	30.2 mBq forTh-233	52
5	Alpha-spectrometry (Soil)	32.5 mBq forTh-230	52
6	Alpha-spectrometry (Soil)	31.0 mBq forTh-228	52
7	Neutron activation analysis	50 ppb	80
8	Liquid scintillation spectrometry	0.2 mBq	81
9	Spectrophotometric methods	0.15 µg	82
10	Inductively coupled plasma atomic emission spectrometry	0.04 µg	83
11	Inductively coupled plasma mass spectrometry	0.1 µg	84

Sample Preparation of Biological Materials

Soft tissues including Lung, Lymph nodes, Liver, Kidney, spleen, Heart, Thyroid and muscle etc. are spiked with thorium. In wet ashing methods, mixtures of HCl, HF, HNO_3 and $HClO_4$ in different proportions are employed, at varying heating temperatures and digestion times. Co-precipitated with $Fe(OH)_3$ and cleaned with complexation electrodeposited. Bones spiked with tracer, dry ashed thorium is co-precipitated with $Fe(OH)_3$, cleaned with complexation, solvent extracted and electro-deposited [87, 88]. Blood, urine, ashed bones samples, dried in quartz ampules, sealed and irradiated in a reactor, ^{233}Pa, the cooled irradiated samples were cleaned by multiple column chromato-graphy, solvent extraction and evaporated on counting planchettes [87, 89]. Acidified sample of Urine coprecipited with NH_4OH, irradiated with thermal neutron, reprecipited with La-hydroxide and the precipitate are dissolved in HNO_3 [90]. The urine sample plus 50% by volume of concentrated HNO_3 is transferred into a beaker and the isotopic tracers ^{232}U and ^{229}Th are added. The solution is heated at about 120^0C until almost dryness; concentrated NH_4OH is added in the centrifuge tube and raised the pH to 7. After centrifugation the precipitate is dissolved in 3 ml of 8N HNO_3. When the amount of the precipitate is less than 10% of the sample volume, 5 ml of concentrated solution of $Ca(NO_3)_2$ and 5 ml of 1.6 M H_3PO_4 are added [91]. A few drops of H_2O_2 are added in order to obtained a clear residue, which is transferred to a centrifuge tube with 30 ml of 0.01N HNO_3.Faecal samples are transferred to a quartz capsule and dried in oven and ashed at 400^0C for 24 h. Thorium-229 and ^{232}U are added as internal tracers

prior to wet-ashing with concentrated HNO_3, H_2O_2 and concentrated HF in platinum capsule. Following the ashing and evaporation, the remaining residue is fused with a 3:1 mixture of a $Li_2B_4O_7$ and $LiBO_2$. The cooled flux is dissolved in boiling 1N HCl and then transferred to a centrifuge tube [92, 93].

Environmental Sample Preparation

Air Sample Preparation

The particulate matters in air are collected on filter wet ashed, fused with LiF and H_2SO_4, interference eliminated by complexation and fluorescence developed in buffered solution with 3,4,7-trihydroxyflavanone [94-96]. Another particulate matter of air are collected on filter wet ashed, fused with $K_2S_2O_7$. Thorium is coprecipitate with $PbSO_4$, dissolved in ADTP and is cleaned by complexation. Finally thorium is extracted in aqueous oxalic acid and is electrodeposited [97-98]. Thorium in drinking water is coprecipited from acidified sample with $Fe(OH)_3$, clean by selective solvent extraction, coprecipited with $Al(OH)_3$ and the colour is develop by arsenazo (III) reagent. After colour development, thorium is co-precipitated with LaF3 and concentrated [99, 100].

Soil and Sediment Sample Preparation

Soil samples are dissolved in HCl, HF, HNO_3 and $HClO_4$, thorium is coprecipited with CeF, cleaned by solvent extraction, oxalate formation and the solution is fused with $NaHSO_4$. In the case of sediment mixture cleaned by anion exchange resin and electrodeposited on silver disc [101, 102, 136].

Extraction /Separation

Extraction Chromatography

Extraction chromatography is commonly used for separation of Thorium-238 and Uranium using commercially available UTEVA resin. In this process thorium and uranium in controlled nitric acid (1–5 mol/dm^3) were extracted with UTEVA resin and recovered with mixture containing 0.1 mol/dm^3 HNO_3 and 0.05-mol/dm^3 oxalic acid. For the extraction of Thorium-238 5 mol/dm^3 HNO_3 solution has been reported to be suitable but thorium fluoride formation interferes with extraction of Th-238. Addition of $Al(NO_3)_3$ and $Fe(NO_3)_3$, which have higher solubility constant with fluoride ion than Th, that improve extractability of Th-238 in 1 mol/dm^3 HNO_3 sample solution [103, 104].

