



Review

Mass spectrometry of long-lived radionuclides

Johanna Sabine Becker*

Central Division of Analytical Chemistry, Research Centre Jülich, D-52425 Jülich, Germany

Received 3 April 2003; accepted 10 July 2003

Abstract

The capability of determining element concentrations at the trace and ultratrace level and isotope ratios is a main feature of inorganic mass spectrometry. The precise and accurate determination of isotope ratios of long-lived natural and artificial radionuclides is required, e.g. for their environmental monitoring and health control, for studying radionuclide migration, for age dating, for determining isotope ratios of radiogenic elements in the nuclear industry, for quality assurance and determination of the burn-up of fuel material in a nuclear power plant, for reprocessing plants, nuclear material accounting and radioactive waste control. Inorganic mass spectrometry, especially inductively coupled plasma mass spectrometry (ICP-MS) as the most important inorganic mass spectrometric technique today, possesses excellent sensitivity, precision and good accuracy for isotope ratio measurements and practically no restriction with respect to the ionization potential of the element investigated—therefore, thermal ionization mass spectrometry (TIMS), which has been used as the dominant analytical technique for precise isotope ratio measurements of long-lived radionuclides for many decades, is being replaced increasingly by ICP-MS. In the last few years instrumental progress in improving figures of merit for the determination of isotope ratio measurements of long-lived radionuclides in ICP-MS has been achieved by the application of a multiple ion collector device (MC-ICP-MS) and the introduction of the collision cell interface in order to dissociate disturbing argon-based molecular ions, to reduce the kinetic energy of ions and neutralize the disturbing noble gas ions (e.g. of $^{129}\text{Xe}^+$ for the determination of ^{129}I). The review describes the state of the art and the progress of different inorganic mass spectrometric techniques such as ICP-MS, laser ablation ICP-MS vs. TIMS, glow discharge mass spectrometry, secondary ion mass spectrometry, resonance ionization mass spectrometry and accelerator mass spectrometry for the determination of long-lived radionuclides in quite different materials.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Environmental monitoring; Glow discharge mass spectrometer; Inductively coupled plasma mass spectrometry; Isotope ratios; Laser ablation ICP-MS; Long-lived radionuclides; Radioactive waste; Trace analysis

*Fax: +49-2461-61-2560.

E-mail address: s.becker@fz-juelich.de (J.S. Becker).

1. Introduction

The determination of long-lived radionuclides [1–11] especially in environmental materials such as waters, geological and biological samples [12–24], medical samples [25–28] nuclear materials and radioactive waste [29–36] and high-purity materials [37–41] ceramics and glass [10,40,42] is of increasing importance. The analysis of long-lived radionuclides is also of interest in areas ranging from radiobioassay, environmental monitoring, decontamination and environmental remediation, health safety, nuclear waste characterization (radioactive waste control) and management of radioactive waste of high radiological toxicity for storage and disposal. Experts estimated that worldwide more than 160 000 tons of highly long-lived radioactive waste (LLRW) have been created and some ten thousands of tons are added every year [43]. Furthermore, the mobilization of radionuclides in the environment has been studied in order to trace the routes from soil, via plants into the food chain which is available for consumption.

Inorganic mass spectrometry is a universal and extremely sensitive analytical method for the simultaneous determination of element concentrations in the trace and ultratrace range and their isotope ratio measurements and has been established in the last few years for the determination of long-lived radionuclides. The application fields of inorganic mass spectrometry for the determination of long-lived radionuclides are expected increase with improvements in sensitivity and precision and decreasing detection limits. The determination of the concentration and the precise isotopic analysis of radioactive elements (e.g. ^{238}U , ^{235}U , ^{232}Th and the decay nuclides) by inorganic mass spectrometry as terrestrial sources of radioactivity is applied in environmental research, geology or in solid-state research and material controlling (e.g. of high-purity metals, alloys, semiconductors and insulators for microelectronics). The characterization of radioactive waste is required especially in respect to long-lived transuranics ^{237}Np ($t_{1/2}$: 2.1×10^6 a) ^{239}Pu ($t_{1/2}$: 2.4×10^4 a), ^{240}Pu ($t_{1/2}$: 6.6×10^3 a), ^{242}Pu ($t_{1/2}$: 3.8×10^5 a), ^{243}Am ($t_{1/2}$: 7.4×10^3 a) and fission

fragments and activated products ^{79}Se ($t_{1/2}$: 7×10^3 a), ^{93}Zr ($t_{1/2}$: 1.5×10^6 a), ^{99}Tc ($t_{1/2}$: 2.1×10^7 a), ^{107}Pd ($t_{1/2}$: 6.5×10^6 a), ^{126}Sn ($t_{1/2}$: 1.0×10^4 a), ^{129}I ($t_{1/2}$: 1.57×10^7 a) and ^{135}Cs ($t_{1/2}$: 2×10^6 a). Also ^{241}Am with relative short half-life ($t_{1/2}$: 432 a) can be determined in waste and environmental samples by mass spectrometry. The determination of ^{238}Pu ($t_{1/2}$: 88 a) is difficult due to isobaric interference with ^{238}U ; therefore, an isotope selective technique such as resonance ionization mass spectrometry (RIMS) or accelerator mass spectrometry (AMS) is advantageous. Besides the analysis of radioactive waste the determination of contamination and enrichments of selected radioactive nuclides (e.g. ^{129}I , which is one of the most important environmental indicator of nuclear accidents, ^{79}Se , ^{99}Tc , ^{237}Np , ^{239}Pu , ^{240}Pu and ^{241}Am) at ultralow concentration levels is useful for environmental monitoring due to fallout from nuclear weapons testing, nuclear power plants or nuclear accidents. Long-lived radionuclide tracers have also been used for tracer experiments in biological, medical and geological research and can also be applied for determining the concentration of monoisotopic elements (e.g. iodine using ^{129}I) by the isotopic dilution method [11]. In Fig. 1 different applications for determination of concentration and isotope ratio of long-lived radionuclides are summarized.

