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Review

Inductively coupled plasma mass spectrometry (ICP-MS) and laser ablation ICP-MS for isotope analysis of long-lived radionuclides

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Abstract

For a few years now inductively coupled plasma mass spectrometry has been increasingly used for precise and accurate determination of isotope ratios of long-lived radionuclides at the trace and ultratrace level due to its excellent sensitivity, good precision and accuracy. At present, ICP-MS and also laser ablation ICP-MS are applied as powerful analytical techniques in different fields such as the characterization of nuclear materials, recycled and by-products (e.g., spent nuclear fuel or depleted uranium ammunitions), radioactive waste control, in environmental monitoring and in bioassay measurements, in health control, in geochemistry and geochronology. Especially double-focusing sector field ICP mass spectrometers with single ion detector or with multiple ion collector device have been used for the precise determination of long-lived radionuclides isotope ratios at very low concentration levels. Progress has been achieved by the combination of ultrasensitive mass spectrometric techniques with effective separation and enrichment procedures in order to improve detection limits or by the introduction of the collision cell in ICP-MS for reducing disturbing interfering ions (e.g., of $^{129}Xe^+$ for the determination of ^{129}I).

This review describes the state of the art and the progress of ICP-MS and laser ablation ICP-MS for isotope ratio measurements of long-lived radionuclides in different sample types, especially in the main application fields of characterization of nuclear and radioactive waste material, environmental research and health controls.

Keyword: Inductively coupled plasma mass spectrometry; Isotope ratio measurements; Laser ablation ICP-MS; Long-lived radionuclides

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1. Introduction

Precise and accurate isotope ratio measurements of long-lived radionuclides at the trace and ultratrace level are necessary for quite different applications, e.g., for analysis of nuclear samples [1–3], radioactive waste [4–6], environmental materials such as biological samples, soils, dust, water [7–17] and especially for geological [18,19] and medical samples [20–23]. For example, environmental contamination by artificial radionuclides and the evaluation of their sources requires precise isotope analysis. Due to the long-term impact of radionuclides with half lives >100 years special attention must be given to the topic of increasing contamination of the environment by artificial radionuclides. Therefore, optimal management of storage sites requires the determination of the radionuclide composition present in waste produced by nuclear fuel reprocessing [24]. Besides radioactive waste characterization and environmental monitoring, also health control of exposed persons (blood, urine, feces, hair and tissue analysis) require powerful and fast analytical techniques which allow many samples to be measured in a short time with a high degree of accuracy and precision. In long-lived radionuclide analysis, radioanalytical methods such as α-spectrometry (a main part of these radionuclides is α-emitter) were used for many decades as the dominant techniques. But conventional radiochemical methods for the determination of long-lived radionuclides at low concentration levels require careful chemical separation and enrichment steps of the analyte, e.g., by liquid–liquid, solid phase extraction or ion chromatography. Furthermore, the major disadvantage of α-spectrometry relates to the long counting period, which can take from days to several weeks depending on the sensitivity, detection limit and precision required. In addition, ^{239}Pu and ^{240}Pu isotopes – relevant for the determination of Pu origin in radioactive waste or environmental samples (as a result of nuclear fallout from nuclear weapons tests or nuclear power plants) – are difficult to analyze due to the very similar α energies of ^{239}Pu and ^{240}Pu (5.24 and 5.25 MeV, respectively). Due to these disadvantages, the radioanalytical techniques have been increasingly replaced by mass spectrometry in the few last years. Thus for example, thermal ionization mass spectrometry has long been the benchmark technique especially for the determination of uranium and plutonium isotope ratios in different matrices. Because of a number of serious drawbacks of TIMS [25] – which is restricted to elements with ionization potential >7 eV, TIMS has no multielement capability, requires time-consuming sample preparation steps – the more powerful ICP-MS (inductively coupled plasma mass spectrometry) has developed into a universal and extremely sensitive analytical method for the isotope analysis of long-lived radionuclides and their concentrations for few years now. ICP-MS has been established for the analysis of radionuclides with long half-lives (>10^4 a) at the ultratrace level due to the easy and small number of sample preparation steps.

Other mass spectrometric techniques such as resonance ionization mass spectrometry (RIMS) [26–29] and accelerator mass spectrometry (AMS) [30–32] possess high isotope selectivity for an extreme ultratrace and isotope analysis of, in particular, radiotoxic isotopes (^{14}C, ^{41}Ca, ^{90}Sr, ^{99}Tc, ^{210}Pb, ^{236}U and plutonium isotopes) in the environment, cosmochemistry, radiodating, nutrition and biomedical research. For example, a minimum detectable isotopic ratio for ^{129}I/^{127}I of about 10^{-12} can be achieved by AMS [33]. However, these methods involve complicated and expensive experimental equipment and the analysis, including sample preparation, is time-consuming, too. In contrast to these techniques, ICP-MS is very advantageous due to relatively low costs and high sample throughput, which is especially required for radwaste or environmental control.

ICP-MS is now the most frequently used mass spectrometric technique for fast and relatively inexpensive element determination at the trace and ultratrace concentration levels in very low-radioactive environmental or waste samples and for precise and accurate isotopic analysis [34,35] at very low radioactivity and extremely low nuclide abundances. In addition, ICP-MS allows mostly simple sample introduction in a normal pressure ion source. Nowadays, the analysis of radionuclides with shorter half-lives, such as ^{90}Sr ($T_{1/2} = 29.1$ years), ^{241}Am ($T_{1/2} = 241$ years) and ^{226}Ra ($T_{1/2} = 1600$ years), can also be carried out by ICP-MS with low detection limits [20,36]. In addition, ICP-MS coupled with a laser ablation system (LA) to create LA-ICP-MS opens up the possibility of direct isotope analysis on solid samples, mostly without additional sample preparation steps.

The development of analytical methods using ICP-MS and LA-ICP-MS for the determination of long-lived radionuclides in quite different types of samples is focused especially on the development of microanalytical techniques (in order to avoid possible contamination of instruments and to reduce the dose to the operator) thus improving the detection limits, the precision (relative standard deviation) and accuracy of mass spectrometry for isotope ratio measurements. Detection limits and precision of the developed analytical method are strongly dependent on the ICP mass spectrometer used (quadrupole-based, sector field with single ion collector or ICP-MS with multiple ion collectors), matrix composition and sample preparation steps (separation and enrichment factors). Problems in ICP-MS due to the isobaric interferences of long-lived radioactive nuclides and molecular ions or stable isotopes of other chemical elements can be solved by the application of double-focusing sector field ICP-MS at the required mass resolution, by the application of ICP-MS with collision cell, or by the application of coupling (hyphenated) techniques such as ion chromatography, HPLC and CE with ICP-MS [5,37–40]. Because long-lived radionuclides occur at extremely low concentrations, especially in environmental or medical samples, matrix separation and enrichment of the analytes has been proposed for their analysis by several authors [20,41–43]. Trace/matrix separation, which is performed off-line or on-line, is used more and more frequently for isotope ratio measurements of long-lived radionuclides in order to avoid possible isobaric interferences, matrix effects and to reduce the detection limits. For example, Egorov et al. [44] developed fully automated flow-based equipment for the microwave-assisted treatment of liquid samples for the oxidation (using peroxydisulfate) of reduced technetium species to pertechnetate in the analysis of ^{99}Tc by ICP-MS in nuclear waste samples from the Hanford site.

This review discusses the capability of ICP-MS and LA-ICP-MS with the available type of ICP mass spectrometers for isotope ratio measurements of long-lived radionuclides in quite different application fields.