Liquid-Liquid Extraction Chromatography

Separation of Th(V) is done either by liquid-liquid extraction or solid phase extraction techniques. A large number of extrants, such as tributyl-phosphate, trioctylphosphineoxide and organo-phosphoric acid are employed [105]. An aliquot of a sample solution containing 1.0-65.0 g of Th(V) is transferred into a 25 ml separating funnel. The pH of the solution is adjusted at 4.5 for Th(V) using buffer solution. The mixture is shaken with 3 ml of 1.08×10^{-4} M C4RAHA and the combined extracts along with washings are diluted with ethyl acetate. The absorbance of the organic phase is measured against the reagent blank at 341 nm. The total concentration of thorium [Tho^{2+}] species in aqueous phase [Tho^{2+}]aq is measured by Inductively Coupled Plasma Atomic Emission spectrometry (ICP-AES). The concentration of Th(V) extracted into organic phase, [Tho^{2+}]org, as a complex can be estimated by [Tho^{2+}]org = [Tho^{2+}](aq, initial) -[Tho^{2+}]aq, where [Tho^{2+}](aq, initial) is the initial concentration of the metal ion in the aqueous phase and the percent extraction (%E) for Th(V) may also be calculated by [106].

Ion-Exchange Chromatography

In ion exchange chromatography thorium (IV) is eluted with 4MHCl, the resin synthesized from XAD-4 comprises of a thioglycolate functional group [107]. In ion exchange chromatography, number of resins has been reported, but they have less specificity and sorption capacities due to the poor loading of metals ions [108]. The macrocycles of the host-guest complex are used for the complexation of several metal ions; however, complexation with Th(V) is scanty [109]. Ligands that can selectively bind Th(V) and strictly discriminate it from other metal ions present in excess in monazite sand and other samples are hydroxamic acids, that have achieved considerable importance for the separation of Th(V) [110]. The octaarmed calyx(iv)resorcinarene-hydroxamic acid, C_4RAHA has been used for the extraction and determination of Th(V) in the presence of several interfering ions. This extraction removes the bulk of the major elements and precentrate Th(V) into small volume simultaneously, the extract is directly aspirated into ICP-AES, which increases the sensitivity and detection limit, by many fold [106].

Electrodeposition Procedure

A chemometric approach was used to evaluate and optimize the parameters of the

procedure. A balanced half- fraction factorial design can be chosen to minimize the number of sample to be run [111]. Samples are prepared by adding the appropriate tracer(s) to a beaker by adding 2 ml of 0.36 M $NaHSO_4$ followed by adding concentrated HNO_3 (5 ml) and subjected to hot plate for dryness twice. Then the samples are dissolved in 5 ml of the appropriate concentration of H_2SO_4 (0.50, 0.75, or 1.0 M), 4 drops of thymol blue indicator is added and finally solution is transferred to a plating cell with a 3 ml polyethylene transfer pipette. The planchet is rinsed with de-ionized water dried under a heating lamp for about 5 to 10 minutes. The planchet is then counted for analyzing alpha-spectrum [112]. The solution is transferred to a deposition cell, which contains stain less steel disc covered with film of tri-noctylphosphinoxide/ vinol/cyclohexanone and is stirred for one hour, after which the steel disc is transferred to a muffle furnace at 400^0C for one hour. The disc is counted in an alpha spectrometry system for 1000 min [91, 113, 114].

Radioactivity Measurement

Biological Materials

The calorimetric methods are not useful for isotope-specific determination of thorium isotopes. Alpha spectrometric and neutron activation analysis have potential to quantify the specific isotopes of ^{230}Th and ^{232}Th, respectively. Alpha spectrometry is commonly used for the determination of ^{232}Th and the ^{230}Th derived from the decay of ^{238}U [115, 116]. In vitro monitoring methods for the analysis of thorium in urine, feces, hair and nails have been reported that none of these biological media is a good indicator of thorium uptake in the human. In vivo monitoring, NaI detectors are relatively suitable for determining thorium lungs burden. In one method, in exhaled air ^{220}Rn is determined as a measure of thorium lung burden. The exhaled air is passed to a delay chamber where the positively charged decay products of thoron (e.g. ^{216}Po and ^{212}Pb) are collected electrostatically with the help of an electrode and are measured using alpha scintillation counter. This method has prerequisite sensitivity to be used as an indicator of thorium uptake. However, because of lack of information regarding the thoron escape rate from the thorium particles in the lungs, the method faces limitations accurate for indicating lung uptake of thorium [117]. Some authors have reported the levels of exhaled thoron or its decay products in human breath [118, 119].