Inorganic mass spectrometry—especially inductively coupled plasma mass spectrometry (ICP-MS)—has developed in the past decade into a congruent method of the well-established classical radioanalytical techniques due to easier sample preparation steps, excellent detection limits and the ability to carry out precise isotope ratio measurements. Conventional radiochemical methods for the determination of long-lived radionuclides at low concentration levels require a careful chemical separation of the analyte, e.g. by liquid–liquid, solid phase extraction or ion chromatography. The chemical separation of the interferents from the long-lived radionuclide at ultratrace level and its enrichment in order to achieve low detection limits is often very time-consuming. Especially inorganic mass spectrometry is advantageous in comparison to radioanalytical techniques for the characterization of radionuclides with long half-lives ($> 10^4$

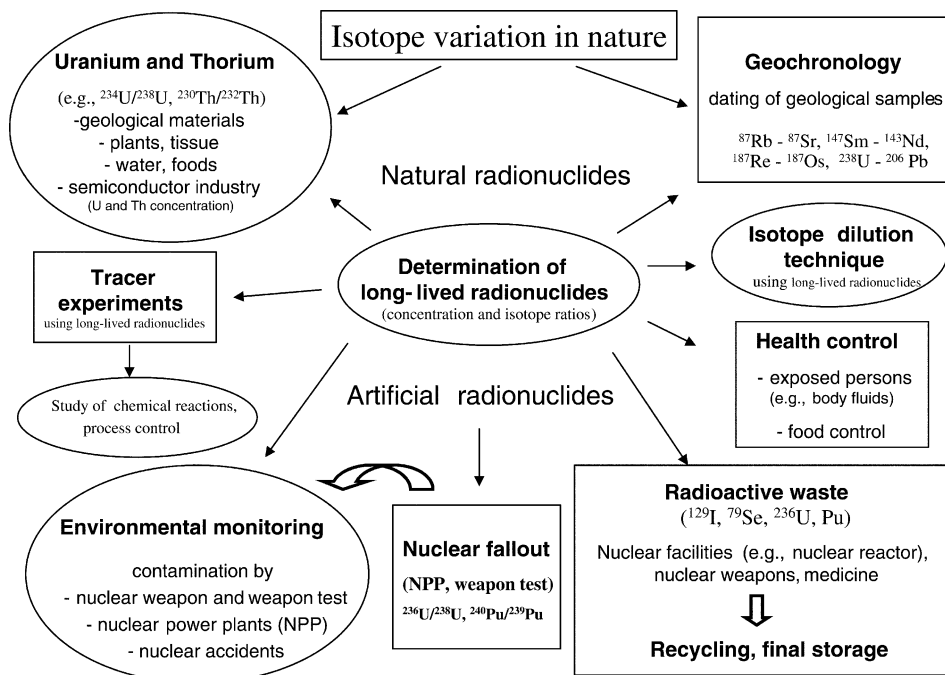


Fig. 1. Overview of application fields for determination of long-lived radionuclides.

a) at ultratrace level and very low-radioactive environmental or waste samples. Henry et al. [2] reported that improvements in quadrupole ICP-MS have resulted in attogram mass detection capability. Following the analysis of radionuclides with shorter half-life is also possible (Fig. 2).

The development of analytical methods for the determination of long-lived radionuclides at ultratrace concentration levels in high-radioactive materials from nuclear reactors—which is also important for waste classification—is focused on improving microanalytical techniques in order to reduce the sample volume (minimize radioactive contamination of instrument and dose to the operator), to improve the detection limits, the precision (relative standard deviation, R.S.D.) and accuracy of mass spectrometric measurements. For example, the quality control of radioactive waste packages or health control of exposed persons (blood, urine, faeces, hair and tissue analysis) requires powerful and fast analytical methods which allow many samples to be measured in a short time with a high degree of accuracy and precision. This review

discusses the different inorganic mass spectrometric techniques and their application for quantitative analysis and determination of isotope ratios of long-lived radionuclides.

2. Mass spectrometric techniques for determination of radionuclides

Solid-state mass spectrometric methods with multielemental capability—such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) [35,36,44–46], glow discharge mass spectrometry (GDMS) [47–50] and secondary ion mass spectrometry (SIMS) [12,51]—allow the direct sensitive trace element determination and isotope analysis of long-lived radionuclides in solid samples without any chemical sample preparation. For the trace and ultratrace analysis of selected radionuclides and the precise determination of isotopic ratios in solid samples also, thermal ionization mass spectrometry (TIMS) [12,52,53], AMS [54,55] and RIMS [22,56] have been used.

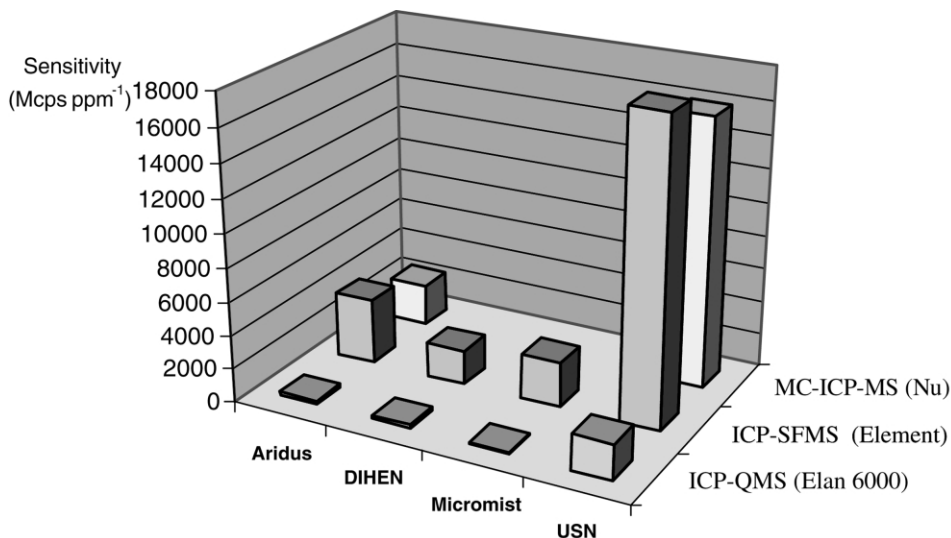


Fig. 2. Comparison of sensitivity for ^{238}U in ICP-MS using different nebulizers (from Ref. [127] with permission).

