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Mass spectrometric analysis of long-lived radionuclides in bio-assays

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ABSTRACT

During the past few decades releases of man-made radionuclides into the biosphere have created environmental contamination that has provoked public concern. This has also raised the need to accurately and in a timely manner determine the quantities of radionuclides in environmental samples and in bio-assays in order to assess their potential impact on public health. The wide spectrum of emission sources has resulted in heterogeneous structures and different isotopic compositions of the contamination that, in turn, has produced new and very specific elemental and isotopic features.

Nowadays, mass spectrometry is increasingly used for the determination of many long-lived radionuclides with low specific activities in environmental and biological samples. In summary, the merits of particular mass spectrometric methods include (i) low detection limits (ICP-MS, TIMS, etc.), (ii) high precision of the measured isotopic ratios (multi-collector ICP-MS and TIMS), (iii) high selectivity and abundance sensitivity (RIMS, AMS), and (iv) possibility for a spatially resolved isotope analysis (SIMS, LA-ICP-MS). Mass spectrometric analysis of long-lived radionuclides has been employed in radiobiology and biomedical studies, environmental monitoring and remediation, climate research, and forensics. The implementation of imaging inorganic mass spectrometry in proteomic research is highly promising for the study of radionuclide speciation mechanisms in organs and tissue on a bio-molecular level.

This paper summarises specific features of major radioactive contaminations that have occurred during the last few decades and discusses the merits of modern mass spectrometric techniques, with examples of the determination of long-lived isotopes of actinides and fission products in biological samples.

1. Introduction

There are more than 60 natural radionuclides in the Earth's biosphere which can be subdivided into primordial, cosmogenic, and radiogenic radionuclides that are derived from the decay of primordial radionuclides in the decay series. When the formation of the Earth took place about 4.5×10^9 years ago, radioactive isotopes were natural components in the planet's material. Among them just a few have sufficiently long half-lives to still be present in measurable amounts in the Earth's crust today. They are called primordial radionuclides. The cosmogenic radionuclides are constantly produced by the interaction of cosmic rays with stable isotopes of terrestrial elements (both in the atmosphere and in the Earth's crust). The natural radioactive isotopes are widely used in environmental research, for instance for tracing climate change or as chronometers. Thus, the many decay products of uranium and thorium decay chains can be separated from their parents because of their differing geochemical properties, and these separations allow the possibility of measuring geological time, depending on the half-life of the particular radionuclide [1]. For instance, the isotopic analyses of U decay products in corals can provide information on their age as well as on the seawater temperatures. In addition to dating the ages of corals, human bones and other artefacts can also be dated.

During the past few decades significant amounts of radionuclides have been released into the biosphere through industrial activities. In particular, the power production industry has played a significant role in polluting the environment with heavy elements and radioactive isotopes, the latter ones of both natural and man-made origin. Potential sources of contamination range from conventional coal-fired stations to nuclear reprocessing and power plants. For instance, a typical release of natural uranium in dust emitted from an average coal-fired power station into the air amounts to ~0.3 GBq per year [2]. In addition, uranium decays into radioactive gaseous products like radon (release into the air of 34 GBq a^{-1}) or metals with low boiling points, such as lead and polonium (typical releases of radioisotopes of corresponding elements from a coal-fired power plant into the air are 0.4 GBq a^{-1} and 0.8 GBq a^{-1}, respectively). Thus, industrial activities result in a re-distribution of natural radionuclide inventories and alter their bio-chemical pathways in the biosphere.

Particularly at the initial stage of the nuclear industry development the environmental regulations were not very strict and did not prevent releases of contaminated waste or by-products, among them transuranium isotopes and fission products from the

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nuclear fuel cycle and from the development and testing of nuclear weapons. Partly, those isotopes were released into the environment as a result of either intended or accidental use of nuclear devices. Specific radioactive contaminations with artificial radionuclides have been produced in numerous places all over the world through accidents of different nuclear devices and plants as well as by the use of particular by-products of nuclear fuel cycle, such as depleted uranium (DU), for industrial and military purposes. Just a few examples of major incidents involving releases of radiological agents include: accidents of US aircraft carrying nuclear bombs in Spain and Greenland; the accident at Chernobyl nuclear power plant; and military conflicts in Iraq, Afghanistan and Kosovo where DU ammunition was used. In 2006 the ^{210}Po poisoning episode in London [3] re-awakened the public's concern about the possible radiological risks for public health. Those incidents raised the necessity for the health agencies and emergency services in several countries to accurately and in a timely manner determine radionuclide amounts in environmental samples and in bio-assays in order to assess their possible impact.

On the other hand, the wide spectrum of emission sources has resulted in strongly heterogeneous structures and different isotopic compositions of the contaminations. These represent new and very specific elemental and isotopic features, which could be used for tracing the sources of corresponding emissions. Nowadays, those isotopic features are increasingly used in forensic studies. In particular, isotopic analysis on a microscopic level is gaining increasing importance as it reveals significantly more specific and persistent isotopic information. For instance, micro-particles with dimensions of <2 μm have been produced and distributed in the environment as a result of impacts with DU ammunition. When inhaled by human beings such particles can reach bronchioles and pulmonary alveoli and remain in lung tissues during relatively long periods after exposure. That fact was used by Rummel et al. [4] to investigate a case of a murdered man, whose body had been recovered in 2004 in Central Eifel in Germany. Investigation of micro-particles in the lung tissue allowed reconstruction of his previous history including his prior stay in Iraq [4]. The latter could be revealed due to the presence of desert-specific minerals, which were associated with a small number of depleted uranium particles in the lung tissue.