Environmental Samples

Standard reference materials (SRMs) for thorium in river and freshwater lake sediment (SRM-4350B and SRM-4354), soils (SRM-4355 and SRM-4353), coal (SRM-1632), and fly ash (SRM 1633) are available [120, 121]. Neither calorimetric nor atomic absorption/emission methods are suitable for the determination of thorium specific isotopes, these methods are also not sensitive enough for the quantification of trace amounts of thorium, e.g., in seawater. The particulate phases are filtered by inert polypropylene fiber filter and adsorption of solution phase thorium onto MnO_2-coated fiber or preconcentration of thorium on XAD-2 resin by using adsorption of thorium-Xylenol Orange complexes which are subjected to alpha spectrometry or neutron activation analysis that relatively better methods for the quantification of low levels of thorium in water [122-125].

The isotope dilution-mass spectrometric method provides the most accurate and sensitive thorium quantification but is rarely used because of the specialized nature and the cost of the analytical technique [126]. The beta counting of thorium deposited on counting discs is useful for the determination of ^{234}Th derived from ^{238}U [99]. The direct gamma radiation counting with a germinium planer detector has been used for the quantification of ^{228}Th in grass samples [49]. The recoveries of thorium from soil and sediment samples are usually poor and special attention should be given to sample treatment during their analysis [87].

Inductively Coupled Plasma Mass Spectrometry (ICPMS) and Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) Procedures

Inductively coupled plasma mass spectrometry (ICPMS) and inductively coupled plasma optical emission spectrometry (ICP-OES) have been routinely used for the elemental analysis of natural thorium (^{232}Th) in a very wide range of sample matrices for many years [126]. The techniques also offer several advantages such as shorter analysis times and have no requirement for the separation of thorium from the sample matrix over the more traditional radiometric methods e.g., alpha spectrometry, gamma spectrometry and neutron activation analysis in the measurement of thorium [85].

In ICP-MS analysis the sample in ionized form is required, having mass of ions, which is the characteristic of the desired analyte. The argon plasma, where the analyte ions are formed, operates under atmospheric pressure whereas a quadrupole mass spectrometer resolves all of the ions formed in the plasma and operates under vacuum. The extraction of the ions from the plasma into this

vacuum system is, therefore, a very important step in ICP-MS analysis [127]. An interface comprising a sampler cones as well as skimmer cone are used to extract the ions. The extracted ions are focused using a lens system, before passing into the quadrupole mass analyzer, where they are sorted according to their mass to charge (m/z) ratio. For the detection of natural thorium (^{232}Th), m/z of 232 is used and the ions are finally detected using a channeltron electron multiplier [85].

The ICP-OES based upon the light that is emitted by the excited atoms which is the characteristic of the element present. Atoms or ions produced in an energised state in the plasma will spontaneously revert to a lower energy state, with the emission photons of energy. In quantitative measurements, the emitted energy is assumed to be proportional to the concentration of the element present. The emitted light passes through the entrance slit of the spectrometer and is resolved into its components by a grating or a prism and grating combination (echelle spectrometers). The light intensity at a specific wavelength for each elemental line is measured either with an exit slit and photomultiplier tube or with a semiconductor device. Thorium has many lines in the spectrum, which can be used for quantitative analysis and the quality of each line in the spectrum depends upon the type of sample being analyzed. This is because emissions from other elements present in the sample solution can often overlap with the analyte lines. Thorium has been measured in zirconia based ceramics, where the major matrix elements were zirconium, cerium and titanium and found two lines appeared at 283.231 nm and 326.267 nm, respectively without interference [126, 128, 129].

Neutron Activation Analysis (NAA)

In Neutron Activation Analysis (NAA), samples are bombarded with thermal neutrons, which render radioactive by the capture of one extra neutron. These radioisotopes are recognized by the characteristic energy of the gamma rays emitted as they decay with specific half-lives. The concent-rations of particular elements are determined by measuring the areas of the photo peaks. NAA is remarkably free of analytical problems such as matrix effects and interferences due to photo peak overlap [130, 131]. Neutron activation analysis is relatively suitable for the determination and measurement of thorium because it forms a radioisotope with a long half-life and it can be determined using a late count when the activity due to most of the other elements has been decayed. Furthermore, the analysis is performed using large samples (typically 10-30 g), thereby reducing the risks of sample in homogeneity. This is particularly important for thorium analysis since it is often concentrated in minor heavy accessory minerals, which can easily become segregated in a sample prior to analysis. The major downside of the NAA technique is that the facility of a nuclear reactor is compulsory and the time for the analysis of thorium is of the order of several weeks making it unrealistic [132].