An advantage of solid state mass spectrometry is that sample preparation steps are reduced to a minimum and, therefore, possible contamination during sample preparation can be avoided. One problem is the quantification of analytical results in solid state mass spectrometry, which is difficult if no suitable (matrix-matched) standard reference materials are available. The quantification problem can be solved, for example, by the preparation and application of synthetic matrix-matched laboratory standards [36,57].

2.1. Thermal ionization mass spectrometry

For many decades TIMS was a frequently used isotope analytical technique allowing isotopic ratios of long-lived radionuclides to be measured with a precision of better than 0.01% [53]. Thermal ionization mass spectrometers with a multiple ion collector system yield the most precise isotope ratios down to 0.001% (R.S.D.). In TIMS a small volume (down to 1 μl) of aqueous solution containing the analyte in the nanogram to microgram range is deposited on a cleaned filament surface (mostly high-purity Re) and evaporated to dryness. The most frequently applied technique in TIMS works with two heated filaments (one for evapo-

ration of the sample the other for ionization of evaporated atoms) which are arranged opposite to each another. Due to the low initial energies (0.1–0.2 eV) of the ions formed on the hot thermal surface mostly single magnetic sector field mass spectrometers have been used for ion separation.

The limiting factors for the accuracy of measured isotopic ratios in TIMS are mass discrimination in the TIMS instrument (e.g. ion optical system or ion detector) and mass fractionation effects (caused during the evaporation of sample, where the measured isotope ratio changes with time). These inherent effects limit the capability of isotope ratio measurements by TIMS can be considered by different internal calibration techniques [11] or by using isotopic standard reference materials with well-known isotopic ratios for an element (e.g. from NIST—National Institute of Standards and Technology, Gaithersburg, USA—or IRMM—Institute of Reference Materials and Measurements, Geel, Belgium).

The capability of TIMS in precise isotopic ratio measurements—as the major application field of this analytical technique—is used in the accurate trace element determination of radiogenic elements for determining element concentration by the isotope dilution method using high-enriched isotopic

Table 1
Application of inorganic mass spectrometry in determination of uranium and thorium in high-purity metals, alloys and glass

Samples	Equipment	Concentration range	Detection limit	References
Indium	ICP-QMS Plasmaquad	U after trace/matrix separation	0.03 $\mu\text{g g}^{-1}$ (U)	Grazhulene et al. [62]
Platinum	LA-ICP-QMS ELAN 6000	U	3 ng g^{-1} (U)	Becker et al. [63]
Aluminium	TIMS, THQ isotope dilution	U and Th after trace/matrix separation	0.018 ng g^{-1} (U) 0.06 ng g^{-1} (Th)	Beer and Heumann [37]
Titanium	TIMS, THQ isotope dilution	U and Th after trace/matrix separation	0.07 ng g^{-1} (U) 0.07 ng g^{-1} (Th)	Beer and Heumann [64]
Cobalt	TIMS, THQ	U and Th after trace/matrix separation	0.007 ng g^{-1} (U) 0.017 ng g^{-1} (Th)	Beer and Heumann [65]
Molybdenum Tungsten	TIMS, MAT 261 isotope dilution	U and Th after trace/matrix separation	0.006 ng g^{-1} (U) 0.008 ng g^{-1} (Th)	Herzner and Heumann [38]
Tantalum	ICP-QMS ELAN 5000	U and Th after trace/matrix separation	0.02 $\mu\text{g g}^{-1}$ (U) 0.01 $\mu\text{g g}^{-1}$ (Th)	Panday et al. [66]
Zircaloy	ICP-QMS ELAN 5000	U and Th after trace/matrix separation	0.01 $\mu\text{g g}^{-1}$ (U) 0.02 $\mu\text{g g}^{-1}$ (U)	Panday et al. [67]
Glass fibers	LA-ICP-SFMS ELEMENT	U and Th	0.03 ng g^{-1} (Th, U)	Becker et al. [68]

spikes. For example, Heumann's group determined U and Th (and other elements) in, e.g. high-purity metals and silicides of Mo, W and Ta and silicon oxide after separation of analytes by TIMS and IDA [38,39,59]. Impurities of the naturally occurring radioactive elements uranium and thorium and their decay products at the picogram per gram level in high-purity refractory metals and their silicides, which have been increasingly used for gate electrodes, interconnections and diffusion barriers in integrated circuits, affect the electronic and physical properties of integrated circuits. The isotope dilution technique using TIMS together with different applications, also for the determination of long-lived radionuclides, is reviewed by Heumann [60].

TIMS was used by Aggarwal and Crain [61] for the determination of the half-life of several transactinium isotopes (e.g. ^{241}Pu , ^{242}Pu , ^{243}Am , ^{242}Cm) and of the fission yield of stable and long-lived fission products in thermal neutron induced fission of ^{233}U , ^{239}Pu and ^{241}Pu .

Selected applications of TIMS in comparison to

other inorganic mass spectrometric techniques in the determination of U and Th in high-purity metals are summarized in Table 1.

TIMS has a number of disadvantages: it requires an often time-consuming sample preparation (including digestion of solid samples and trace-matrix separation), it lacks multielement capability and is restricted to elements with ionization potential <6 eV; as a result this technique is being replaced by the more sensitive ICP-MS in recent years.