In general, the analysis of long-lived radionuclides is of interest in different areas ranging from radiobiology and health safety, environmental decontamination and remediation, archaeology and forensics [5]. This paper focuses on mass spectrometric determination of radionuclides of actinides and fission products in biological tissues as well as in environmental compartments, which can serve as sources of contamination of living organisms. The relatively low specific activity of long-lived radionuclides limits the application of radiometric techniques that are based on registration of emitted radiation. But also the modern mass spectrometric methods, which are based on atom (ion) counting, are challenged by the very low amounts of artificial actinides in bio-assays.

2. Nuclear and other radiological materials in the biosphere

2.1. Contamination by nuclear weapon tests

Atmospheric nuclear weapons tests, mainly explosions of megaton-range weapons that took place before 1963, have released about 1.1×10^{16} Bq of ^{239,240}Pu and significant amount of fission products, which have been globally distributed onto the Earth's surface [2,6]. The majority of Pu has been incorporated in sea-bed sediments and upper soil layers [7]. Nowadays, the median Pu content in soils of the Northern Hemisphere is about 10^{-13} g/g and the Pu amounts in the human body can vary between 0.05 and 0.5 ng (Table 1) [8,9]. Together with 'global fallout' from atmospheric tests, local contaminations have occurred on test sites, such as the Marshall Islands, Maralinga (Australia), Mururoa (French Polynesia), the Nevada test site (USA), Novaya Zemlya (Russia), Semipalatinsk (Kazakhstan), etc. [2,20–23].

2.2. Emission from the nuclear fuel cycle

Another source of environmental contamination with both actinides and fission products is the nuclear fuel cycle [24]. Different levels of contaminations can occur at all stages of the nuclear fuel cycle including mining and milling of ores, uranium enrichment, fabrication of fuel, reactor operation, spent fuel storage, fuel reprocessing and waste storage. Contamination of the environment by radioactive materials has also occurred at the facilities for the production of nuclear materials for nuclear weapons fabrication, which exist in several places in the United States, United Kingdom, France, China and Russia [2]. At the early stage of nuclear weapons development the production reactors were cooled by water that was drained off into natural water reservoirs. For instance, at the Hanford facility (USA), whose original mission was production of plutonium by irradiation of uranium fuel elements in reactors, the water coolant was drained into the Columbia River. At the chemical plant "Mayak" (Russia, the Southern Ural) the water was drained into the Techa River and a lake near the plant, some fraction of the radiochemical production liquid wastes was also drained into the Techa River in 1949–1951 [25].

Later, reprocessing plants were built taking into account the increased requirements for operational safety. However, as a result of accidents at some plants, several local contamination incidents have also taken place [26]. For example, a major fire occurred at the Rocky Flats Plant, in Colorado, USA in 1969 and the total amount of plutonium deposited at the site was 1.6×10^{11} Bq [21]. Discharges into the sea and into the atmosphere from commercial reprocessing plants located in the UK at Sellafield and in France at Cap de la Haque have also been reported. The cumulative total emission of ^{239,240}Pu from the reprocessing plant of Sellafield into the Irish Sea has been 6.9×10^{14} Bq [27].

2.3. Accident at Chernobyl NPP

The world's most serious nuclear accident occurred at the Chernobyl nuclear power plant (NPP) in the Ukraine in 1986. The estimated atmospheric releases of radionuclides from the Chernobyl NPP are listed in Table 1. According to numerous studies [28–35], three forms of radioactive release could be generally distinguished according to their radiological effects: volatile short-lived radionuclides such as radioactive iodine (^{131}I), radio-caesium, and the fallout that contained radioactive particles. The latter ones included 'ruthenium particles' (with diameters of up to tens μm) and particles of irradiated fuel matrix or its mixture with constructive materials (with diameters of several μm). The fuel particles were found mainly within the 30 km exclusion zone around Chernobyl NPP. Long-lived and non-volatile radionuclides such as Pu and Sr-isotopes (^{239}Pu and ^{90}Sr) were initially incorporated into the fuel particles.

2.4. Contamination with depleted uranium

Depleted uranium is a by-product of enrichment processes of natural uranium and reprocessing of spent nuclear fuel. DU consists mainly of ^{238}U, it has only about one-third of the natural ^{235}U abundance (0.2–0.3% vs. 0.72% in natural uranium). Areas of applications include both civilian and military uses. Civilian usage included colouring of glassware and dental ceramics (until the middle of the 20th century), employment as a chemical catalyst, for counterbalancing weights and ballast, and as radiation shielding

Table 1
Major sources of long-lived radionuclides in biosphere and reported radionuclide concentrations in environmental and biological assays.