Alpha Spectrometry

This technique is able to quantify individual isotopes of thorium independently and is based upon the measurement of energies of the specific alpha particles emitted as a result of decay of thorium isotopes. The essential requirement in alpha spectrometry is the preparation of an extremely radiochemical pure source having thorium yield from the original sample. The essential step in this analytical technique is the sample preparation and most of the research on this technique has been concerned with the development of protocol for producing satisfactory sources for alpha counting [86]. Alpha-spectrometry with solid-state detectors is the benchmark of today's methods for determining alpha emitting elements. The other methods are being investigated that may surpass the detection capabilities of alpha-spectrometry for long-lived radionuclides which might be expensive and complex such as inductively coupled plasma mass spectro-metry. Although alpha-spectrometry typically requires long counting times, the spectra are relatively simple to analyze and the equipment is relatively inexpensive and durable. Alpha-spectrometry affords high confidence in the analytical results through the use of isotopic dilution techniques such as isotopic tracers and allows analyst to determine the quality of the chemical separation by review of the spectra [59, 112].

Gamma Spectrometry

Thorium is frequently measured by passive gamma spectrometry, which has an advantage over other techniques since it is a non-destructive with low detection limits. It can also be performed directly on solid and liquid samples. Only total thorium is determined based on the indirect quantification of ^{232}Th. This technique involves the measurement of rays of specific energies emitted by the decay of progeny nuclides ^{228}Ac, ^{208}Tl and ^{212}Pb using a high purity germanium-based detector. The disadvantages of this technique are that erroneous results can be obtained for samples in which progeny nuclides are

not in equilibrium with ^{232}Th and prolonged counting times, more then 20 h, may be required for samples having low thorium concentrations [86]. The biological and environmental samples were taken, cleaned with acetone as well as 33% hydrogen peroxide and are dried in open air. In the cleaning procedure the samples are cleaned once in acetone, then in isopropanol and finally are dried in an oven at 60^0C for about 40 min. In order to homogenize the sample and to get a well-defined geometry for gamma ray spectrometry, the samples are ground to a grain size of about 1–3mm, and then weighed [133]. ^{228}Th and ^{228}Ra contents of all the bone samples are measured by the 208Tl (583.2 and 2614.5 keV) gamma ray lines and the ^{228}Ac (911.2 and 969.0 keV) gamma ray lines respectively using ultra low-level gamma ray spectrometry. For all the measurements three very sensitive spectrometers, two coaxial HPGe detectors having 60% and 106% relative efficiencies and one semi-planar HPGe detector of 8% relative efficiency are used [134].

Conclusion

Sensitive analytical techniques are available for the qualitative as well as quantitative analyses of thorium in the environmental samples such as air, water, soil and vegetation etc. Knowledge of the different levels of thorium compounds in environmental media can be used to indicate human exposure to thorium through inhalation of air and ingestion of drinking water and foods containing thorium compounds. In drinking water and foods the concentration of thorium is very low; however, more sensitive analytical methods are required. The significance of ICP-MS, in precise isotope ratio measurements at ultra-trace levels can be increase especially when multicollector and or double focusing sector field instruments are used. This is also an excellent tool for the determination of long-lived radionuclides in the environment and radioactive waste. In the environment, thorium and its compounds do not degrade or mineralize like many organic compounds, but speciate into different chemical compounds and form radioactive decay products. Analytical methods for the quantification of radioactive decay products, such as radium, radon, polonium and lead are available. The determination of Rn-220 and its decay product in the environment may serve indirect measure of percent compound in the environment if a secular equilibrium is reached between thorium-232 and all its decay products.

Knowledge of the environmental transformation processes of thorium and its compounds formation is important in understanding their transport in environmental media. The radiation dose scenarios described, for both workers and the population, needs to be analysed thoroughly in order to highlight the radionuclides involved. The level of radioactivity in the environment due to the presence of natural radionuclides and human activities should be assessed regularly. There is a need to develop a radioactivity level map regionally and globally. Any nuclear activity may alter the level in specific region. Also the detection of the radionuclides, qualitative as well as quantitative, in the food chain is also important in order to evaluate the risk assessment. Indeed, in recent years the non-nuclear industry has received greater attention and is at the top of the interest of the radiation protection community. This paper has described the measurement and invest-igative approaches, which are being pursued to determine the transport properties of various natural and artificial products.