2. Limits for precision and accuracy of isotope ratio measurements

The precision and accuracy of isotope ratio measurements in ICP-MS and LA-ICP-MS is limited by several effects [45,46]. For example, the mass discrimination effect, which is the result of space charge effects, plays an important role in mass spectrometry. A time-independent discrimination of ions with different mass occurs if the ions – formed in the inductively coupled plasma – leave the skimmer cone, whereby the Coulomb repulsion of positively charged ions results in a loss of transmission through the ion optical lens system. During ion extraction the light ions are deflected more than the heavy ones. Therefore in ICP-MS the measured isotope ratio of lighter to heavier isotope is smaller than the true value [e.g., $^{24}\mathrm{Mg}/^{26}\mathrm{Mg}_{\mathrm{measured}} < {}^{24}\mathrm{Mg}/^{26}\mathrm{Mg}_{\mathrm{true}}$]. In general, mass discrimination depends on the experimental parameters used and decreases with increasing atomic weight of the element investigated. The mass discrimination can be corrected in ICP-MS by the mass discrimination factor—this is the ratio of the true and measured isotope ratio ($R_{\mathrm{true}}/R_{\mathrm{measured}}$) determined using an isotope reference material with the certified isotope ratio [47].

A further source of uncertainty in isotope ratio measurements in ICP-MS is the dead time of the ion detector. Dead time correction of the detector is required if extreme isotope ratios are measured by channel electron multipliers and pulsed counting systems. For counting rates higher than 10^6 cps mostly a lower number of counts are registered than actually occur [48].

Another limitation in ICP-MS is if mass spectrometer with relatively low abundance sensitivity is used for isotope ratio measurements. The abundance sensitivity, which is the contribution of the neighboring peak to the intensity of a measured isotope, influences the accuracy of isotope abundance measurements [49]. For example, the determination of ^{239}Pu or ^{236}U ultratraces in the presence of a high uranium concentration is not possible at low abundance sensitivity of the mass spectrometer [50]. Also ^{90}Sr determination in aqueous solution, bones or urine is difficult in the presence of natural strontium due to peak tailing of ^{88}Sr on $m/z = 90$ [20]. The abundance sensitivity can be improved in sector field ICP-MS using medium mass resolution in comparison to the low-resolution mode [50].

An important limit in isotope ratio measurements is the occurrence of a multitude of different isobaric interfaces with analyte ions such as isobaric atomic or molecular ions. The measurement of ^{238}Pu in solution by ICP-MS is only possible if the Pu concentration is high enough and/or uranium has been careful separated. Isobaric interferences of atomic ions can be separated with a Fourier transform ion cyclotron resonance mass spectrometer (ICP-FT-ICR-MS) equipped, for example, with a 3-T superconducting magnet as described by Barshik et al. [51]. Interfering ions can be selectively removed prior to transfer to the FT-ICR collision cell by ion molecule reaction in an octapole ion guide. Interferences of single-charged with double-charged atomic ions and with molecular ions can often be separated using double-focusing sector field ICP-MS with a maximum mass resolution of 12 000 or by the application of a collision cell in ICP-MS.

Further limits on isotope ratio measurements are the instrumental background, contamination on the solution introduction system, on the sampler and skimmer cone and lens system, mass scale drift effects, plasma instabilities, drifts of ion intensities and matrix effects [45,47].

3. Isotope ratio measurements of long-lived radionuclides using quadrupole-based ICP-MS without and with collision cell

At present, several types of quadrupole-based ICP mass spectrometers with and without collision cell (e.g., from companies such as Perkin Elmer Sciex, Agilent, Thermo Electron, GV Instruments, Varian, etc.) are available on the analytical market. All these mass spectrometers can be used for isotope ratio measurements of long-lived radionuclides in any matrices. In comparison to the commercial double-focusing sector field ICP-MS (ICP-SFMS applied mostly at low-resolution mode) the element sensitivity of quadrupole instruments is lower (the sensitivity, e.g., for uranium measurements by ICP-QMS “Elan 6000” (Perkin Elmer Sciex, Canada) was found to be 70 Mcps/ppm versus 2100 Mcps/ppm ICP-SFMS ELEMENT (Thermo Electron, Bremen) using Meinhard nebulizer in both measurements) [6,52,53] The background signals are higher in ICP-QMS resulting in higher detection limits (e.g., for uranium determination using ICP-QMS Elan 6000 of 350 pg L^{-1} versus 0.3 pg L^{-1} using ICP-SFMS ELEMENT) and lower precision of measured isotope ratios. By the application of a collision cell in ICP-MS (ICP-CC-QMS Platform Micromass) a significant increase in sensitivity in comparison to ICP-QMS without collision cell was observed. For example, for uranium ICP-CC-QMS using Meinhard nebulizer the sensitivity was found to be 1600 Mcps/ppm, but the detection limit at 35 pg L^{-1} was relatively worse (owing to the high background of the Daly detector used). For all three different types of ICP mass spectrometers, the application of ultrasonic nebulization leads to an increase in the sensitivity for uranium by one order of magnitude and an improvement of the detection limit of about one order of magnitude (ICP-QMS, 26 pg L^{-1}; ICP-CC-QMS, 3 pg L^{-1} and ICP-SFMS, 0.07 pg L^{-1}) [52]. The disadvantage of ultrasonic nebulization for analyzing radioactive solutions is the relatively high solution uptake rate of 2 mL min^{-1} (versus 1 mL min^{-1} for the Meinhardt nebulizer) and consequently a greater danger of possible contamination of ICP-MS with radioactive materials. Therefore especially micronebulizers with solution flow rates of 0.1 mL min^{-1} and lower were used to an increasing extent for the introduction of radioactive solution into the ICP source. The performance of different nebulizers in quadrupole-based ICP-MS was discussed in [53]. The precision of isotope ratio measurements depends on the isotope ratio measured and the concentration of analyte. Isotope ratios were measured in quadrupole ICP-MS in a few minutes by a routine method with a precision of 0.1–0.3%. This precision is sufficient, for example, for radioactive waste characterization. In long-term measurements of 1 μg L^{-1} uranium isotope standard solution with $^{235}U/^{238}U \sim 1$ using a microconcentric Micromist nebulizer a precision of 0.05% (R.S.D., relative standard deviation of eight independent measurements in 16 h) was observed [54]. $^{230}Th/^{232}Th$ isotope ratios of 10^{-2}, 10^{-3} and 10^{-4} were determined in ICP-QMS with a precision of 0.17, 0.6 and 2.6% relative standard deviation, respectively. The thorium concentration was 1 μg L^{-1} in these experiments [53].

$^{235}U/^{238}U$ isotope ratios were measured in fish and marine invertebrates from the North Adriatic Sea by ICP-QMS (Elan 5000, Perkin Elmer Sciex) for the investigation of possible contamination from depleted uranium as a consequence of the war operations previously conducted in the area. The $^{235}U/^{238}U$ isotope ratio measurements in shellfish and echinoderm samples gave values very similar to the natural ratio.

Barrero Moreno et al. [38] determined ^{237}Np and plutonium in UO_2 fuel in the presence of high concentrations of uranium by ion chromatography coupled to ICP-MS. A novel sample cleanup procedure (using three analytical chromatographic columns to carry out the lanthanide/actinide speciation) for ^{241}Am determination in environmental samples (soils and sediment core samples from the Irish Sea) using ICP-QMS was described by Perna et al. [39]. The behavior of the columns was studied by coupling the chromatograph to ICP-MS. For the analysis of plutonium and neptunium oxidation state (species analysis) in different aqueous samples capillary electrophoresis (CE) was coupled to ICP-QMS by Kuczewski et al. [40] to study the reduction of Pu(IV) in a humic-acid-containing groundwater at different pH values.