Isotope	Origin	Major contamination sources	Some figures to illustrate the inventories of radionuclides in the biosphere	Reported concentrations of radionuclides in water and bio-assays
^{234}U ^{235}U ^{238}U	Natural	Depleted uranium	Typical concentrations of uranium in Soil 0.3–11.7 mg/kg Air 2.5×10^{-8}–10^{-7} mg/m^3 Water 3×10^{-3}–2.1 μg/l	U amount in human body in unexposed individuals is ca. 56 μg [10] The worldwide mean value found for uranium in the skeleton was 2.4 μg (U)/kg wet bone [12] Daily excretion rate (urine) in unexposed persons is ca. 13.6 ng/day [11]
^{210}Po	Natural (decay product of ^{238}U); artificial (activation of bismuth)		Natural concentration of ^{210}Po in the Earth crust is ca. 2×10^{-17} g/g	Average ^{210}Po concentrations In bone ca. 6 fg/kg In liver ca. 2.4 fg/kg [12]
^{236}U	Artificial, activation product	Nuclear fuel cycle, weapon tests	The total global fallout of U-236 on the Earth is ca. 900 kg [13]	<3 fg in 24 h urine samples [11]
^{239}Pu ^{240}Pu	Artificial, activation product	Nuclear fuel cycle, weapon tests	Release of Pu into atmosphere from the above-ground tests of nuclear weapons in 1950s and 1960s was ca. 5 tons [9] The estimated Pu release from Chernobyl NPP (including fuel particles) was ca. 19.7 kg [2]	Pu amount from global fallout and other sources in human body varies from ca. 0.05 to ca. 0.5 ng [8,9]
^{129}I	Artificial, fission product	Nuclear fuel cycle, weapon tests	Natural ^{129}I inventory is ca. 263 kg [14], for comparison: the annual discharge from European nuclear reprocessing facilities (Sellafield and La Hague) in 1997 was ca. 330 kg/year [15]	^{129}I/^{127}I isotope ratio in open ocean surface water: 1.2×10^{-10} to 9×10^{-10} [16] ^{129}I/^{127}I isotope ratio in the Northern Sea: 5.1×10^{-7} to 1.5×10^{-6} [16,17] (corresponds to ^{129}I concentration of ca. 8×10^{-14} g/g) ^{129}I/^{127}I isotope ratio in thyroid glands $<4 \times 10^{-11}$ (pre-nuclear) to 4×10^{-7} (post nuclear) [18]
^{90}Sr	Artificial, fission product	Nuclear fuel cycle, weapon tests	The global release of atmospheric weapon testing was ca. 120 kg The estimated atmospheric release from Chernobyl NPP was ca. 2 kg [2]	Peak concentration of ^{90}Sr of ca. 60 fg/g (Ca) was measured in human bones in 1964–1966 and it was attributable to atmospheric weapons testing in 1961–1962 [12][a] ^{90}Sr in milk teeth of children born in 1994 was ca. 6 fg/g (Ca) [19]
^{137}Cs	Artificial, fission product	Nuclear fuel cycle, weapon tests	The global release of atmospheric weapon testing was ca. 300 kg The estimated atmospheric release from Chernobyl NPP was ca. 26 kg [2]	Concentration of ^{137}Cs in human body (residents of Berkshire and Oxfordshire, UK) has varied between 20 fg/g (K) and 2 pg/g (K) [12][b] Peak concentration was measured in 1964–1966 and it was attributable to atmospheric weapons testing in 1961–1962

[a] Strontium is deposited principally in bone and hence this has been the organ of interest for virtually all studies of ^{90}Sr in autopsy samples. The data have been usually expressed as Bq/g Ca, because of the very limited discrimination between the two elements from foodstuffs [12]. Here the ^{90}Sr concentrations are reported in fg per g of calcium.

[b] In general the body caesium (^{137}Cs and ^{134}Cs) values have been often reported in the literature in terms of Bq of caesium per g of potassium. This was because there was a stronger correlation between total body radiocaesium and total body potassium than between total body radiocaesium and body weight [12]. Here the ^{137}Cs concentrations are reported in fg per g of potassium.

in hospitals (although DU itself is weakly radioactive, it provides a suitable protection against gamma radiation) [36].

Depleted uranium has become an environmental contaminant of considerable concern in many combat zones and weapons-testing sites around the world. Its dispersion from the application of DU-bearing ammunition in military conflicts led to local contamination in certain areas, representing an example of a specific non-natural isotopic signature in the environment. The use of DU ammunition was recognized in several conflicts, including the first Gulf War (Iraq and Kuwait, 1990), in Bosnia-Herzegovina in 1995; in the NATO air strike on Serbia and Montenegro in 1999; and more recently in the conflicts in Afghanistan and in Iraq [37–39]. Although DU is less radioactive than natural or enriched uranium, it represents a health risk to people. As a result of combat activities, penetrator fragments may remain in wounds; furthermore, aerosols are created during the impact of DU rounds on hard surfaces. These aerosols immediately burn and produce micrometer-sized uranium oxide particles, which can be inhaled and penetrate into organisms [40].

2.5. Other examples of incidents with nuclear devices

Further local contaminations with actinides of specific non-natural isotopic composition occurred, for example, after the collisions of US Air Force bombers, which where mounted with thermonuclear bombs, in Spain (Palomares, 1966) and in Greenland (Thule, 1968) [41,42], and after a crash of a cargo plane in the Netherlands, that was ballasted with DU as a counterweight (Ams-

terdam, 1992) [43]. In those accidents Pu and U particles were released into the environment. Atmospheric contamination with plutonium-238 occurred from the SNAP (System for Nuclear Auxiliary Power) device in an American satellite (SNAP 9A), which burned up some 46 km above the Mozambique channel shortly after take-off in April 1964. It contained plutonium metal, primarily as ^{238}Pu, and about 6.3×10^{14} Bq of ^{238}Pu was released into the environment [6,20]. In 1978, a Soviet satellite COSMOS-954 burned up in the atmosphere and contaminated a large area of Canada with reactor fuel particles, which had sizes of 0.1–1 mm and activities of up to 5×10^9 Bq per particle [44].

3. Figures of merit of mass spectrometric techniques

Conventional radioanalytical techniques, such as α-spectrometry or liquid scintillation radiometry [45,46], are based on the measurement of activities of radioisotopes. They require careful chemical separation of the analyte (for instance, via precipitation, solvent extraction or chromatography), which is delicate and time-consuming. Although radioanalytical techniques are well established for the determination of most actinide isotopes especially those having a half-life of less than 1000 years, 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. This means that analysis can take several days or even several weeks. Determination of long-lived radionuclides is especially difficult if only small amounts of sample materials (e.g. human tissue obtained by a biopsy) are available. 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 α energies (5.24 MeV and 5.25 MeV, respectively). Although some sophisticated methods, such as for instance implanted passivated junction silicon detectors and special spectra deconvolution software [47], were proposed to improve α-spectrometry resolution, those approaches are mainly restricted to high-activity samples, as a relatively high peaks are needed to define the spectrum well enough so that the multivariate analysis techniques can be applied. 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 [5,48,49].