2.2. Glow discharge mass spectrometry

GDMS was established as a powerful and efficient analytical method for the direct trace element and depth profile analysis of solids [47,49,50]. In GDMS an argon gas glow discharge at a pressure of 0.1–10 Torr is used as an ion source [58]. The cathode surface consisting of the sample material is sputtered by Ar^+ ions, which are formed in low-pressure argon plasma and accelerated towards the cathode. Sputtered neutral particles of the

sample are ionized in the glow discharge plasma ('negative glow') by Penning and/or electron impact ionization and charge exchange processes. For the direct analysis of solid samples the commercial direct current glow discharge mass spectrometer VG-9000 (VG-Elemental, Thermo Instruments, UK)—a double-focusing sector field mass spectrometer with inverse Nier-Johnson geometry—has been available on the analytical market for many years. This instrument was used mainly for the determination of trace elements in electrically conducting materials with detection limits in the nanogram per gram concentration range and lower (reproducibility of $\approx \pm 10\%$ R.S.D.). The analysis of nonconducting materials by d.c. GDMS is difficult due to charge-up effects on the sample surface. Different techniques such as mixing nonconducting powdered samples with a high-purity metal powder (or high-purity graphite) or the use of a secondary cathode have, therefore, been applied for the analysis of electrically insulating samples by d.c. GDMS. Betti and co-workers [47–49,69] used the VG 9000 for different applications to characterize radioactive waste materials in electrically conducting and non-conducting materials, e.g. for different types of nuclear fuels, alloys containing Pu and U, cladding materials, nuclear waste glasses. It was thus possible to determine the neptunium concentration in Irish Sea sediment samples with d.c. GDMS with a detection limit of 80 pg g^{-1} [48]. In this work, a certified marine sediment doped with ^{237}Np was used for the calibration strategy. The ^{237}Np concentrations in sediments determined in the low nanogram per gram range are in good agreement with results of γ spectrometry. Detection limits in the low picogram per gram range measured by d.c. GDMS on soil, sediment and grass were reported by Betti et al. [47]. Table 2 summarizes selected applications of mass spectrometry for the determination of long-lived radionuclides in biological, geological and environmental samples.

2.3. Resonance ionization mass spectrometry

RIMS is a highly selective and ultrasensitive method for ultratrace and isotope analysis of especially radiotoxic isotopes (^{41}Ca , ^{90}Sr , ^{99}Tc , ^{135}Cs ,

^{210}Pb , ^{236}U , ^{238}Pu , ^{239}Pu , ^{240}Pu , ^{242}Pu , ^{244}Pu) in environment, cosmochemistry, radiodating, nutrition and biomedical research [22,56,75–78]. In RIMS the solid or liquid samples are vaporized and atomized by an atomic beam source (e.g. in an atomic beam oven by thermal vaporization on a hot Re filament or by evaporation of sample using an electron beam). One or in most cases more lasers are tuned precisely to the wavelength required for the excited states and ionization of evaporated atoms in order to obtain a highly selective resonance ionization of the element of interest. RIMS has been successfully applied in environmental samples at the ultratrace concentration level with detection limits of $\sim 3 \times 10^6$ atoms ^{90}Sr per sample ($\sim 2 \text{ mBq}$) and the isotopic selectivity of $\geq 10^{10}$ [56,75]. The determination of Pu after electrolytic separation from soil, air filters or urine was described by Erdmann et al. [78] with detection limits of 10^6 – 10^7 atoms. Nunne-mann et al. [22] determined Pu isotope ratios in environmental samples in order to distinguish between Pu from nuclear power plants and from global nuclear fallout due to nuclear weapons tests or from Chernobyl nuclear fallout. Recently, Trautmann [79] described the progress of RIMS in the determination of extremely small isotope ratios for different applications. Besides the determination of 238 – ^{244}Pu in soil, sea water and sediment, house dust and urine, RIMS was used at the University of Mainz for the determination of ^{99}Tc in sea water, $^{90,89}\text{Sr}$ in aerosols from Chernobyl samples, soil, plant, milk and urine and for the surveillance of nuclear reactor coolant, ^{41}Ca in nuclear reactor concrete, meteorites and biomedical samples [76,77].

2.4. Accelerator mass spectrometry

AMS started approximately 25 years ago at nuclear physics laboratories [55,80–84] as a highly selective and ultrasensitive mass spectrometric technique. The sensitive determination of exotic radionuclides such as ^3He , ^{14}C , ^{10}Be , ^{26}Al , ^{129}I , ^{32}Si , ^{182}Hf , ^{210}Pb , ^{236}U or ^{244}Pu is carried out by ion sputtering (e.g. using a Cs^+ primary ion source). The sputtered secondary negative ions were extracted into a two-stage mass filter. The

Table 2
Application of inorganic mass spectrometry in trace and ultratrace analysis of long-lived radionuclides in biological, geological and environmental samples

Samples	Equipment	Radionuclides	Detection limits	References
Soil, sediments, grass	GDMS 'VG 9000'	^{137}Cs , ^{90}Sr , ^{239}Pu ^{240}Pu , ^{241}Pu , ^{232}Th	Low pg g^{-1}	Betti et al. [47]
Zeolites	LA-ICP-QMS 'ELAN 6000'	U and Th	0.09 $\mu\text{g g}^{-1}$ (U) 0.03 $\mu\text{g g}^{-1}$ (Th)	Pickhardt et al. [46]
Meteorites (chondrites)	ICP-QMS	U and Th	0.28 ng g^{-1} (Th)	Shinotsuka and Ebihara [70]
Irish sediments	GDMS 'VG 9000'	^{237}Np	80 pg g^{-1}	Aldave de las Heras [48]
Biological SRMs, sea and river water	ICP-QMS, ELAN 5000 'PlasmaQuad PQ2' ETV, on-line solid phase extraction	^{238}U , ^{232}Th	0.9 pg ml^{-1} (^{238}U) 0.3 pg ml^{-1} (^{232}Th)	Truscott et al. [71]
Sediments, fish samples	ICP-SFMS Element	^{226}Ra , ^{230}Th , ^{233}U , ^{237}Np , ^{239}Pu , ^{241}Am	4.0 pg l^{-1} (^{235}U) 1.2 pg l^{-1} (^{239}Pu , ^{240}Pu , ^{241}Am)	Chiappini et al. [72]
Thermal water	ICP-QMS + USN 'PlasmaQuad PQ2' extraction, ion exchange	^{226}Ra	2 fg g^{-1}	Joannon and Pin [73]
Food	ICP-SFMS + USN 'ELEMENT', ion extraction	Pu	0.03 pg g^{-1}	Evans et al. [74]

mass-separated ions were accelerated in a tandem accelerator to energies of some mega electron volt and were stripped in a gas target (or foil) stripper where they lose electrons and gain a high positive charge states (e.g. $^{236}\text{U}^{5+}$) and, therefore, are accelerated a second time by the same potential. The stripping process has the advantage that it dissociates molecular ions if enough electrons are stripped off which results in an elimination of isobaric interferences [55]. After the deceleration of ions and a final mass separation the ions were sensitively detected.