References

1. D. G. Mose, G. W. Mushrush, F. V. Simoni, R. R. Strzlecki and S. Wolkowicz, *Energy and Sources*, **25**, 467 (2003).
2. R. Lopez, M. Garcia-Talavera, R. Pardo, L. Deban and J. C. Nalda, *Radiation Protection Dosimeter*, **111**, 83 (2004).
3. R. L. Kathren and R. L. Hill, *Health Physics*, **63**, 72 (1992).
4. World Nuclear Association (WNA), htt://www.world nuclear.org/info/info.html (2002).
5. Webelements.com, Thorium key information. Internet Publication (2003).
6. K. H. Wedepohl, *Geochim. Cosmochim. Acta*, **59**, 1217 (1995).
7. J. Fruchter D. Robertson and J. Evans, *Science*, **29**, 1116 (1980).
8. P. Kuroda, T. Barbod and S. Bakhtiar, *Journal of Radioanalytical and Nuclear Chemistry*, **111**, 137 (1987).
9. S. J. Hu, S. Kandaiya and T. S. Lee, *Applied Radiation and Isotopes*, **46**, 147 (1995).
10. P. Zoriy, P. Ostapczuk, H. Dederichs, J. Höbig, R. Lennartz and M. Zoriy. *Journal of Environmental Radioactivity*, **101**, 414 (2010).
11. C. Galindo, L. Mougin and A. Nourreddine, *Applied Radiation and Isotopes*, **65**, 9 (2007).
12. C. Sill, *Health Physics*, **33**, 393 (1977).
13. T. Poston, *Bulletin Environmental Contamination Toxicology*, **28**, 682 (1982).
14. N. Fisher, J. Teyssie and S. Krishnaswami, *Limnol Oceanogr*, **32**, 131 (1987).
15. B. Torstenfelt, *Radiochem Acta*, **39**, 105 (1986).