Different mass spectrometric methods have been applied for actinide isotopic measurements, such as thermal ionization mass spectrometry (TIMS) [50–52], accelerator mass spectrometry (AMS) [53,54], resonance ionization mass spectrometry (RIMS) [55,56], glow discharge mass spectrometry (GDMS) [57–59], secondary ion mass spectrometry (SIMS) [59–62], inductively coupled plasma mass spectrometry (ICP-MS) [5,63–67], laser ablation ICP-MS (LA-ICP-MS) [68–70], etc. In summary, the merits of particular mass spectrometric methods include (i) low detection limits (ICP-MS, TIMS, etc.), (ii) high precision of the measured isotopic ratios (multi-collector ICP-MS and TIMS), (iii) high selectivity and abundance sensitivity (RIMS, AMS), and (iv) high spatial resolution (SIMS, LA-ICP-MS).

3.1. Detection limits and precision of isotope ratio measurements

Mass spectrometry is being increasingly used for the determination of the majority of long-lived radionuclides with low specific activity in environmental and biological samples. During the last two decades, especially ICP-MS has become an important tool in radiology, biomedical and environmental research [5,65–70] because it provides low detection limits, involves simple experimental procedure and reliable isotopic ratio measurement and is more universal in comparison to radio-analytical techniques. Arguably this technique presently surpasses other mass spectrometric methods in terms of the absolute registration sensitivity for actinide isotopes. Therefore, this method, with its ability to provide precise and, if required, simultaneous analysis of a wide range of elements, has turned into a powerful tool for monitoring long-lived radionuclides in water [71], urine [72,76–79], biological tissues [74,75] and other environmental samples [63,68,73]. ICP-MS is an especially promising technique for the analysis of small amounts of biological tissues, which are, for instance, obtained by biopsy [80] and for the determination of ultra-low concentrations of long-lived radionuclides in complex matrices [71]. The limits of detection for ^{239}Pu in 1 L of urine and for ^{236}U in 0.5 l of urine were reported as low as 1×10^{-18} g/ml [77] and 2×10^{-19} g/ml [79], respectively.

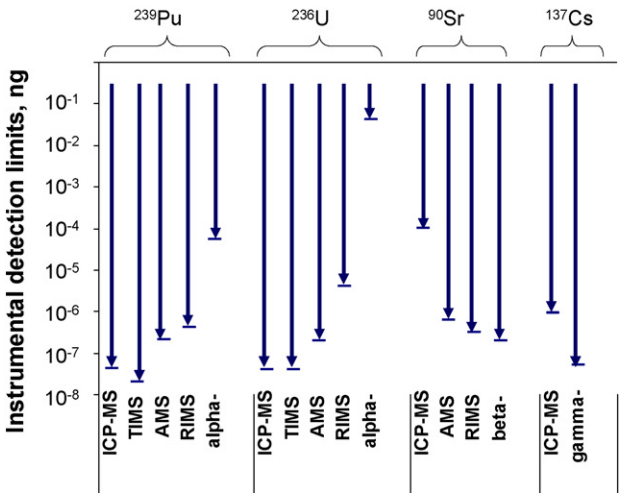

Fig. 1. Instrumental detection limits of radioanalytical and mass spectrometric techniques for analysis of ^{239}Pu, ^{236}U, ^{90}Sr, and ^{137}Cs (alpha-, beta- and gamma-abbreviations refer to alpha-, beta- and gamma-spectrometry).

Fig. 1 compares instrumental detection limits of several radioanalytical and mass spectrometric techniques for radionuclide analysis and Tables 2 and 3 list reported minimal detectable amounts of radionuclides in urine and tissue samples. It can be clearly seen from the presented data that mass spectrometric techniques have significantly lower detection limits for radionuclides with half lives that are longer than 1000 years (^{239}Pu, ^{236}U, ^{238}U, etc.); however, they are less sensitive than the radioanalytical or 'decay-counting' techniques for detection of short-lived nuclides, which have high specific activity (such as ^{90}Sr and ^{137}Cs). The

Table 2
Reported minimal detectable amounts of radionuclides in urine samples by radioanalytical and mass spectrometric methods.

Isotope	Analytical techniques	Minimal detectable amount of radionuclide in urine sample
^{238}U	Alpha spectrometry	80 ng (1 mBq) [81]
	ICP-MS	20 pg (0.25 μBq) [11]
^{236}U	ICP-MS	ca. 3 fg (7 nBq) [11]
^{239}Pu	Alpha spectrometry	(^{239}Pu + ^{240}Pu): ca. 0.05–0.01 pg (0.1–0.2 mBq) [83,84]
	AMS	ca. 0.44 fg (1 μBq) [83]
	TIMS	0.53 fg (1.2 μBq) [85]
	ICP-MS	1 fg (2.3 μBq) [80]
	RIMS	ca. 4 fg for ^{244}Pu [129]
^{241}Am	Alpha spectrometry	9.5 fg (1.2 mBq) [81]
	ICP-MS	3.7 pg (0.5 Bq) [86]
^{90}Sr	Beta-counting	0.2–20 fg (1–100 mBq) [87,88]
	ICP-MS	0.4 pg (ca. 2 Bq) [105] (desired for radiation protection: 20 fg/l)

Table 3
Reported minimal detectable amounts of radionuclides in solid biological tissues by radioanalytical and mass spectrometric methods.