An analytical method for the separation and enrichment of ^{99}Tc from sea water by anion exchange was developed by Eroglu et al. [55]. Using a quadrupole-based ICP-MS (HP 4500, Hewlett-Packard) the detection limit was found to be 0.03 ng L^{-1}.

Joannon and Pin [56] analyzed ^{226}Ra in environmental samples (highly saline thermal waters) by ICP-QMS with ultrasonic nebulization after preconcentration and isolation from the matrix elements by selective extraction using a radium-specific solid phase extraction membrane disk designed for radioactive counting methods. A very low detection limit was achieved in quadrupole ICP-MS when the pressure in the interface was reduced from approx. 2 to 0.85 mbar in these experiments. A selective extraction procedure for preconcentration of ^{226}Ra from uranium ores and biological samples was proposed by Larivière et al. [57]. ICP-QMS with hexapole collision cell was used in order to reduce possible interferences, whereby an absolute detection limit of 0.02 fg (0.75 mBq) for the ^{226}Ra determination was obtained.

An analytical procedure for the determination of ^{79}Se (β-emitter; $T_{1/2} \sim 10^6$ a) in solutions of fission products from nuclear fuel reprocessing after pre-treatment by ion exchange chromatography and ETV-ICP-QMS (Elan 6000) was described by Compte et al. [24]. The method developed using synthetic fission product solutions allows the determination of ^{79}Se in fission product solutions at the sub-mg L^{-1} level after separation of analyte from isobaric interferences due to argon plasma and $^{79}Br^+$. The detection limit for ^{79}Se determination in aqueous solution was 13 ng L^{-1}. An improvement of detection limit for ^{79}Se determination in comparison to, for example, sector field ICP-MS [58] is made possible by the introduction of a collision cell in ICP-QMS, which represents progress in isotope ratio measurements for selected applications. Collision-induced reactions result in a reduction of disturbing isobaric interferences (e.g., $^{79}Br^+$, $^{39}K^{40}Ar^+$, $^{38}Ar^{40}Ar^1H^+$, $^{63}Cu^{16}O^+$ at mass 79). The ^{79}Se determination by ICP-CC-QMS Platform in combination with hydride generation for analyte introduction in ICP [58] and using a H_2/He mixture as collision gas is possible with detection limit at 5 ng L^{-1} level. A precision for $^{79}Se/^{80}Se$ isotope ratio measurement of 0.26% (concentration of Se was 100 μg L^{-1}) by ICP-CC-QMS was obtained [47]. Lower detection limits were also observed in ICP-CC-QMS for ^{236}U and ^{239}Pu with 3 pg L^{-1}. A further improvement in the detection of ^{236}U and ^{239}Pu is limited by isobaric interference with uranium hydride $^{235}U^1H^+$ and $^{238}U^1H^+$, respectively, and by the abundance sensitivity of ICP-MS used. The abundance sensitivity of the mass spectrometer used is restricted by ions with higher kinetic energy so that reducing the kinetic energy of ions from several eV to <0.1 eV by collisions with gas atoms (He, Xe, Ar) or molecules (H_2, O_2, CH_4, NH_3) introduced in a collision cell of ICP-MS leads to improved abundance sensitivity. For example, the collision of analyte ions with He (at a flow rate of 10 mL min^{-1}) in the hexapole collision cell results in a reduction of kinetic energy from several eV down to 1 eV and an improvement of abundance sensitivity lower than 6×10^{-8} was achieved (e.g., for $^{236}U/^{238}U$ ratio) in quadrupole ICP-MS (Platform) with a hexapole collision cell [49]. In comparison to ICP-CC-QMS, the abundance sensitivity for $^{236}U/^{238}U$ was observed in ICP-QMS (Elan 6000), ICP-SFMS (ELEMENT) and MC-ICP-MS (Nu Plasma) as 6×10^{-7}, 5×10^{-6} and 3×10^{-7}, respectively. Collision-induced processes and reaction chemistry in a gas-filled collision or reaction cell for resolving interference problems in ICP-MS were reviewed by Tanner et al. [59]. ICP-MS with a band-pass reaction cell using different reaction gases (ethylene, carbon dioxide and nitride oxide) were studied by Tanner et al. [60] to suppress disturbing interferences for plutonium and americium analysis. An efficient reaction of U^+ and UH^+ with CO_2 (and non-reaction with Pu^+) allows the sub-ppt determination of ^{239}Pu, ^{240}Pu and ^{242}Pu (single ppt for ^{238}Pu) in the presence of seven orders of magnitude excess uranium matrix without prior chemical separation [60].

For ^{129}I determination at the ultratrace level in contaminated soils and waters the ICP-CC-QMS is advantageous for solving the high background problem caused by xenon impurities in Ar plasma (isobaric interference of $^{129}Xe^+$). Using a He and H_2 mixture as the collision gases in ICP-MS with a hexapole collision cell an efficient reduction of the disturbing background intensity of $^{129}Xe^+$ ions was found [47]. Furthermore, an improved abundance ratio sensitivity of ICP-CC-QMS was required [61], which is relevant for $^{129}I/^{127}I$ measurements because of the $m/z = 129$ a peak tailing of iodine from $m/z = 127$.

Izmer et al. [8] determined ^{129}I in contaminated soil samples by hot extraction in an oven (at 1000 °C with oxygen) coupled online to ICP-CC-QMS with detection limits of 30 pg g^{-1}. Oxygen was further used as the reaction gas for eliminating isobaric interference with $^{129}Xe^+$. By using a cooling finger for the collection of iodine between the oven for the hot online extraction of volatile analyte iodine and ICP an improvement of the detection limit for ^{129}I analysis in sediments (without any additional sample preparation) down to 0.4 pg g^{-1} was found. $^{129}I/^{127}I$ isotope ratios were measured in two sediments with 2.1×10^{-6} (R.S.D. = 9%) and 6.9×10^{-6} (R.S.D. = 7.6%), respectively [62].

4. Isotope ratio measurements of long-lived radionuclides using sector field ICP-MS with single ion collector

The high element sensitivity of double-focusing sector field ICP-MS (at low mass resolution) permits ultratrace analysis down to the sub-fg mL^{-1} concentration range (without preconcentration) and precise and accurate isotope ratio measurements in aqueous solution [1,6,47,63,64]. For the characterization of small volumes of radioactive solution, micronebulizers (Aridus, CETAC Technologies, MicroMist from Glass Expansion; or DIHEN—Direct Injection High Efficiency Nebulizer, Meinhard) were used for solution introduction in ICP [6,35]. Accurate results were obtained for uranium isotope analysis in ICP-SFMS using a desolvating microconcentric nebulizer system (Aridus) with a minimum hydride formation rate (UH^+/U^+) of 9×10^{-7}. A limit for $^{236}U/^{238}U$ isotopic ratio measurements of 3×10^{-7} in ICP-SFMS was observed. The comparison of uranium isotope analysis measurements in environmental samples using sector field ICP-MS with single collector and multiple collector ICP-MS (MC-ICP-MS) results in a good agreement of isotope ratios [65]. In order to characterize the DIHEN in ICP-SFMS for radionuclide analysis the sensitivity for ^{238}U, ^{239}Pu (in aqueous solution) was studied under hot plasma conditions (rf power, 1200 W; nebulizer gas flow rate, 0.21 mL min^{-1}) and ^{90}Sr under cold plasma conditions in order to avoid $^{90}Zr^+$ interference (rf power, 750 W; nebulizer gas flow rate, 0.35 mL min^{-1}) as a function of solution uptake rate (see Fig. 1). Maximum ion intensity for $^{238}U^+$ and $^{239}Pu^+$ was observed at 60 μL min^{-1}. This behavior of $^{238}U^+$ sensitivity for a solution uptake rate from 10 to 60 μL min^{-1} is in agreement with measurements by McLean et al. [35] using the DIHEN for solution introduction in ICP-SFMS. In contrast, for ^{90}Sr measurement at cold plasma condition significant lower sensitivity and a small increasing of sensitivity with increasing solution uptake rate was observed. The limits of detection of long-lived radionuclides in MilliQ water using DIHEN in ICP-SFMS are mostly in the sub-pg L^{-1} range except for ^{238}U due to a possible contamination in the solution introduction system and for ^{90}Sr determination because the measurements were performed under cold plasma conditions in order to avoid the isobaric interference with $^{90}Zr^+$ ions (see Table 1). The limits of detection measured by ICP-SFMS at low mass resolution increased at medium mass res-