Today with 63 accelerator mass spectrometers installed worldwide (including recycled tandem accelerator and new facility instruments) AMS has been established as a powerful routine method especially for ^{14}C dating (^{14}C : $t_{1/2} = 5.7 \times 10^3$ a), in which extremely small isotope ratios 10^{-12} – 10^{-16} can be measured very fast in routine mode in very small samples [81]. Recently, Kutschera and Müller [82] dated the Alpine Iceman Oetzi and associated materials using ^{14}C dating by AMS. AMS revolutionized the use of long-lived radionuclides by detecting radioactive atoms directly at the ultratrace level and it thus became possible to measure many long-lived radionuclides such as ^{10}Be , ^{41}Ca , ^{236}U or ^{244}Pu at natural abundances [55]. AMS can, therefore, be used to determine $^{236}\text{U}/^{238}\text{U}$ isotope ratios in the range from 10^{-8} to 10^{-14} for evidence of ^{236}U in environmental samples [83]. However, since a standard material for ^{236}U determination at this level is not established, the result of $^{236}\text{U}/^{238}\text{U}$ isotope ratio measurement by AMS of $(6.1 \pm 0.4)10^{-11}$ for the ‘K.k. Uranfabrik Joachimsthal’ uranium can be only considered preliminary [55]. With AMS absolute detection limits of 10^6 atoms are reached for isotopes such as ^{239}Pu [84]. Furthermore, with its capability of providing isotopic abundance ratios as low as 10^{-15} for very small samples, AMS has been applied for the detection of extremely low concentrations of long-lived radionuclides for research in geochronology and archaeology.

2.5. Secondary ion mass spectrometry and secondary neutral mass spectrometry

SIMS [85] is the most important mass spectrometric surface analytical technique and can be

applied for analysis of long-lived radionuclides. Secondary neutral mass spectrometry (SNMS) [86] is less significant in this topic due to its lower sensitivity. In SIMS the solid sample surface is sputtered by bombardment with a focused primary (keV) ion beam (Ar^+ , Ga^+ , Cs^+ , O_2^+ or O^-) and the sputtered ions are analyzed mass spectrometrically. In contrast, in SNMS the secondary neutrals, which were postionized, e.g. by electron bombardment or using a laser beam, were analyzed mass spectrometrically. SIMS and SNMS are mainly applied for depth profiling, reaching depth resolution in the low nanometer range. Both techniques are able to perform a microlocal analysis in the sub-micrometer range (e.g. for analysis of local inclusion or impurities) and can be used for the determination of lateral element distribution and isotope analysis, e.g. for the characterization of small particles, aerosols, and liquid or solid inclusions. Whereas in SNMS the detection limits for trace analysis are in the microgram per gram range, SIMS can be applied for the characterization of bulk material with detection limits down to the low nanogram per gram range (but very element dependent). Both surface analytical techniques allow precise isotope ratio measurements with precisions between 0.01 and 1%. By the application of multiple ion collector SIMS (NanoSIMS, CAMECA), e.g. in geochronology, a precision of 0.002% can be reached [11]. In contrast to SNMS, the quantification of analytical results in SIMS is very difficult due to large matrix effects. Nevertheless, if a matrix matched standard reference material is available for SIMS accurate analytical data were obtained. SIMS and SNMS are advantageous for determining surface contamination and investigation of interdiffusion of elements in solid materials or in layered systems. More details of this surface analytical mass spectrometric technique are given in Refs. [85,86].

SIMS has been applied for the characterization of single uranium and plutonium particles by Betti et al. [87,88]. The identification of uranium micro-particles and the determination of their isotopic composition by SIMS is discussed by Tamborini et al. [87]. The mapping of an entire sample surface was performed by the use of the resistive anode encoder, avoiding charging effects during

sputtering by a coating with 20 nm carbon. Working in the microprobe mode the isotopic composition of the particles was obtained with good accuracy and precision. A detection limit for uranium in the nanogram per gram to picogram per gram range was obtained by optimization of different instrumental parameters. Erdmann et al. [89] described a determination of isotopic composition with an accuracy better than 0.4% for ^{235}U in single uranium oxide particles. Control particles were produced consisting of isotopically certified monodisperse uranium oxide microspheres of 1 μm in diameter. These particles were obtained by dissolving uranium isotopic standard reference materials, nebulizing the solution in droplets and collecting the particles after their desolvation and calcination.

2.6. Inductively coupled plasma mass spectrometry

ICP-MS [11,57,90] is at present the most frequently used mass spectrometric technique for fast single- and multielement determination and isotope ratio measurements in the trace and ultratrace concentration range. This powerful analytical technique is also increasingly used for analysis of radionuclides at very low activity and low nuclide abundances [1–11,70–74,91]. ICP-MS is applied as well in aqueous radioactive solutions or on solid samples after digestion. In contrast to conventional inorganic solid mass spectrometric techniques, ICP-MS allows a simple sample introduction in a normal pressure ion source and an easy quantification procedure using aqueous standard solutions. The principle of ICP-MS is described in detail in Ref. [90]. The chemical compounds contained in the sample solution are decomposed into their atomic constituents in an inductively coupled argon plasma at a plasma temperature of approximately 6000–8000 K and ionized at a high degree of ionization (>90% for most chemical elements) with a low fraction of multiply charged ions ($\approx 1\%$). The positively charged ions are extracted from the inductively coupled plasma (at atmospheric pressure) into the high vacuum of the mass spectrometer via an interface. The major problem in determining long-lived radionuclides in radioactive waste or environmental samples is the

Table 3
Figures of merit of ICP-MS for determination of long-lived radionuclides [11]

Analytical method	Detection limits
Solid state mass spectrometry ($\mu\text{g g}^{-1}$)	
SSMS	1–0.001
GDMS	0.1–0.0001
SIMS	10–0.002
LA-ICP-MS	0.010–0.00001
ICP-MS (ng l^{-1})	
Quadrupole ICP-MS	0.01–0.6
ICP-SFMS ($m/\Delta m=300$)	0.00004–0.005
ICP-QMS with collision cell	0.003–0.01
ICP-TOFMS	0.1–1
MC-ICP-MS (sector field)	0.0001–0.0002 [75]

appearance of isobaric interferences of long-lived radioactive nuclides and stable isotopes of other chemical elements at the same mass. ICP-MS offers some interesting advantages to solve these inherent interference problems. Isobaric interferences of radionuclides especially with molecular ions can be resolved using double-focusing sector field ICP-MS at the required mass resolution. Furthermore, by the application of ICP-MS with collision cell, disturbing interfering isobaric ions can be suppressed or special sample introduction and coupling techniques such as high-performance liquid chromatography (HPLC) and capillary electrophoresis (CE) can be helpful to avoid interference problems by separating the analytes.