Isotope	Analytical techniques	Minimal detectable amount of radionuclide in urine sample
^{236}U	ICP-MS	Soft tissue and bone: 15 fg (36 nBq) [82]
^{239}Pu	Alpha spectrometry	(^{239}Pu + ^{240}Pu): ca. 0.02 pg (0.4 mBq) [9]
	TIMS	Bone: 8 fg (0.02 mBq) [91]
	ICP-MS	Bone: ca. 1 fg (2.3 μBq) [98]
	Fission track radiography	Gall stones: ca. 0.1 pg (0.23 mBq) [8][a]
^{241}Am	Alpha spectrometry	Bioassays: 8 fg (1 mBq) [92]
	ICP-MS	0.6 fg (0.08 mBq) [92]
^{90}Sr	Beta-counting	Bone: 1 fg (5 mBq) [19]
	ICP-MS	0.4 pg (2 Bq) [107][b]

[a] Fission track radiography can achieve, in theory, significantly lower detection limits for ^{239}Pu, however, the ability of this method to detect fissile isotope ^{239}Pu in environmental samples is limited by the presence of interfering isotope ^{235}U from natural uranium.
[b] Estimated from the detection limits reported in [107] for soil samples with account to the elemental composition of bone tissue.

mass spectrometry can still be used for express-monitoring of higher concentrations of ^{90}Sr in emergency cases because it allows much faster analysis. However, mass spectrometry is generally much less suited for ^{137}Cs analysis. Thus, ICP-MS had a detection limit of 0.9 fg/ml (0.0027 Bq/ml) [89], which is worse than the corresponding detection limit of gamma-spectrometry. In general, gamma-spectrometry provides more accurate results for ^{137}Cs, as it usually does not suffer from significant interferences, and the analytical procedure is much simpler than the mass spectrometric analysis (further detailed discussion of particular merits of radiometric and mass spectrometric methods for the determination of radionuclides in environmental, biological and nuclear waste samples can be found in a work by Hou and Roos [90]).

LA-ICP-MS together with isotope dilution technique offered a possibility for plutonium and americium isotope ratio analysis in lichen and moss samples, which had been collected from a bog in the eastern Italian Alps, at a concentration level of 5×10^{-14} g/g to 2.5×10^{-13} g/g [73]. Table 4 compares detection limits provided by LA-ICP-MS and alpha spectrometry for several actinide isotopes. There again, the 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. The isotopic results from that work [73] allowed one to draw the conclusion that the detected contamination with artificial transuranium elements was due to the global fallout after nuclear weapons tests in the 1960s. Although the anthropogenic radionuclide concentrations in the samples were extremely low, those moss samples appeared to be suitable for investigating atmospheric contamination with actinides and to provide a record of the history of atmospheric fallout.

Table 4
Estimated detection limits of LA-ICP-MS and alpha-spectrometry for some actinide isotopes in moss samples [73].

Isotope	Half-life, years	Detection limit, Bq	
		LA-ICP-MS	Alpha spectrometry
^{230}Th	7.54×10^{4}	2.9×10^{-6}	2.0×10^{-5}
^{232}Th	1.41×10^{10}	2.8×10^{-11}	5.0×10^{-5}
^{233}U	1.59×10^{5}	1.4×10^{-6}	–
^{234}U	2.44×10^{5}	8.8×10^{-7}	2.0×10^{-5}
^{235}U	7.04×10^{8}	3.9×10^{-10}	2.0×10^{-5}
^{236}U	2.34×10^{7}	9.5×10^{-8}	3.0×10^{-5}
^{238}U	4.47×10^{9}	8.8×10^{-11}	5.0×10^{-5}
^{237}Np	2.14×10^{6}	1.0×10^{-7}	2.0×10^{-5}
^{238}Pu		–	8.0×10^{-5}
^{239}Pu	2.41×10^{4}	9.0×10^{-6}	5.0×10^{-5}
^{240}Pu	6.56×10^{3}	3.1×10^{-5}	
^{241}Pu	1.49×10^{1}	1.4×10^{-2}	–
^{242}Pu	3.87×10^{5}	5.1×10^{-7}	2.0×10^{-5}
^{244}Pu	8.26×10^{7}	2.4×10^{-9}	–
^{241}Am	4.32×10^{2}	4.7×10^{-4}	8.0×10^{-5}
^{243}Am	7.37×10^{3}	2.7×10^{-5}	4.0×10^{-5}

Traditionally, TIMS has been the technique of choice for achieving the highest accuracy and precision of isotope ratios. Recent developments in multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) made possible accurate and precise determination of isotope ratios, with precision reaching, which is comparable to that achieved with MC-TIMS [93,94]. Highly precise uranium isotope analysis by MC-TIMS and MC-ICP-MS has been employed for the detection of depleted uranium in urine to assess the risk of depleted uranium uptake in military personnel as well as in civilians who had been affected by DU-bearing ammunition in military conflicts [95–97]. Other biological indicators, such as lichen, moss, etc., have also been used to assess DU contamination in combat regions and weapons testing sites [97–99].

An impressive example of MC-ICP-MS application for monitoring of depleted uranium in urine can be found in a work by Gerdes [79]. After the inhalation of uranium oxide aerosols formed during fires and explosions, the uranium may remain in the lungs for years and only tiny fractions, which can be as small as one part per million of the initially inhaled fraction may be excreted per day in urine over several years. Therefore, the screening of human exposure to DU dust demands precise and sensitive methods of analysis. The developed methodology [79] allowed detection of deviations of ^{238}U/^{235}U from the natural values, which was also accompanied by clearly elevated ^{236}U/^{238}U ratios. That study demonstrated the capability of the modern MC-ICP-MS to detect urinary excretion of depleted uranium in the low fg/ml range or at fractions down to 0.5% of the total urinary uranium concentration. It suggested that the assessment of up to a few micrograms of insoluble non-natural uranium particles in the lung would be possible several months or even years later.