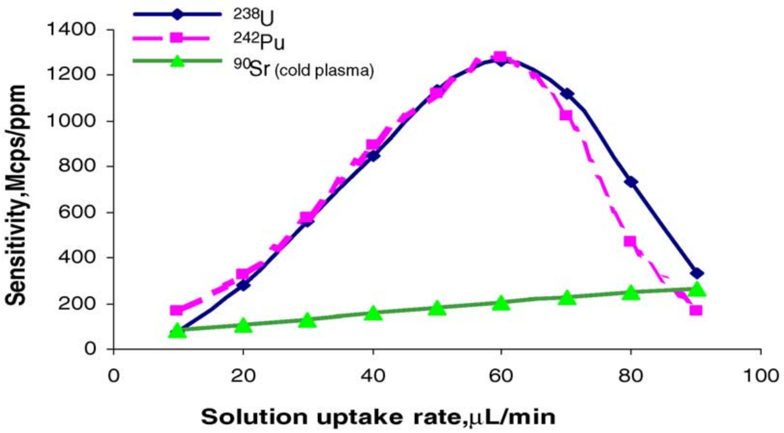

Fig. 1. Dependence of sensitivity for $^{238}U^+$, $^{242}Pu^+$ and $^{90}Sr^+$ on solution uptake rate using DIHEN in ICP-SFMS. Parameters hot plasma: rf power, 1200 W; nebulizer flow gas rate, 0.21 mL/min; cold plasma: rf power, 750 W; nebulizer flow gas rate, 0.35 mL/min.

Table 1
Limit of detections of long-lived radionuclides in MilliQ water using DIHEN in ICP-SFMS (solution uptake rate: 60 μL/min)

Isotopes	LOD (pg L^{-1})	Absolute sensitivity (counts fg^{-1})
^{90}Sr	35.4[a]	206[a]
^{234}U	0.46 (1.2)[b]	1360
^{235}U	1.5	
^{236}U	0.3	
^{238}U	97	
^{239}Pu	0.43	1282
^{242}Pu	0.9 (77)[b]	

[a] Cold plasma conditions (in order to avoid $^{90}Zr^{+}$ interference).
[b] Medium mass resolution [66].

Table 2
Precision and accuracy of DIHEN-ICP-SFMS measuring uranium isotope standard solutions NIST U005, U350, U930 and U(nat) (U_{conc} = 0.1 ppb, $n = 6$)

	Isotope ratios		Precision (R.S.D., %)	Accuracy (%)
	Measured	Certified		
U005				
$^{235}U/^{238}U$	0.0049435	0.0049194	1.4	0.5
$^{234}U/^{238}U$	0.0000218	0.0000219	1.8	−0.12
$^{236}U/^{238}U$	0.0000472	0.0000468	4.3	0.9
U350				
$^{235}U/^{238}U$	0.540114	0.546488	1.6	−1.2
$^{234}U/^{238}U$	0.003863	0.003879	3.2	−0.41
$^{236}U/^{238}U$	0.002644	0.002598	1.3	1.8
U930				
$^{235}U/^{238}U$	17.3472	17.3487	2.0	−0.01
$^{234}U/^{238}U$	0.2005	0.2010	1.9	−0.23
$^{236}U/^{238}U$	0.03783	0.03768	2.8	0.4
U(nat)				
$^{235}U/^{238}U$	0.007227	0.007253	1.1	−0.3
$^{234}U/^{238}U$	0.000054	0.000055	0.1	−0.52

olution as demonstrated for ^{242}Pu and ^{234}U [66]. Fig. 2 shows the results of isotope ratio measurements on uranium isotope standard reference material with natural isotope composition by DIHEN-ICP-SFMS ($n = 10$). The $^{235}U/^{238}U$ isotope ratio was found to be 0.007227 ± 0.00008 (R.S.D., 1.1%). The precision and accuracy of DIHEN-ICP-SFMS measured on NIST U005, U350, U930 isotope standard reference materials and U(nat) (U_{conc} = 100 ng L^{-1}, $n = 6$) are summarized in Table 2. The accuracy of isotope ratios measured by DIHEN-ICP-SFMS is mostly better than 1% [66]. This experimental arrangement, which is advantageous for the characterization of small volumes of radioactive waste solutions with respect to isotope composition, can be improved by applying the flow injection technique [67].

Of similar interest is the determination of ^{90}Sr ($T_{1/2} = 29.1$ years) at ultratrace concentration since ^{90}Sr appears as a radionuclide in the decay series of nuclear fission and can therefore be found in nuclear waste or may be released by nuclear accidents. Current methods for the detection of this radionuclide are time-consuming and may be prone to a large variety of interferents. Vonderheide et al. [20] applied ICP-SFMS for sensitive ^{90}Sr determination in the presence of stable zirconium in urine, which leads to an isobaric interference with ^{90}Zr isotope. Specific techniques such as measurements under cold plasma conditions are investigated to remove the isobaric interference caused by the formation of $^{90}Zr^{+}$ ions. As a result of these studies ICP-SFMS at medium mass resolution allows ^{90}Sr to be measured under cold plasma conditions (optimum rf power: 750 W) at the ultratrace level. In addition to reducing $^{90}Zr^{+}$ ion formation also other potential interferences (such as $^{38}Ar^{40}Ar^{12}C^{+}$, $^{58}Ni^{16}O_2^{+}$ or $^{60}Ni^{16}O^{14}N^{+}$) were minimized and the detection limit for ^{90}Sr analysis was measured under optimized conditions by ICP-SFMS as 3 pg L^{-1} for water samples. For urine samples, this mass spectrometric method was combined with an extraction step of Sr from matrix using a crown ether extraction resin and Sr was concentrated (enrichment factor: 200). The limiting factor of ^{90}Sr determination is the high levels of strontium with natural isotopic composition in the separated fraction (of about 1 μg mL^{-1}), which leads to higher detection limits (80 pg L^{-1}) due to $^{88}Sr^{+}$ peak tailing at $m/z = 90$. If an ICP-SFMS at low mass resolution and at low abundance sensitivity is used. The abundance sensitivity of ICP-SFMS at medium mass resolution was measured for ^{90}Sr measurements as 6×10^{-7}. This detection limit in separated fractions corresponds to the detection limit of 0.4 pg L^{-1} in the original urine sample. The recovery of ^{90}Sr, determined by the analytical method in spiked urine samples, was in the range

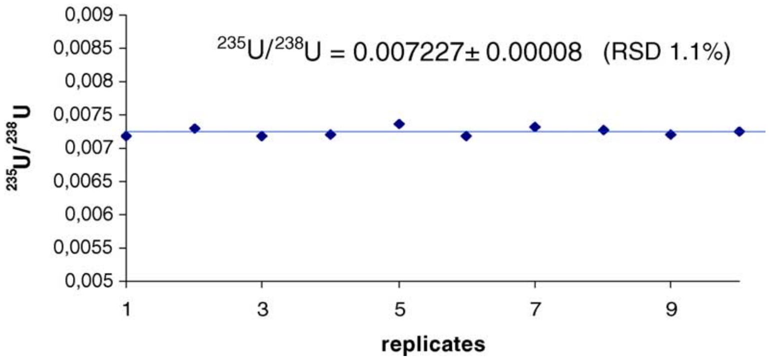

Fig. 2. Stability of DIHEN-ICP-SFMS for $^{235}U/^{238}U$ isotope ratio measurements (U_{conc} = 0.1 ng mL^{-1}, natural isotopic composition).

of 82–86%. The abundance sensitivity can be improved using MC-ICP-MS Neptune up to 2×10^{-10}, which results in an improved detection limit for ^{90}Sr measurements by more than one order of magnitude. Similar analytical methods for ^{90}Sr determination at ultratrace level can be applied to the analysis of other body fluids, such as blood or human milk or in addition of bones, foods, environmental, nuclear and radioactive waste samples.