At present several quadrupole-based ICP mass spectrometers without and with collision cell (e.g. Perkin Elmer Sciex, Agilent, ThermoElemental, Varian GmbH analytical instruments, Micromass, etc.), a time-of-flight ICP-MS from Leco and several commercial double-focusing sector field ICP-MS with single and multiple ion collectors, e.g. 'ELEMENT' and 'NEPTUNE' (Thermo-Finnigan, Bremen, Germany) and a single magnetic sector field ICP-MS with collision cell 'Isoprobe' (Micromass Ltd, UK), 'Nu Plasma' (Nu Instruments) are available on the international market. In Table 3 the detection limits for the determination of long-lived radionuclides measured by ICP-MS are compared with those of solid mass spectrometry. In the low-resolution mode, the element sensitivity of commercial double-focusing sector field ICP-MS is significantly higher than

conventional quadrupole ICP-MS. The extreme element sensitivity of double-focusing sector field ICP-MS permits ultratrace analysis down to the sub-femtogram per milliliter concentration range in aqueous solution [7]. Whereas the precision for isotope ratio measurements in quadrupole ICP-MS varies between 0.1 and 0.5%, double focusing sector field ICP-MS with single ion detection allows isotope ratio measurements with a precision of 0.02% [11]. A better precision of isotope ratio measurements (one order of magnitude) was achieved by the introduction of the multi-ion collector device in sector field ICP-MS. The capability of the double-focusing sector field 'Nu Plasma' from Nu Instruments (with Nier-Johnson geometry) with 12 Faraday cups is demonstrated by measurements from Halicz [92,93] on a lead and strontium NIST isotope standard reference material. With these measurements a precision at 20 ppm (0.002% R.S.D.) and an excellent agreement with certified values was achieved. Also small isotope ratios as demonstrated for $^{234}\text{U}/^{238}\text{U}$ [$^{234}\text{U}/^{238}\text{U}_{\text{measured}} = 63.0(0.5) \times 10^{-6}$ vs. $^{234}\text{U}/^{238}\text{U}_{\text{recommended}} = 62.58(0.12) \times 10^{-6}$] in ocean water can be measured with good precision and accuracy [94].

Similar to solid state mass spectrometric techniques, ICP-MS possesses the multi-element capability for the quasi-simultaneous determination of long-lived radionuclides, but single element determination was performed especially for selected applications (e.g. determination of ^{129}I or ^{79}Se) or in isotope ratio measurements.

The oxide formation of long-lived radionuclides ^{226}Ra , ^{230}Th , ^{237}Np , ^{238}U , ^{239}Pu and ^{241}Am in double-focusing sector field ICP-MS and their applications is described by Becker and Dietze [95]. In ICP-MS and LA-ICP-MS the authors found a good correlation of oxide intensities of long-lived radionuclides with bond dissociation energies. From this correlation it was possible to estimate bond energies for AmO and NpO.

2.6.1. Application of collision cell in ICP-MS for determination of long-lived radionuclides

The introduction of the collision cell in ICP mass spectrometers is one of the most significant improvements in ICP-MS instrumentation for more

sensitive analysis of radionuclides and more precise determination of isotope ratios in comparison to commercial quadrupole ICP-MS without collision cell [96–102]. The principles and possible application of collision-induced reaction in a gas target for increasing the sensitivity in an inorganic mass spectrometer for ultrasensitive trace analysis was already studied 20 years ago [103]. The collision-induced reaction of ions—formed in the inductively coupled plasma—with molecules or atoms of the collision gas or gas mixture (e.g. He and /or H_2 , O_2 , Xe, CH_4 , NH_3) introduced by one or two mass flow controllers in the collision or reaction cell results in a reduction of the energy spread ('cooling') of the ions from several eV to <0.1 eV, in dissociation of the molecular ions and neutralization of disturbing atomic ions of noble gas of the plasma gas (Ar and Xe contaminants) used. Whereas the collision cell was introduced in ICP-MS in order to dissociate disturbing argon-based molecular ions (ArX^+ , X=O, N, C, H or Ar) and to neutralize the plasma gas ions (Ar^+), more and more newly formed interference free molecular ions were used as analyte ions [11,98–101]. Tanner et al. [100] reviewed fundamentals in the reaction chemistry and collision processes in the gas cell for resolving isobaric interferences in ICP-MS.

ICP-MS with collision cell is the method of choice for the sensitive determination of the long-lived rare ^{129}I ($t_{1/2} \approx 1.6 \times 10^7$ a), which is of great interest for environmental monitoring of nuclear fallout (e.g. as a result of the Chernobyl accident) and for monitoring of radioactive emissions from nuclear facilities and for radioactive waste control. The main problem for ^{129}I determination by ICP-MS is an impurity of Xe in the high-purity argon gas used which results in an isobaric $^{129}\text{Xe}^+$ interference, leading to a high background at mass 129 u and an increased detection limit. Furthermore, the determination of the $^{129}\text{I}/^{127}\text{I}$ ratio in environmental samples requires an abundance sensitivity down to 10^{-10} – 10^{-11} . Analytical methods which are mostly applied for the ultrasensitive determination of ^{129}I —such as AMS and neutron activation analysis—are very expensive, require special equipment and laboratory facilities. For the determination of ^{129}I , ICP-MS with collision cell

is a powerful tool for an ultrasensitive determination of the extremely rare ^{129}I radionuclide. Using He and H_2 as the collision gases in ICP-MS with a hexapole collision cell (Platform, Micromass) an efficient reduction of the disturbing background intensity is possible which results in a lowering of the detection limit in comparison to ICP-SFMS by nearly two orders of magnitude from 100 to 3 ng l^{-1} [11,104]. Recently, a further improvement of the detection limit for ^{129}I determination by ICP-MS with hexapole collision cell using oxygen as the collision gas was demonstrated in our working group [105]. For the sample introduction of volatile ^{129}I from solid geological material (soil) an electrothermal vaporization technique was developed. The detection limit for the analysis of ^{129}I in aqueous solution and in soils could be reduced to the sub-ppt and low ppt range, respectively.