Recently, Froidevaux et al. [100,101] reported application of sector-field ICP-MS technique for determination of ^{239}Pu data in the whole milk teeth of children at the femtogram (10^{-15} g) level. They measured plutonium levels in the milk teeth of children born between 1951 and 1995 to assess the potential risk that plutonium incorporated by pregnant women might pose to the radiosensitive tissues of the fetus through placenta transfer. Based on the measured ^{240}Pu/^{239}Pu isotope ratios Froidevaux et al. concluded that the Pu source in the analyzed samples was atomic bomb test fallout. Those works [100,101] also demonstrated that plutonium found in milk teeth was caused by fallout that was inhaled around the time the milk teeth were shed and not from any accumulation during pregnancy through placenta transfer. The obtained data were useful to make more precise estimation of the retention time of plutonium in the skeleton of humans.

The improved sensitivity of mass spectrometric determinations, as compared to alpha counting, has also enhanced the uranium disequilibrium series dating and enabled, for instance, the use of ^{230}Th chronometer to investigate the ages of human bones, coral reefs and other marine archives [1], thus, further increasing the application spectrum of mass spectrometric isotope analysis.

3.2. Selectivity and abundance sensitivity

The determination of ultra-low amounts of long-lived radionuclides (such as ^{41}Ca, ^{99}Tc, ^{129}I, ^{239}Pu, ^{240}Pu, ^{241}Am, ^{230}Th or ^{236}U) by ICP-MS can be affected by a number of isobaric atomic (Ar_2^+ vs. $^{80}Se^+$, $^{129}Xe^+$ vs. $^{129}I^+$, ^{241}Pu vs. ^{241}Am, etc.) and molecular ion interferences (e.g. $^{235}UH^+$ vs. $^{236}U^+$, $^{238}UH^+$ vs. $^{239}Pu^+$) as well as by peak tailing of the adjacent major isotopes (e.g. effect of the peak tail of $^{238}U^+$ on $^{236}U^+$). Therefore, efficient chemical separa-

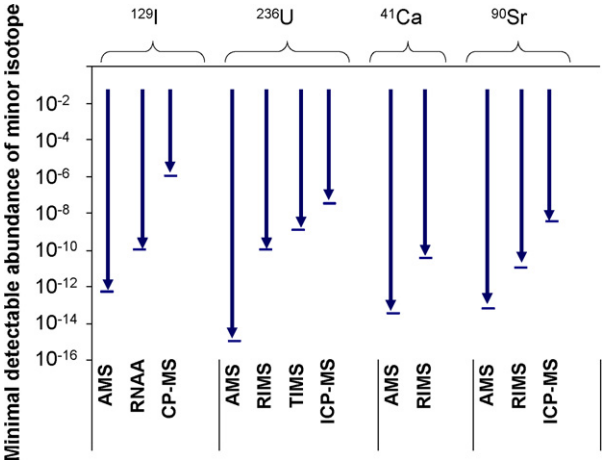

Fig. 2. Ability of different mass spectrometric techniques to analyze minor isotopes ^{129}I, ^{236}U, ^{41}Ca, and ^{90}Sr, expressed as minimal detectable abundance of minor isotope in matrix of major isotope(s).

tion techniques and the application of special sample introduction devices are required to extract the element of interest from the sample matrix. Many studies have reported different approaches to solve the interference problems of molecular and atomic ions in LA-ICP-MS by the application of higher mass resolution [102–105], the use of heavy water (D_2O) as a solvent for the dissolution and dilution of samples (reducing $^{235}U^1H^+$ interference on $^{236}U^+$) [102] or the implementation of a cool plasma (on-line separation of ^{90}Sr from ^{90}Zr) [105]. Reaction and collision cell technologies have been extensively applied for on-line separation of radionuclides, such as reduction of $^{90}Zr^+$ ion intensity for ^{90}Sr determination [105–107], reduction of $^{129}Xe^+$ ion intensity for ^{129}I determination [108,109], for on-line separation of actinides (U, Pu and Am) in the reaction cell [110–112] and for analysis of a number of other nuclides (^{135}Cs, ^{137}Cs, ^{210}Pb, and ^{226}Ra) [113].

A rapid technique for the determination of Pu in urine samples after matrix separation using TRU resin and implementation of a dynamic reaction cell (DRC) for on-line separation of U and Pu was reported by Epov et al. [112]. However, collision and reaction cells might introduce new interferences by molecular ions, which are produced in the cell and which can significantly affect the determination of low-abundant radionuclides.

High isotopic abundance sensitivity is desirable for the measurement of low-abundant isotopes in the presence of neighbouring high-abundant ones. This is of importance for analyzing ultra-low concentrations of trace elements or isotopes in the presence of elements or isotopes with much higher concentrations (e.g. radionuclides included in a matrix of stable isotopes). An improvement of abundance sensitivity in a quadrupole-based inductively coupled plasma mass spectrometer with a hexapole collision cell could be achieved by reducing the kinetic energy of ions [114]. On the other hand, the application of ion deceleration filters in sector-field MC-ICP-MS improved the abundance sensitivity by about two orders of magnitude accompanied by only a small loss of absolute sensitivity [115,116]. Thus, an MC-ICP-MS with a high-efficiency solution introduction systems allowed the determination of $^{236}U/^{238}U$ isotope ratios down to 10^{-8}, which surpassed by more than one order of magnitude the capabilities of conventional sector-field ICP-MS. However, the abundance sensitivity of MC-ICP-MS is still significantly lower than that of TIMS, with which a lower limit of detection for $^{236}U/^{238}U$ ratio of about 3×10^{-9} could be achieved [52].