A sensitive analytical procedure based on nanovolume flow injection (FI) and ICP-SFMS was developed for the isotope analysis of uranium and plutonium at the ultratrace concentration level. Using a nanovolume nebulizer, a 54-nL sample was injected into a continuous flow of carrier liquid solution at 7 μL min^{-1} prior to ICP-SFMS [67]. The absolute detection limits were 9.1×10^{-17} g (3.8×10^{-19} mol, ∼230 000 ^{238}U atoms) and 1.5×10^{-17} g (6×10^{-20} mol, ∼38 000 ^{242}Pu atoms) for uranium and plutonium, respectively. The method was validated for determining the uranium isotope ratios by the analysis of 100 pg mL^{-1} solutions of a certified isotope reference material (NIST U350) and applied to the determination of the ^{235}U/^{238}U isotope ratio in a urine sample at sub-ppb level. The precision of isotope ratio measurements increased with decreasing isotope ratio. The most accurate isotope ratio (R.S.D. of 0.7%, $n = 10$) was measured for ^{235}U/^{238}U in NIST 350. The precision of the measurements of uranium isotope ratios via transient signals (54 nL solution volume) in the NIST U350 material was in the low % range. Furthermore, flow injection was used to analyze contaminated urine samples. In order to avoid clogging of the nebulizer, the urine sample was microwave-digested. Owing to a very small injection volume (54 nL) in the FI mode matrix effects were minimized allowing preconcentration by evaporation. The ^{235}U/^{238}U isotope ratio obtained of 0.037 ± 0.005 demonstrated a contaminated urine sample with enriched uranium [67].

Recently, an improved analytical procedure for the ultrasensitive determination of ^{236}U or ^{239}Pu was developed in our laboratory. The main factors affecting the accurate and precise determination of ^{236}U using ICP-MS are instrumental background, the isobaric interference of ^{235}UH$^+$ molecular ion on ^{236}U$^+$ analyte ions, and the presence of ^{238}U$^+$ and ^{235}U$^+$ peak tails. In order to reduce ^{235}UH$^+$ formation, D_2O (heavy water) is used as a solvent for the dissolution and dilution of uranium samples [50]. Abundance sensitivity was improved by the use of medium mass resolution ($m/\Delta m = 4450$) in comparison to low mass resolution in double-focusing sector field ICP-MS. For solution introduction the performances of several different sample introduction systems (Aridus, Meinhard nebulizer and ultrasonic nebulizer) were studied with respect to improving ^{236}U/^{238}U isotope ratio measurements. It has been shown that for all nebulization systems, a decrease in UH$^+$/U$^+$ is observed in D_2O in comparison to H_2O as the solvent [50].

^{236}U radionuclides (produced in nuclear reactors) can be monitored as radioactive tracers for nuclear fallout in the environment. Therefore, ^{236}U/^{238}U isotope ratio measurements are of interest for the characterization of hot particles which were found in soils contaminated by Chernobyl fallout. Hot particles were characterized by ICP-SFMS with respect to uranium isotope ratios by Entwistle et al. [68] and Boulyga and Becker [69]. ^{236}U/^{238}U isotope ratios in the range from 10^{-5} to 10^{-3} were found [69].

As demonstrated in several papers [34,36,70], also the analysis of plutonium isotopic composition is useful in “fingerprinting” studies, which attempt to distinguish between Chernobyl Pu and other sources such as global nuclear fallout.

An analytical method for ^{237}Np, ^{239}Pu and ^{240}Pu determination in contaminated soils, sediments and biological samples has been developed using ICP-SFMS in combination with an automated sequential injection (SI) separation system by Kim et al. [71]. The purification of actinides was carried out using extraction chromatography (TEVA resin) in an automated SI system. Detection limits in the low fg mL^{-1} range were obtained for ^{237}Np (2.5 fg mL^{-1}), ^{239}Pu (2.1 fg mL^{-1}) and ^{240}Pu (0.42 fg mL^{-1}).

Nygren et al. [72] proposed an optimized sample preparation procedure for the determination of ^{240}Pu/^{239}Pu isotope ratios at ultratrace level in soils (IAEA Soil 6) and sediment reference materials (IAEA 300 and IAEA 135) with ICP-SFMS. Samples were digested by lithium borate fusion and acid leaching. Pu was separated by an extraction chromatographic resin such as TEVA resin or a combination of UTEVA and TRU followed by elution with 0.1% HEDPA. To avoid interference problems the medium mass resolution in ICP-SFMS was applied. Sector field ICP-MS with a single ion collector (VG Axiom) was used for Pu isotope analysis after a chemical separation in environmental samples by Agarande et al. [73]. The ^{240}Pu/^{239}Pu isotope ratio in different environmental samples (aquatic moss, semi-aquatic plant, soil and sediment) collected in France varies between 0.19 and 0.26 depending on the contamination source.

Muramatsu et al. [14] described the determination of Pu isotope ratios in Japanese soils by ICP-SFMS. ^{240}Pu/^{239}Pu isotope ratios observed in soils were usually between 0.17 and 0.19, except for ^{240}Pu/^{239}Pu = 0.37 found in the Nagasaki area. The $^{239+240}$Pu activity profile is determined by ICP-SFMS for a sediment core collected from a depth of 170 m in Loch Ness, Scotland, UK, for the rapid determination of the chronology of post-1950 sediments by Ketterer et al. [74]. The ^{240}Pu/^{239}Pu isotope ratios measured in the range of 0.15–0.20 are in agreement with the expected range of 0.166–0.194 for northern hemisphere fallout and do not suggest the presence of other contamination sources.