The determination of the long-lived radionuclide ^{79}Se ($t_{1/2} \approx 65\,000$ a) can be performed by ICP-MS using a hydride generator for solution introduction in order to reduce the interference problem (possible isobaric interferences of ^{79}Se with $^{79}\text{Br}^+$, $^{39}\text{K}^{40}\text{Ar}^+$, $^{63}\text{Cu}^{16}\text{O}^+$, $^{158}\text{Gd}^{2+}$ and $^{158}\text{Dy}^{2+}$). The detection limit of ^{79}Se determination in sector field ICP-MS was 100 pg ml^{-1} [106]. An improvement of sample introduction by hydride generation coupled to ICP-QMS with hexapole collision cell for selenium determination in biological samples was described in Ref. [107]. By applying hydride generation in quadrupole ICP-MS with a hexapole collision cell the detection limit could be reduced to 5 pg ml^{-1} because the disturbing argon hydride molecular ions $^{38}\text{Ar}^{40}\text{Ar}^1\text{H}^+$ were additionally suppressed [11].

The application of a collision cell in ICP-MS results in an improved sensitivity for heavy elements due to increasing ion transmission as discussed in Ref. [16]. An $^{238}\text{U}^+$ ion intensity of up to 27 000 Mcps/ppm in ICP-QMS with hexapole collision (using an ultrasonic nebulizer) cell was found.

2.6.2. Application of ICP-MS for determination of long-lived radionuclides after trace/matrix separation

Long-lived radionuclides occur at extremely low concentrations especially in environmental sam-

ples; therefore, matrix separation and enrichment of the analytes is proposed for their analysis by several authors [19,71–74,108–117]. Trace/matrix separation, which is performed off-line or on-line, is also advantageous in order to avoid possible isobaric interferences, matrix effects and to reduce the detection limits for the determination of long-lived radionuclides.

For example, Yamamoto et al. [91] suggested for the determination of ^{99}Tc in environmental and radioactive waste samples by ICP-MS—which is disturbed by isobaric interference with $^{99}\text{Ru}^+$ (and $^{98}\text{MoH}^+$) ions—a separation of ^{99}Tc using different solvent extraction and purification techniques with anion exchange. In this work, the determination of ^{99}Tc in sediments from the Irish Sea is described with an absolute detection limit of 0.25 pg, (0.16 mBq), using a double-focusing sector field ICP-MS (PlasmaTrace, VG Elemental Ltd).

^{99}Tc in a highly radioactive evaporator concentrate from a nuclear power plant [118] was measured in our laboratory after chemical separation procedures using ICP-MS. The detection limit for ^{99}Tc determination in separated solutions was determined by double-focusing ICP-SFMS to be 5 pg l^{-1} , corresponding to an activity of 3 $\mu\text{Bq ml}^{-1}$, in comparison to quadrupole-based ICP-MS (ELAN 6000, Perkin Elmer Sciex) with a detection limit of 0.1 ng l^{-1} [7].

Eroglu et al. [19] studied separation and enrichment of ^{99}Tc from sea water by anion exchange with a detection limit of 0.03 ng l^{-1} using a quadrupole-based ICP-MS (HP 4500, Hewlett-Packard). An IC-ICP-MS spectrum for the separation of ^{99}Ru and ^{99}Tc in an environmental sample is demonstrated by Betti in Ref. [14].

Barrero Moreno et al. [108] determined neptunium and plutonium in the presence of high concentrations of uranium by ion chromatography coupled to ICP-MS. The determination of natural uranium and thorium in environmental samples by ETV-ICP-MS after matrix removal by on-line solid phase extraction was described by Truscott et al. [71].

Recently, Evans et al. [74] developed a rapid and accurate method for the determination of plutonium in food using double focusing ICP-SFMS with an ultrasonic nebulizer with desolva-

Table 4
Concentration of different spallation nuclides of the lanthanides ($\mu\text{g g}^{-1}$) in an irradiated tantalum target [114]

Nuclide	Half-life	Sample 1	Sample 2	Sample 3
^{141}Pr	Stable	9.6 ± 1.7	2.1 ± 0.6	0.7 ± 0.2
^{145}Pm	17.7 y	21.2 ± 3.6	4.4 ± 1.1	0.9 ± 0.3
^{150}Gd	1.8×10^6 y	28.7 ± 4	6.3 ± 1.2	1.1 ± 0.3
^{163}Ho	33 y	80.3 ± 10.4	21 ± 4	3 ± 0.6
^{173}Yb	Stable	111.1 ± 13.3	29.6 ± 5.3	4.6 ± 0.8
^{173}Lu	1.4 y	16.5 ± 2.8	5 ± 1	0.8 ± 0.2

tion unit (Cetac USN 6000 AT+) and ion chromatography. 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 on-line separation using a polystyrene–divinylbenzene ion chromatography column ^{239}Pu and ^{238}U were separated in order to reduce the $^{238}\text{U}^1\text{H}^+$ interference. A further reduction of $^{238}\text{U}^1\text{H}^+$ interference was achieved by application of an ultrasonic nebulizer (USN). The detection level for Pu of 0.020 pg g^{-1} ($4.6 \times 10^{-2} \text{ Bq kg}^{-1}$) is significantly below 1/10 of the European Union legislation for baby food (1 Bq kg^{-1} – 0.436 pg g^{-1}) [74].