Fig. 2 demonstrates the ability of different mass spectrometric techniques to analyze minor isotopes, such as ^{129}I, ^{236}U, ^{41}Ca, and ^{90}Sr. AMS and RIMS have the great advantage as compared to other mass spectrometric techniques, in that they do not suffer from molecular isobaric interferences, and they are therefore extremely selective techniques [48,117,118]. Thus, AMS has the sensitivity and selectivity to perfectly meet requirements for ^{14}C analysis and is now the predominant method in use for the ^{14}C-dating methodology [1] as well as for bio-medical investigations that use ^{14}C-labelled biologically active compounds to obtain pharmacokinetic and metabolism data [119]. Isotopic labelling of bone using ^{41}Ca, a long-living radiotracer, has also been proposed for measuring changes in bone metabolism. After isotopic labelling of bone, changes in urinary ^{41}Ca excretion, that reflect changes in bone Ca balance, can be efficiently monitored by AMS or RIMS [120,121].

AMS is well established 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} [122–124]. The plutonium isotopic measurements in tissue samples of marine organisms have been performed by using ultra-high sensitivity accelerator mass spectrometry by Hamilton et al. [125]. 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 plutonium (as well as other radionuclides) from low-level radioactive waste repositories.

AMS has been implemented for monitoring of sources of environmental and bioassay contamination with iodine-129 via analysis of this radionuclide in lichen, thyroids and other environmental samples [18,126]. Michel et al. [127] investigated the feasibility of this technique for the retrospective dosimetry of the ^{131}I exposure after the Chernobyl accident. Based on the total ^{129}I inventories and on literature data for the atomic ratio of $^{129}I/^{131}I$ for the Chernobyl emissions and on aggregated dose coefficients for ^{131}I, the thyroid exposure due to ^{131}I after the Chernobyl accident was estimated for the inhabitants of several villages in the areas, which had been affected by radioactive fallouts from the Chernobyl NPP.

AMS has also been established as a very sensitive method for pharmacological studies of radionuclide-labelled drugs, which have been used to obtain pharmacokinetic data [128]. The very low doses of drug administered consequently lead to very low concentrations of drug appearing in the body. AMS has been able to measure drug concentrations in the ag/ml range.

RIMS has been developed during the past decade into a very versatile experimental method for highly selective ultra trace determination of radioisotopes [117,118,129–131]. Apart from providing nearly complete isobaric suppression and high overall efficiency, the possibility for combining optical isotopic selectivity with that of the mass spectrometer has led to remarkable specifications. The widespread analytical potential and applicability of different techniques based on resonant laser ionization has been demonstrated in investigations on the lowest quantities of radioactive isotopes in bio-medical samples. Along with the isotopic selectivity of 3×10^{12} in the suppression of neighbouring isotopes, a very high isobaric suppression of $>10^8$ and a good overall sensitivity of 5×10^{-5} were also obtained, resulting in overall detection limits in the pg/g region.

Due to its high selectivity and good sensitivity RIMS has been successfully applied for monitoring of Pu in urine and soft tissues for radiological studies [129,132]. Analytical applications of high resolution RIMS have also concerned ^{41}Ca determination in human bones and other bioassays with a wide spectrum of biomedical research interests (e.g. study of bone calcium metabolism), as well as ^{90}Sr determination in radiation protection, and analysis of gadolinium isotopes in tumour tissues and other bioassays [117,118,121,133,134].

3.3. Spatially resolved analysis

The specific toxicity of alpha-emitting radionuclides largely depends on their spatial distribution within organs and tissues. The health hazard produced by radioactive aerosols is also determined by the size distribution of particles. Large particles with a diameter of more than 50 μm are retained in the nasal cavity and nasopharynx, whereas small particles with sizes of a few micrometers reach the bronchioles and can penetrate to the alveoli. By inhaling particles with high specific activity, high doses can be absorbed in a limited tissue volume within the range of alpha emission.

Mass spectrometric methods, such as SIMS and LA-ICP-MS, can be employed for a spatially resolved analysis of long-lived actinide isotopes in biological tissues and aerosol samples. However, SIMS is mainly applied in nuclear forensics to characterize and identify particles and reveal isotopic ratios of plutonium and uranium [135,136], but its application for analysis of bio-assays is complicated. The limitations of SIMS include the need for rather high concentrations of the analyte, the occurrence of isotopic fractionation during various stages of the analysis, pronounced matrix effects, and complicated sample preparation and measurement procedures that are required for biological tissues.

LA-ICP-MS with double-focusing sector field and quadrupole-based mass spectrometers has been successfully applied as a powerful imaging (mapping) technique to produce quantitative images of detailed regionally specific element distributions in thin biological tissue sections, for instance in human lymphatic and respiratory tissues, brain, bones, etc. [74,71,137–141]. The first imaging of long-lived radionuclides in brain tissues was done by Becker et al. [74] and the first detection of uranium binding to protein in 2D gels was also reported by the same group in 2005 [142]. Imaging LA-ICP-QMS has also been applied to investigate distributions and isotopic composition of uranium in plant tissues and single hairs to study, for example, the uptake of uranium and thorium from environmental contaminations [143–144] or the uptake of natural uranium from drinking water [145].

Near-field laser ablation inductively coupled plasma mass spectrometry (NF-LA-ICP-MS) has been proposed for nanometer-scale spatially resolved analysis of biological surfaces doped with uranium [146]. Those experiments suggested a new potential path for future applications in nano-imaging of elements in life science, biology and medicine, e.g., for analyses of single cells, cell organelles or biological structures at nanometer range in order to detect neurodegenerative diseases, but also in material science, nanotechnologies and nano-electronics.