ICP-MS is increasingly being applied especially for the precise and accurate determination of ^{235}U/^{238}U isotope ratios at the trace and ultratrace level in medical samples (especially in body fluids) in order to demonstrate possible contamination with uranium. Of the various body fluids urine is the most frequently investigated medical matrix [20,22,75–81] because samples for evidence of possible contamination with long-lived radionuclides can be easily collected and only a short analysis time by ICP-MS is neces-

Table 3
Application of ICP-MS in isotope analysis of long-lived radionuclides in nuclear materials and radioactive waste

Samples	Method	Radionuclides	Detection limits/isotope ratio	References
UO_2 fuel	ICP-QMS, Elan 5000 ion chromatography isotope dilution	^{238}U, ^{237}Np, ^{239}Pu	0.06 μg L^{-1} (^{237}Np)	[83]
Fission product solution	ETV-ICP-MS	^{79}Se	13 ng L^{-1}	[24]
Radioactive waste solution	ICP-SFMS ELEMENT (USN)	^{226}Ra, ^{230}Th, ^{233}U, ^{237}Np, ^{239}Pu, ^{241}Am	0.05 pg L^{-1} (^{241}Am), 0.04 pg L^{-1} (^{239}Pu), $^{236}U/^{238}U \sim 0.02$ (flow injection)	[6]
Radioactive waste solution	ICP-SFMS ELEMENT (DIHEN)	^{226}Ra, ^{230}Th, ^{230}Th, ^{233}U, ^{237}Np, ^{238}U, ^{241}Am	0.1 pg L^{-1} (^{241}Am), 0.1 pg L^{-1} (^{237}Np), $^{236}U/^{238}U \sim 0.00002–0.0001$	[35]
Spent uranium in soils (Chernobyl)	ICP-SFMS ELEMENT (Aridus) ion exchange	^{236}U, ^{239}Pu	0.2 pg L^{-1} (solution), 0.04 pg g^{-1} (soil), $^{236}U/^{238}U \sim 0.000056–0.00098$	[3]

sary. Sector field ICP-MS is used daily in our laboratory for sensitive and precise isotope ratio measurements of uranium at the ultratrace level in urine samples in a routine mode. An analytical procedure for the rapid determination of both long-lived radionuclides (Th and U) in urine samples was proposed in [22], where different sample preparation and quantification procedures (e.g., isotope dilution) were studied. In order to avoid matrix effects during the mass spectrometric measurements and clogging effects on the nickel cones and torch the urine samples were digested in a mixture of nitric acid, hydrogen peroxide and hydrogen fluoride by closed-vessel microwave digestion. Because no certified standard reference material (SRM) exists laboratory standards were prepared in order to check the accuracy of the analytical method [22]. The detection limits for the determination of uranium and thorium in urine samples using double-focusing sector field ICP-MS were determined down to sub-ng g^{-1}.

Validation procedures for uranium isotope ratio measurements in human urine samples using ICP-MS were also discussed in other laboratories [23,80]. Bleise et al. [82] reported on the properties, use and health effects of depleted uranium.

Besides uranium analysis, Pu isotope analysis in urine at the ultratrace level is attracting increasing interest in order to detect possible contamination and the origin of plutonium. We have developed an analytical method using ICP-SFMS for Pu isotope analysis at the low attogram per milliliter concentration level with the aid of tracer experiments [79]. One liter of urine was doped with pg ^{242}Pu. The Pu was separated by co-precipitation with $Ca_3(PO_4)_2$ followed by extraction chromatography on TEVA resin in order to enrich the Pu and remove uranium and matrix elements. The capability of double-focusing ICP-SFMS for Pu isotope analysis was studied using two nebulizers, PFA-100 and DIHEN for solution introduction with uptake rates of 0.06 and 0.58 mL min^{-1}, respectively. The sensitivity for Pu in ICP-SFMS was found to be 2000 and 1380 Mcps ppm^{-1} for the PFA-100 and DIHEN nebulizers, respectively. Due to the low solution uptake rate of DIHEN the absolute sensitivity was about seven times better and yielded 1380 counts fg^{-1} in comparison to 207 counts fg^{-1} measured with the PFA-100 nebulizer. Recovery using ^{242}Pu tracer was about 70%. The limits of detection (LOD) for ^{239}Pu in 1 L of urine, based on an enrichment factor of 100 for the PFA-100 nebulizer and 1000 for DIHEN, were 9 and 1.02 fg L^{-1} (1 fg L^{-1} = 10^{-18} g g^{-1}), respectively.

Measurements of $^{240}Pu/^{239}Pu$ isotopic ratio at the ultratrace level in synthetically prepared urine standard solution yielded a precision of 1.8 and 1.9% and accuracy of 1.5 and 1.8% for the PFA-100 and DIHEN nebulizers, respectively [79].

Recently, Evans et al. [83] developed a rapid and accurate method for the determination of plutonium in food using double-focusing ICP-SFMS with an ultrasonic nebulizer with desolvation unit (Cetac USN 6000) and ion chromatography. This method can also be used for precise and accurate $^{240}Pu/^{239}Pu$ isotope ratio measurements. The samples were prepared by HNO_3 closed-vessel microwave digestion, evaporated to dryness and diluted into a mobile phase (1.5 M HNO_3 and 0.1 mM 2,6-pyridinedicarboxylic acid). By online separation using a polystyrene-divinylbenzene ion chromatography column ^{239}Pu and ^{238}U were separated in order to reduce the $^{238}U^1H^+$ interference. A further reduction of $^{238}U^1H^+$ interference was achieved by applying an ultrasonic nebulizer (USN). The detection level for Pu of 0.020 pg g^{-1} (4.6×10^{-2} Bq kg^{-1}) is significantly below 1/10th of the European Union legislation for baby food (1 Bq kg^{-1} = 0.436 pg g^{-1}).

Several applications of ICP-MS in the isotope analysis of long-lived radionuclides in nuclear and radioactive waste materials, and biological, geological, environmental and medical samples are summarized in Tables 3 and 4, respectively.

5. Multiple collector ICP-MS for isotope ratio measurements of long-lived radionuclides

Using multiple ion collector ICP-MS in comparison to sector field ICP-MS with single ion collector, the precision of isotope ratio measurements was improved by one order of mag-

Table 4
Application of ICP-MS in isotope analysis of long-lived radionuclides in biological, geological, medical and environmental samples

Samples	Method	Radionuclides	Detection limits/isotope ratio	References
Soils	ICP-SFMS (VG Axiom) after separation	^{239}Pu, ^{240}Pu, ^{241}Pu	^{240}Pu/^{239}Pu ∼ 0.18–0.35, ^{241}Pu/^{239}Pu ∼ 0.003–0.004	[39]
Urine	ICP-SFMS (ELEMENT) after separation (1 L urine)	^{239}Pu, ^{240}Pu	1×10^{-18} g mL^{-1}, ^{240}Pu/^{239}Pu ∼ 0.14 (synth. sample)	[79]
Urine	ICP-SFMS (ELEMENT), ICP-CC-MS (Platform)	^{90}Sr	0.4 fg mL^{-1} (ELEMENT), 2 pg mL^{-1} (Platform)	[20]
Soils and sediments	ICP-SFMS (ELEMENT)	^{239}Pu, ^{240}Pu	^{240}Pu/^{239}Pu ∼ 0.18–0.2	[72]
Thermal water	ICP-QMS + USN (PlasmaQuad PQ2) extraction, ion exchange	^{226}Ra	2 fg g^{-1}	[56]
Food	ICP-SFMS + USN (ELEMENT), ion extraction	Pu	0.03 pg g^{-1}	[83]
Sediments	ICP-CC-MS (Platform), hot extraction	^{129}I	0.4 pg g^{-1}, ^{129}I/^{127}I ∼ 5×10^{-7}	[62]
Sea water	ICP-SFMS (ELEMENT), MC-ICP-MS (NuPlasma) after separation	^{239}Pu, ^{240}Pu (in 100 L sea water)	≈10^{-19} g mL^{-1} (ELEMENT), ≈10^{-20} g mL^{-1} (NuPlasma), ^{240}Pu/^{239}Pu ∼ 0.17	[13]
Moss, plant, soil, sediment	ICP-SFMS (VG Axiom) after separation	^{239}Pu, ^{240}Pu,	^{240}Pu/^{239}Pu ∼ 0.19–0.26	[73]

nitude. Thorium and uranium isotope ratios in geological materials at low-concentration (<0.1 μg g^{-1}) were determined by Turner et al. [18] with MC-ICP-MS (“Nu Plasma” from Nu Instruments using an Aridus microconcentric nebulizer with desolvator). Isotope ratio measurements of ^{230}Th/^{230}Th equal to 6×10^{-6} (at Th concentration of 5 μg L^{-1}) were performed with a precision of 1.1% (R.S.D.).