16. C. J. Garten, *Environmental Research*, **17**, 437 (1978).
17. S. Ibrahim and F. Whicker, *Health Physics*, **54**, 413 (1988).
18. J. Lambert and F. Wilshire, *Analytical Chemistry*, **51**, 1346 (1979).
19. C. R. Cothern and W. L. Cothern, *Research Technology*, **158**, 160 (1987).
20. C. R. Cothern and W. L. Cothern, Lappenbusch and J. Michel, *Health Physics*, **50**, 33 (1986),
21. R. Bulman, Concentration of actinides in the food chain. 17803, 11-12 (1976).
22. L. Hannibal, *Health Physics*, **42**, 367 (1982).
23. S. Hu, W. Koo and K. L. Tan, *Health Physics*, **46**, 452 (1984).
24. P. Kotrappa, D. Bhanti and V. Menon, *American Industrial Hygiene Association Journal*, **37**, 613 (1976).
25. J. McKlveen and R. Jenkins, *Health Physics*, **39**, 69 (1980).
26. I. Fisenne, P. Perry and K. Decker, *Health Physics*, **53**, 357 (1987).
27. T. H. Zeevaert, L. Sweeck and H. Vanmarck, *Journal of Radioanalytical and Nuclear Chemistry*, **85**, 1 (2006).
28. P. H. Holloway and E. B. Evans, *Chemistry and Material Science*, **4**, 27 (1972).
29. D. Coles, R. Ragaini J. Ondov, *Environmental Science Technology*, **13**, 455 (1979).
30. J. Tadmor, *Health Physics*, **50**, 270 (1986).
31. S. Weissman, R. Carpenter and G. Newton, *Environmental Science Technology*, **17**, 65 (1983).
32. D. Roeck, T. Reavey and J. Hardin, *Health Physics*, **52**, 311 (1987).
33. R. Mustonen and M. Jantunen, *Health Physics*, **49**, 1251 (1985).
34. Z. Pietrzak-flis, M. M. Suplinska and L. Rosiak, *Journal of Radioanalytical and Nuclear chemistry*, **222**, 189 (1997).
35. L. Jensen, G. Regan and S. Goranson, *Health Physics*, **46**, 1021 (1984).
36. A. E. Metzger, M. I. Etchegaray-Ramirez and E. L. Haines, Thorium concentrations in the lunar surface. V - Deconvolution of the central highlands region, Lunar and Planetary Science Conference, 12th, Houston, TX, March 16-20, 1981, Proceedings. Section 1. (A82-31677 15-91) New York and Oxford, Pergamon Press, p. 751, NASA-supported research (1982).
37. S. Hu and S. Kandaiya, *Health Physics*, **49**, 1003 (1985).
38. EPA, Background information document (integrated risk assessment). Final rules for radionuclides. Vol I. U.S. Environmental Protecton Agency, 520 (1984).
39. A.M. Arogunjo, V. Höllriegl, A. Giussani, K. Leopold, U. Gerstmann, I. Veronese and U. Oeh. *Journal of Environmental Radioactivity*, 100, 232 (2009).R. Platford and S. Joshi, *Health Physics*, **54**, 63 (1988).
40. S. Akyil, A.M. Yusof, *Journal of Hazardous Materials*, **144**, 564 (2007).
41. P. McKee, W. Snodgrass and D. Hart, *Journal of Fish Aquaculture Science*, **44**, 390 (1987).
42. W. Cottrell, F. Haywood and F. F. Witt, Radiological survey of the shpack landfill, norton, Massachusetts, Report DOE/EV-ORNL-5799 (1981).
43. J. J. Harrison, A. Zawadzki, R. Chisari and H. K.Y. Wong, *Journal of Environmental Radioactivity*, article in press (2011)
44. R. Platford and S. Joshi, *Journal of Radioanalytical and Nuclear Chemistry*, **106**, 333 (1986).
45. B. LaFlamme and J. Murray, *Geochim Cosmochim Acta*, **51**, 243 (1987).
46. K. Harmsen and F. DeHaan. *Netherlan Journal of Agriculture Science*, **28**, 40 (1980).
47. Lutfullah, S. Sharma, N. Rahman, S. N. H. Azmi, *Arabian Journal of Chemistry*, article in press (2011).
48. J. J. Harrison, A. Zawadzki, R. Chisari, H. K.Y. Wong, *Journal of Environmental Radioactivity*, **102**, 896 (2011).
49. P. Gamaletsos, A. Godelitsas, T. J. Mertzimekis, J. Göttlicher, R. Steininger, S. Xanthos, J. Berndt, S. Klemme, A. Kuzmin and G. Bárdossy, *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, **269**, 3067 (2011).
50. EPA, U.S. Environmental Protecton Agency, EPA 540 (1988).
51. G. Jia. G. Torri, R. Ocone, D. A. Lullo, D. A. Angelis and R Boschetto, *Applied Radiation Isotopes*, **66**, 1478 (2008).
52. A. E. Gates and L. C. S. Gundersen, *Geological Society of America*, **271**, 53 (1993).
53. V. Höllriegl, W. B. Li, K. Leopold, U. Gerstmann and U. Oeh, *Science of the Total Environment*, **408**, 5794 (2010).
54. A. F. Stehney and H. F. Lucas, *Health Physics*, **78**, 8 (2000).
55. C. W. Mays, *Health Physics*, **63**, 33 (1992).
56. P. Zoriy, P. Ostapczuk, H. Dederichs, J. Höbig, R. Lennartz and M. Zoriy, *Journal of Environmental Radioactivity*, **101**, 414 (2010).