In order to better understand the uranium-protein binding mechanisms, uranium speciation was investigated by doing an in vivo screening of target proteins likely to bind it in kidneys of exposed rats. Kidneys were dissected out and protein extract was prepared. Then, separation of renal proteins by isoelectric focusing gel electrophoresis (IEF) and two-dimensional gel electrophoresis (2-DE) followed by LA-ICPMS analysis were performed [147]. The results of IEF-LA-ICP-MS suggested that uranium could be observed chelated with some renal proteins that was very encouraging to understand the entry, storage and elimination of this element in kidneys. Thus, the combination of imaging LA-ICP-MS of metals with proteomic studies made available a new powerful technique for investigation of uranium accumulation in organs on a biomolecular level [74,75,137,147].

The forensic study of the corpse that was found in Central Eifel [4] emphasized the importance of particle analysis: in the lung tissue of the dead person micro-particles (with a size of <5 μm) were found, which proved to contain depleted uranium. It was very likely that those particles had derived from aerosols, which had been generated after the impact of DU-penetrators. The finding of DU particles that were associated with desert-specific minerals suggested a prior stay of the murdered person in Iraq. That finding, together with other results of criminalistic and forensic investigations, provided important evidence to determine the history of the murdered person.

The isotopic analysis of particular elements in biological tissue samples with a high spatial resolution is a great challenge. Application of laser ablation ICP-MS with multiple ion counters, as proposed in a recent work [148] for highly sensitive isotope ratio measurements of long-lived radionuclides in radioactive microsamples, could be of potential interest in bio-medical and forensic applications. The highly sensitive simultaneous measurement of all isotopes of interest is crucial for achieving precise isotope ratios from transient signals, which are obtained from the ablating of micro-samples; and therefore, employment of multiple secondary ion multipliers represent definite advantages for simultaneous recording of low-intensity signals. The advantage of the LA-MC-ICP-MS approach reported in [148] consisted of a possibility for direct isotope analysis of radionuclides in complex sample matrices that included organic components and minerals. Such a methodology would represent a promising approach for isotopic analysis of radionuclides in microscopic areas of soft bio-tissues.

4. Conclusions

Mass spectrometry is playing an increasingly important role in the determination of ultra-low concentrations of long-lived radionuclides with low specific activities in different kinds of biological samples. Nowadays, the mass spectrometric analysis of radionuclides is being widely employed in radioprotection, radiobiology, biomedicine, nutrition science, forensics, and in many other scientific fields. Modern mass spectrometric techniques and equipment are superior in terms of sensitivity and selectivity for the majority of the required applications; but newer and more powerful methods have to be constantly developed to enable, for instance, the investigations of micro-distribution of radionuclides in biological tissues for an assessment of irradiation doses on individual cells, or to study radionuclide behaviour in living organisms on bio-molecular level. A few pioneering studies in those directions have already been reported, thereby opening new and important horizons in our understanding of bio-toxic effects of radionuclides. Implementation of ^{234}U–^{230}Th and ^{235}U–^{231}Pa chronometers for age determination of bone tissues, corals, and other archives has an important value in climate research and archaeometry [1]. The highly sensitive mass spectrometric techniques promise to significantly extend the range and accuracy of the measured ages even if much smaller samples are available for analysis.

Development of the highly sensitive and highly precise mass spectrometric techniques demands also the production of the new certified isotopic reference materials with lower uncertainties of the certified isotope ratios. The measurement of radionuclides by mass spectrometry is a special challenge because of the comparably wide dynamic range of the isotope abundances typically found in nature [149]. High precision isotopic measurements are particularly needed for forensics and radioprotection purposes (for instance, for monitoring of depleted uranium in urine of potentially exposed persons). The accuracy, reliability, and traceability of such measurements depend heavily on suitable isotope reference materials.

Mass spectrometry cannot be expected, however, to completely replace radio-analytical methods. In particular, the radionuclides with relatively short half-times are normally measured by decay-counting techniques. For instance, the use of gamma-spectrometry for ^{137}Cs measurements ($T_{1/2}$ = 30.07 years) is more accurate and much simpler than the mass spectrometric analysis. Thus, gamma-spectrometry allows direct non-destructive measurement of ^{137}Cs

in sealed samples (that can be in solid or liquid form), whereas the ICP-MS requires a time-consuming sample preparation and matrix separation procedures. In addition, the ICP-MS analysis contaminates equipment, the laboratory environment and the exhaust system due to evaporation of radionuclides in the ion source. Fortunately, the wide spectra of presently available analytical methods and the constant development of new techniques provide a nice palette, where the analyst can select or even combine appropriate tools for a particular object of investigation.

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The author had the pleasure to work for several years in the Central Department of Analytical Chemistry at the Research Center Jülich, which was led by Dr. Hans-Joahim Dietze. My research was devoted to the investigation of concentrations and micro-distribution of heavy metals and radionuclides, which were suspected to be potential promoters of pathogenic mechanisms in human thyroid tissues. In 1998 Dr. Dietze invited me to discuss my project and suggested the use of ICP-MS instead of the previously applied radioanalytical methods for the determination of toxic trace elements and radionuclides in bio-assays. That idea resulted in a very efficient analytical approach that combined high sensitivity with the possibility of a simultaneous determination of many toxic and vital elements in one small specimen of human tissue; in addition, Dr. Dietze's proposal initiated a major change in my scientific career. The idea was realized in a new research project, which was supported by the Alexander von Humboldt Foundation. Several years of research in Jülich under the supervision of and in a very fruitful cooperation with Dr. Hans-Joahim Dietze and Dr. Sabine Becker provided me a great opportunity to gain an insight into new mass spectrometric methods and approaches. I remember with appreciation the daily scientific life in the Jülich mass spectrometry group with its challenging research goals, seminars and discussions, and joint exploration of the new ways to solve current analytical problems. On the occasion of the 75th birthday of Dr. Dietze I would like to express my gratitude to him for his intellectual curiosity, perspicacity, openness, and for his willingness to share his knowledge and ideas with younger colleagues.

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