For example, Taylor et al. [84] described the plutonium isotope ratio measurements at ultratrace level by MC-ICP-MS using multiple ion counting. The ^{240}Pu/^{239}Pu isotope ratio can be reproduced to better than 3% with less than 120 fg of Pu. Quétel et al. [85] compared the precision of ^{233}U/^{238}U solutions for different isotope ratios (from 1 down to about 10^{-3}) using the sector field ICP-MS with single and multi-ion collectors in comparison to quadrupole ICP-MS. As expected, using the MC-ICP-MS (Nu Plasma) the best precision of isotope ratio measurements was achieved at a relative high concentration of analyte of 1 mg L^{-1} in aqueous solution, whereas the uranium concentration in ICP-SFMS and ICP-QMS was 1 and 10 μg L^{-1}, respectively.

Most applications of isotope ratio measurements by MC-ICP-MS focus on the study of isotope variation in nature and on geological applications, especially geochronology. The physical method of geochronology as an essential field in the earth sciences, which would not have been possible without mass spectrometry, is based on isotope ratio measurements, i.e., age dating using the following radioactive decay: ^{87}Rb → ^{87}Sr, ^{147}Sm → ^{143}Nd, U/Th → Pb, ^{187}Re → ^{187}Os, ^{176}Lu → ^{176}Hf. Textbooks on isotope ratio measurements, including several applications in age dating by MC-ICP-MS, have been published by Platzner [25] and De Leater [86]. Accurate and reproducible U and Th isotope data for carbonate geochronology using very small sample sizes (0.05–0.34 ng of Th measured by MC-ICP-MS compared with 0.3–1.4 ng Th for TIMS to obtain comparable precision) were presented by Seth et al. [87]. Pietruska et al. [88] discussed an analytical technique for the measurement of ^{226}Ra–^{230}Th–^{238}U disequilibria in volcanic rocks using MC-ICP-MS. MC-ICP-MS, which is much less time-consuming than TIMS, also yielded a better precision (2–3 times) for ^{232}Th/^{230}Th isotope ratios.

Small isotope variations of uranium in nature in the Sea of Galilee and the Sahina spring were described in [47]. For the ^{234}U/^{238}U isotope ratio, a significant enrichment by factor 1.5 was found in comparison to the IUPAC table value of the isotopic composition of elements [89] by ICP-SFMS with a single ion collector (Element) and multiple collector system (Nu Plasma). MC-ICP-MS yielded more precise isotope ratio measurements by factor 3–5. The reason for the variation of ^{234}U/^{238}U in natural water samples from the Sea of Galilee (enrichment in ^{234}U abundance can be explained as a result of the α decay of ^{238}U) ($T_{1/2} = 4450$ Ma) via short-lived ^{234}Th and ^{234}Pa nuclides (due to β^- decay with $t_{1/2}$ of 2.4 days and 6.7 h, respectively) in ^{234}U ($T_{1/2} = 0.245$ Ma). The leaching of ^{234}Th and ^{234}Pa in an aquatic environment leads to ^{234}U enrichment in water. Also the Sahina spring shows a significant enrichment of 16% in comparison to the ^{234}U/^{238}U isotope ratio from the IUPAC table of 5.54×10^{-5}. An analytical method for the determination of Pu isotope ratios (after separation on TEVA resin and enrichment of Pu) at the 3.6×10^{-19} g mL^{-1} concentration level in the Sea of Galilee is described in [13]. The measured ^{240}Pu/^{239}Pu isotope ratio using an MC-ICP-MS (Nu Instruments) of 0.17 is evidence for plutonium contamination as a result of global nuclear fallout after the weapons tests in the 1960s. The detection limits for Pu measurement by MC-ICP-MS was 3×10^{-20} g mL^{-1}.

Ketterer et al. [90] analyzed Polish forest soils with respect to ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu isotope ratios by double-focusing sector ICP-MS (Axiom MC-ICP-MS), operated in the single collector (electron multiplier) mode and showed clear evidence of non-global fallout $^{239+240}$Pu originating from the 1986 Chernobyl disaster. The isotopic composition of plutonium in Polish soils is described by two-component mixing between global fallout and Chernobyl emissions.

Identification of the contamination sources of groundwater samples at the Hanford Site in Washington was performed via high precision uranium isotope ratio measurements by MC-ICP-MS (IsoProbe, Micromass) [91].

Regelous et al. [92] reported on the application of the isotope dilution technique (using ^{233}Pa spike with a half-life of 26.97 days) for the measurement of a femtogram of protactinium (^{231}Pa half-life: 32 760 years) in silicate rock samples after chemical separation of actinide from rock matrix by MC-ICP-MS (Neptune, Thermo Electron, Bremen—equipped with nine Faraday detectors, one secondary electron multiplier and a retarding potential quadrupole for high abundance sensitivity measurements). ^{231}Pa/^{233}Pa isotope ratios can be measured with a precision of 0.5%, and a reproducibility (for rock samples) of 1.2% on as little as 20 fg of Pa. Further reductions in sample size and analysis time could be achieved by using multiple ion counting to measure the 231 and 233 ion beams simultaneously. Detection limits could be decreased to 200 ag mL^{-1}.

MC-ICP-MS (Nu Instruments) was used for the simultaneous collection of ^{226}Ra and ^{228}Ra (isotope spike) for the determination of ^{226}Ra in the Ross Sea via the isotope dilution technique [93]. The ^{226}Ra concentration ranges from 0.36 to 0.42 fmol kg^{-1}.

A method for the measurement of isotope ratios on various transient signals (with a time duration of 30–60 s) by coupling high performance liquid chromatography to the MC-ICP-MS (NEPTUNE, Thermo Electron, Bremen) using a flow injection device for solution introduction was proposed by Gunther-Leopold et al. [94].

6. Laser ablation inductively coupled plasma mass spectrometry

LA-ICP-MS as a sensitive mass spectrometric technique has been used for the direct sample introduction of solid samples in ICP-MS [95]. To an increasing extent, LA-ICP-MS is the method of choice for the direct analysis of solid samples with respect to the analysis of long-lived radionuclides. This powerful analytical technique uses the evaporation of sample material by a focused laser beam (mostly using a Nd-YAG laser with $\lambda/4 = 266$ nm) in an inert gas atmosphere (e.g., Ar) under normal pressure and the postionization of evaporated and ablated material in an inductively coupled plasma of the ion source of an ICP-MS. The majority of commercial laser ablation systems (e.g., LSX-200 or LSX-500, CETAC, USA and LUV 266, Merchantek, USA) are coupled to quadrupole analyzers. Most applications of LA-ICP-MS are described with respect to the analysis of the naturally occurring radioactive elements U and Th in geological and environmental samples.

LA-ICP-MS was also applied for screening of soils for residual depleted uranium using a quadrupole-based instrument (PQ ExCell, Thermo Elemental, Franklin, MA) coupled to a UP 266 laser ablation system (New Wave/Merchantek, Fremont, CA) by Seltzer [96]. An ultrasonic nebulizer with desolvator was used to generate a thallium-containing aerosol for an independent internal standardization to consider the mass discrimination effect by isotope ratio measurements of uranium and possible plasma instabilities, mass scale drift effects, etc. Differentiation between depleted uranium, an anthropogenic contaminant, and naturally occurring uranium was accomplished on the basis of uranium isotope analysis. ^{235}U/^{238}U isotope ratios measured for field samples were in good agreement with those derived from gamma spectrometry measurements.