57. L. C. Scholten and C. W. M. Timmermans, *Fertilizer Research*, **43**, 103 (1996).
58. J. C. Lozano, F. Vera Tomé, P. Blanco Rodríguez and C. Prieto, *Applied Radiation and Isotopes*, **68**, 828 (2010).
59. P. Guo, X. Jia, T. Duan, J. Xu and H. Chen, *Journal of Environmental Radioactivity*, **101**, 767 (2010).
60. D. Baybaş and U. Ulusoy, *Applied Clay Science*, **51**, 138 (2011).
61. F. Jiang and P. Kuroda, *Radiochim Acta*, **42**, 123 (1987).
62. C. Venchiarutti, M. R. Van Der Loeff and I. Stimac, *Topical Studies in Oceanography*, article in Press, (2010).
63. J. Bigu, *Journal of Aerosol Science*, **16**, 157 (1985).
64. C. Rangarajan, C. Eapen and S. Gopalakrishnan, *Water Air Soil Pollution*, **27**, 305 (1986).
65. I. Bodek, W. Lyman and R. Reehl, SETAC Special Publication Series, New York, NY: Pergamon Press, **9**, 2 (1988).
66. K. Hunter, D. Hawke and L. Choo, *Geochim Cosmochim Acta*, **52**, 627 (1988).
67. N. B. Milic and T. Suranji, *Candian Journal of Chemistry*, **60**, 1298 (1982).
68. M. Sheppard, The environmental behavior of uranium and thorium. At Energy Can Ltd [Rep.] AECL, AECL-6795 (1980).
69. R. Carpenter, T. M. Beasley and D. Zahnie, *Geochim Cosmochim Acta*, **51**, 1897 (1987).
70. J. Cochran, *Estuary Filter Journal*, **179**, 220 (1984).
71. P. Santschi, *Particle Limnol Oceanogr*, **29**, 1100 (1984).
72. P. Santschi, Y. Li and D. Adler, *Geochim Cosmochim Acta*, **47**, 201 (1983).
73. N. Miekeley and I. Kuchler, *Inorganic Chim Acta*, **140**, 315 (1987).
74. D. Raymond, J. Dufield and D. Williams, *Inorganic Chim Acta*, **140**, 309 (1987).
75. H. Simpson, R. Trier and Y. Li, *Nuclear Waste Geochem*, **32**, 326 (1984).
76. E. Premuzic, A. Francis and M. Lin, *Archives Environmental Contamination Toxico1ogy*, **14**, 759 (1985).
77. P. Linsalata, R. Morse and H. Ford, *Health Physics*, **56**, 33 (1989).
78. A. Taskayev, O. Popova and R. Alexakhin, *Health Physics*, **50**, 589 (1986).
79. M. Mantel, S. T. Propai and S. Amiel, *Analytical Chemistry*, **42**, 267 (1970).
80. G. Wallner, *Applied Radiation and Isotopes*, **48**, 511 (1997).
81. M. E. Khalifa and M. A. H. Hafez, *Talanta*, **47**, 547 (1998).
82. M. Gopalkrishnan, K. Radhakrishnan, P. S. Dhami, V. T. Kulkarni, M. V. Joshi, A. B. Patwardhan, A. Ramanujam and J. N. Mathur, *Talanta*, **44**, 169 (1997).
83. R. Hill and K. H. Lieser, *Journal of Analytical Chemistry*, **342**, 337 (1991).
84. L. Holmes, *Radiation Protection Dosimeter*, **97**, 117 (2001).
85. M. A. White, A. M. Howe, P. Rosen and L. Holmes, *Radiation Protection Dosimeter*, **96**, 101 (2001).
86. N. Singh, M. Wrenn, *Science of the Total Environment*, **70**, 187 (1988).
87. A. Kumar, M. Ali, B. N. Pandey, P. A. Hassan and K. P. Mishra, *Biochimie*, **92**, 869 (2010).
88. M., Picer and P. Strohal, *Analytical Chim Acta*, **40**, 131 (1968).
89. B. Twitty and M. Boback, *Analytical Chim Acta*, **49**, 19 (1970).
90. A. M. Azeredo, G. F. Melo, D. R. Dantas and B. M. Oliveira, *Radiation Protection Dosimeter*, **37**, 51 (1991).
91. C. D. Ingamells, *Analytical Chim. Acta*, **52**, 323 (1970).
92. S. Barillet, C. Adam-Guillermin, O. Palluel, J. Porcher and A. Devaux, *Environmental Pollution*, **159**, 495 (2011).
93. C. Sill and C. Willis, *Analytical Chem*, **34**, 954 (1962).
94. T. Filer, *Analytical Chemistry*, **42**, 1265 (1970).
95. P. Zoriy, P. Ostapczuk, H. Dederichs, J. Höbig, R. Lennartz and M. Zoriy, *Journal of Environmental Radioactivity*, **101**, 414 (2010).
96. D. Percival and D. Martin, *Analytical Chemistry*, **46**, 1742 (1974).
97. K. Hirose, Y. Igarashi, M. Aoyama and Y. Inomata, *Journal of Environmental Radioactivity*, **101**, 106 (2010).
98. R. Velten and B. Jacobs, Determination of thorium in drinking water, Method 910. Environmental Monitoring and Support Laboratory, U. S. Environmental Protection Agency, Cincinnati (1982).
99. D. Lauria and J. Godoy, *Science of the Total Environment*, **70**, 83 (1988).
100. N. Golchert and F. Iwami and J. Sedlet, Analytical Chemistry in Energy Technology, Gatlinburg, TN, Ott 9-11, 1979. Ann Arbor, MI: Ann Arbor Science Publishers, Inc, 215 (1980).
101. L. J. Mandić, R. Dragović and S. Dragović, *Journal of Geochemical Exploration*, **105**, 43 (2010).