Several applications of laser ablation inductively coupled plasma mass spectrometry concern the isotope analysis of long-lived radionuclides in radioactive filters, reactor graphite or silt samples [97]. For example, ^{234}U/^{238}U isotope ratio down to 6.7×10^{-5} can be determined in radioactive reactor graphite with a good precision (R.S.D., 1.1%). The ^{236}U/^{238}U isotope ratio of 10^{-4} was determined with a precision of 0.7%. Results of isotope ratio measurements of Th and U in different radioactive waste materials by LA-ICP-MS are comparable to measurements using ICP-SFMS after separation of analyte, even if no isobaric interferences of atomic ions of analyte and molecular ions were observed.

In our laboratory, Pu isotope ratios and americium were determined in moss samples – collected from the eastern Italian Alps (1500 m a.s.l.) – by LA-ICP-MS as described in [10]. The frozen samples were cut into 1–2 cm sections and analyzed separately to obtain the distribution curves of vertical concentrations. Estimated limits of quantification of LA-ICP-MS for actinide radionuclides deposited on stainless steel plates after chemical separation are at the 10^{-15} g g^{-1} concentration level. The ^{240}Pu/^{239}Pu isotope ratio was almost constant within experimental errors for all samples analyzed with a weighted average value of 0.212 ± 0.003. The probable Pu contamination source was global fallout after nuclear weapons tests in the 1960s.

Borisov et al. [98] described methodological developments for the characterization of PuO$_2$ materials disposed of by immobilization in glass or ceramic form. The sample preparation discussed by pressing of pellets with and without binder can be applied for isotope ratio measurements of Pu.

In order to detect contamination of uranium und thorium in urine by isotope ratio measurements, ICP-MS after digestion or dilution only is the method of the choice. For the analysis of small dried urine samples (in forensic science) or to reduce the contamination problem during sample preparation an analytical method using LA-ICP-MS was developed in our laboratory for sensitive ^{235}U/^{238}U isotope ratio measurements on urine samples after deposition on a quartz substrate [21]. After careful homogenization, the dried urine samples were analyzed directly by LA-ICP-MS without any time-consuming digestion procedure. For study of the figures of merit of the analytical methods developed, matrix-matched synthetic laboratory standards doped with ^{230}Th (IRMM 60), uranium

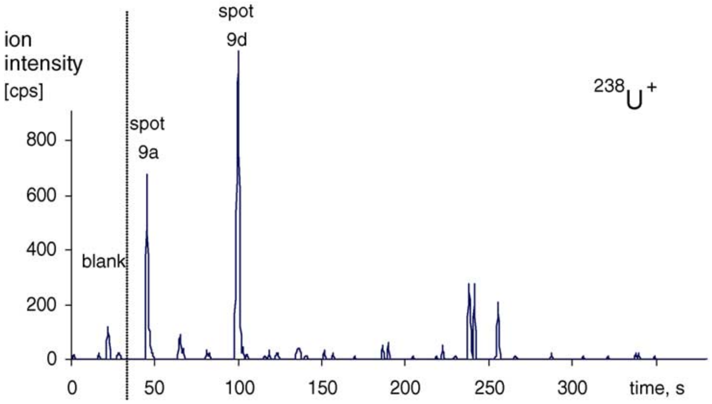

Fig. 3. Transient signals of $^{238}U^+$ in protein spots 9a and 9d from a human brain sample.

with natural isotope composition ($^{235}U/^{238}U = 0.00725$) and uranium isotope standard reference material (NIST U930) at low pg mL^{-1} level were prepared (recovery for thorium and uranium concentration varied between 91 and 100%). The analytical technique developed was applied for $^{235}U/^{238}U$ isotopic ratio measurements in urine samples, whereby possible contamination with depleted or enriched uranium was detected.

Recently, a direct method for determining Pu in soils and sediment samples was proposed by Boulyga et al. [99] using a modified laser ablation system providing a high ablation rate (LINA-Spark Atomizer system) coupled to double-focusing sector field ICP-MS. In order to minimize uranium hydride formation and peak tailing of $^{238}U^+$ on $m/z = 239$, LA-ICP-MS measurements were performed under optimized conditions at a mass medium resolution of the mass spectrometer. Isotope ratios of $^{240}Pu/^{239}Pu \sim 0.4$ were measured in contaminated Chernobyl soil samples, the detection limit for direct Pu determination was 3×10^{-13} g g^{-1}. For determination of Pu concentration in soil samples the authors applied the isotope dilution technique.

Recent developments in LA-ICP-MS at our laboratory focus on the application of LA-ICP-MS in protein research in order to identify metal-containing protein spots [100]. Protein spots separated by two-dimensional gel electrophoresis were fast screened by microlocal analysis using LA-ICP-MS with respect to uranium. Fig. 3 shows transient signals of $^{238}U^+$ from a human brain sample, whereby uranium was detected with high intensity e.g., in protein spots 9a and 9d. $^{235}U/^{238}U$ isotope ratio measurements indicated that uranium of natural isotope pattern was detected in selected human brain proteins.

Selected applications of LA-ICP-MS in the isotope analysis of long-lived radionuclides in radioactive waste, biological, geological and environmental samples are summarized in Table 5.

7. Conclusions

ICP-MS allows sensitive isotope ratio measurements of long-lived radionuclides in the pg g^{-1} down to fg g^{-1} range in radioactive waste solutions, water samples or body fluids, such as urine, using special sample preparation steps developed for matrix separation and analyte enrichment. ICP-MS is an excellent tool for the analysis of aqueous solutions,

Table 5
Application of LA-ICP-MS in isotope analysis of long-lived radionuclides in biological, geological and environmental samples

Samples	Method	Radionuclides	Detection limits/isotope ratio measured	References
Radioactive waste graphite, concrete, glass, silt	LA-ICP-SFMS (ELEMENT)	^{234}U, ^{235}U, ^{236}U ^{238}U, ^{230}Th, ^{232}Th, ^{237}Np, ^{99}Tc	0.0013 ng g^{-1} (^{233}U), $^{236}U/^{238}U \sim 0.00011$ (R.S.D., 0.7%), $^{234}U/^{238}U \sim 0.000067$ (R.S.D., 1.1%), $^{230}Th/^{232}Th \sim 0.003$ (R.S.D., 1.7%)	[97]
Moss (environmental monitor for nuclear fallout)	LA-ICP-SFMS (ELEMENT) after chemical separation and electrolytic deposition	^{230}Th, ^{232}Th, ^{234}U, ^{235}U, ^{236}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Am	$\sim 4 \times 10^{-15}$ g g^{-1}, $^{240}Pu/^{239}Pu = 0.21$	[9]
Soils (Chernobyl)	LA-ICP-SFMS (ELEMENT) (LINA-Spark)	^{239}Pu, ^{240}Pu	2.5×10^{-13} g g^{-1}, $^{240}Pu/^{239}Pu = 0.4$	[99]
Urine	LA-ICP-SFMS (ELEMENT)	^{232}Th, ^{235}U, ^{238}U	0.01 ng L^{-}1(^{238}U), 0.01 ng L^{-1} (^{232}Th), $^{235}U/^{238}U = 0002$	[21]

especially with on-line coupling techniques (ETV, HPLC, ion chromatography, flow injection) achieving detection limits in the sub-fg mL^{-1} range. A wide variety of applications demonstrates the excellent capability of ICP-MS and LA-ICP-MS for environmental or health control for the determination of very low levels of radioactive nuclides and for evidence of contamination from radioactive isotopes in biological, medical samples, soils and sediments.

The significance of ICP-MS in precise isotope ratio measurements at ultratrace levels is increasing, especially when multicollector and/or double-focusing sector field instruments are used.

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