102. F. Asaka, K. Yutaka, H. Akiko, H. Tomoko and N. Mikio, *Journal of Chromatography*, **1140**, 163 (2006).
103. M. E. Nasab, A. Sam and S. A. Milani, *Hydrometallurgy*, article in Press (2010).
104. M. L. P Reddy and R. Meena, *Radiochim. Acta*, **89**, 453 (2001).
105. K. J. Vinod, G. P. Shibu, A. P. Rujul, K. A. Yadvendra and S.S. Pranav, *Analytical Science*, **21**, 129 (2005).
106. A. James, *American Chemical Society*, 400 (1987).
107. J. Ramkumar, S. K. Nayak, B. Maiti, *Journal of Membrane Science*, **196**, 203 (2002).
108. G. W. Gokel, *The Royal society of Chemistry*, London (1991).
109. K. S. Rao, P. D. D. Sarangi and G. R. Chauchuary, *Journal of Chemistry Technology Biotechnology*, **78**, 55 (2003).
110. G. E. P. Box, W. G. Hunter and J. S. Hunter, Statistics for Experimenters: An Introduction to Design, Data Analysis, and Model Building, John Wiley & Sons, New York (1978).
111. S. E. Glover, R. H. Filby, S. B. Clark and S. P. Grytdal, *Journal of Radioanalytical and Nuclear Chemistry*, **234**, 213 (1998).
112. I. A. Sachet, A. W. Nobrega and D. C. Lauria, *Health Physics*, **46**, 133 (1984).
113. P. Chamelot, L. Massot, L. Cassayre and P. Taxil, *Electrochimica Acta*, **55**, 4758 (2010).
114. M. E. Wrenn, N. P. Singh, N. Cohen, S. A. Ibrahim and G. Saccomanno, Thorium in human tissues. US Nuclear Regulatory Commassion. Washington, NUREG/CR-1227 (1981).
115. I. Shtangeeva, *Journal of Environmental Radioactivity*, **101**, 458 (2010).
116. M. Davis, Radiological significance of thorium processing in manufacturing. Report. Info-0150 (1985).
117. A. Keane and D. Brewster, *Health Physics*, **45**, 801 (1983).
118. Y. Mayya, S. Prasad and P. Nambiar, *Health Physics*, **51**, 737 (1986).
119. K. G. W. Inn, *Journal of Radioanalytical and Nuclear Chemistry*, **115**, 91 (1987).
120. J. Ondov, W. Zoller and I, Olmez, *Analytical Chemistry*, **47**, 1102 (1975).
121. K. Hirose, *Journal of Radioanalytical and Nuclear Chemistry Letters*, **127**, 199 (1988).
122. C. A. Huh and M. Bacon, *Analytical Chemistry*, **57**, 2138 (1985).
123. H. Livingston and J. Cochran, *Journal of Radioanalytical and Nuclear Chemistry*, **115**, 299 (1987).
124. J. J. Harrison, A. Zawadzki, R. Chisari, H. K.Y. Wong, *Radioactivity*, article in Press, (2010).
125. R. Saran, *Atomic Spectroscopy*, **18**, 60 (1997).
126. A. L. Gray, *Spectrochim Acta* B, **40**, 1525 (1985).
127. S. R. Marin, *Journal Analytical Atomic Spectrometery*, **9**, 93 (1994).
128. J. S. Becker, *International Journal of Mass Spectrometry*, **242**, 183 (2005).
129. P. J. Potts, *Applied Radiation and Isotopes*, **68**, 511 (2010).
130. D. E. Collier, S. A. Brown, N. Blagojevic, K. H. Sholdenhoof, *Radiation Protection Dosimeter*, **97**, 177 (2001).
131. M. J. Martinez Canet, M. Hult, P. Johnston and I. Lambrichts, *Radiation Protion Dosimeter*, **97**, 169 (2001).
132. R. Wordel, D. Mouchel, A. Bonne and H. Vanmarcke, Proc. 3rd Int. Summer School on Low-Level Measurements of Radioactivity in the Environment: Techniques and Applications, Huelva, Spain, 1993. Ed. M. Garcia Leon and R. Garcý´ a-Tenorio, 141 (1994).
133. N. N. Mirashi and S. Chaudhury, *Microchemical Journal*, **94**, 24 (2010).
134. R. Bernabee, *Health Physics*, **44**, 688 (1983).