An analytical method for ^{226}Ra determination in environmental samples (highly saline thermal waters) by ICP-QMS with ultrasonic nebulization were developed by Joannon and Pin [73]. Radium was preconcentrated and isolated from the matrix elements by selective extraction using a radium-specific solid phase extraction membrane disk designed for radioactive counting method. A very low detection limit was achieved in quadrupole ICP-MS when the pressure in the interface was reduced from approximately 2 to 0.85 mbar. Lari-vière et al. [112] developed a selective extraction procedure for preconcentration of ^{226}Ra from uranium ores and biological samples. The measurements were performed by ICP-QMS with hexapole collision cell in order to reduce possible interferences. An absolute detection limit of 0.02 fg (0.75 mBq) was obtained using less than 4 mg of solid sample or 25 ml liquid sample.

In past years especially on-line ion chromatography ICP-MS has been increasingly used for the

characterization of radioactive materials and environmental samples using ICP-MS [111,117,119,120]. For example, we developed analytical procedures for the determination of spallation nuclides in the tantalum target of a spallation neutron source irradiated with 800 MeV protons [32,119,120]. In order to separate isobars of rare earth elements, such as radioactive ^{173}Lu , from stable ^{173}Yb , on-line HPLC (for a chromatographic separation of a lanthanide mixture into the individual elements) was coupled to the mass spectrometer. The concentrations of different spallation nuclides (Table 4) in the first tantalum plate of the spallation neutron source (sample 1 was collected from the centre of the plate, sample 3 is from the edge, sample 2 was collected between) were measured by HPLC-ICP-MS using reverse isotope dilution technique [114]. With increasing distance from the centre of the plate, that means with decreasing irradiation density of 800 MeV proton beam on the tantalum target, the concentration of the spallation nuclides decreases. We also coupled CE to a double-focusing sector field ICP-MS for the same analytical task [120]. This approach reduces the sample volume from the 100 μl range using HPLC-ICP-MS to the nanoliter range, which is extremely important for the analysis of high-radioactive solutions. The spallation nuclides in the irradiated tantalum were measured using both mass spectrometric coupling techniques after dissolution of high-radioactive tantalum in a HNO_3/HF mixture and after (off-line) matrix separation by liquid–liquid extraction of the tantalum matrix (in order to reduce the high ^{182}Ta activity). The theoretical results of spallation yields of tantalum are verified by mass spectrometric measurements of the concentration of spallation nuclides of the irradiated tantalum target by HPLC-ICP-MS and CE-ICP-MS as well [32,119,120]. One example is demonstrated in Table 5 where the nuclide abundances of gadolinium produced via spallation reactions in an irradiated tantalum target and measured by HPLC-ICP-MS and CE-ICP-MS are compared.

The simultaneous separation and determination of lanthanides and actinides by ion chromatography ICP-MS combined with the isotope dilution technique was studied by Perna et al. [109]. A

Table 5
Nuclide abundances of gadolinium (%) produced via spallation reactions in an irradiated tantalum target via spallation reactions

Nuclide	Nature	Theory	CE-ICP-MS	HPLC-ICP-MS
¹⁴⁸ Gd	–	15.8	19.4	20.7
¹⁵⁰ Gd	–	18.3	18.8	18.4
¹⁵² Gd	0.2	27.2	22.1	22.7
¹⁵⁴ Gd	2.15	2.6	<3.4	<1.1
¹⁵⁵ Gd	14.7	34.4	33.4	33.9
¹⁵⁶ Gd	20.5	0.57	–	<1.1
¹⁵⁷ Gd	15.7	0.40	–	<1.9
¹⁵⁸ Gd	24.9	–	–	–
¹⁶⁰ Gd	21.9	–	–	–

further application of ion chromatography for the determination of fission products and actinides in nuclear applications is discussed by Betti et al. [14,121]. An on-line trace enrichment by flow injection using a microcolumn of activated alumina and mass spectrometric determination of uranium in mineral, river and sea water was described by Dadfarnia and McLeod [122].

Flow injection with on-line preconcentration using solid-phase adsorption on a mini-column of ⁹⁹Tc, ²³⁰Th and ²³⁴U at ultratrace level in soils is described by Hollenbach et al. [123]. Detection limits in the soil for ⁹⁹Tc, ²³⁰Th and ²³⁴U were 11

mBq g⁻¹ (0.02 ng g⁻¹), 3.7 mBq g⁻¹ (0.005 ng g⁻¹) and 0.74 mBq g⁻¹ (0.003 ng g⁻¹), respectively.

Different applications of mass spectrometry in trace, ultratrace and isotope analysis of long-lived radionuclides in nuclear fuel, solid radioactive waste samples and radioactive solutions are summarized in Table 6.

2.6.3. Ultratrace analysis of long-lived radionuclides in very small sample volumes

The development and application of micro-analytical techniques for the precise isotope analysis and concentration determination of long-lived radionuclides at the ultratrace concentration level is a challenging task for analytical chemistry. Micro-analytical techniques are of special importance in order to reduce the radioactivity of the sample analyzed, the waste, contamination of instruments and tools, and the dose to the operator. Furthermore, for a multitude of applications especially for biomonitoring (for monitoring contamination from radioactive waste in the environment and for evidence of nuclear fallout) the concentrations of long-lived radionuclides are extremely low and the sample amount is often restricted. In order to analyze small sample volumes, micronebulizers (MCN Aridus, Cetac Technologies, USA and

Table 6
Application of inorganic mass spectrometry in trace and ultratrace analysis of long-lived radionuclides in nuclear fuel, radioactive waste solid samples and radioactive solutions

Samples	Method	Radionuclides	Detection limits	References
UO ₂ fuel	ICP-QMS, ELAN 5000 ion chromatography isotope dilution	²³⁸ U, ²³⁷ Np, ²³⁹ Pu	0.06 µg l ⁻¹ (Np)	Barrero Moreno et al. [108]
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)	Becker and Dietze [7]
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)	McLean et al. [124]
Spent uranium	ICP-SFMS Element, (Aridus) ion exchange	²³⁶ U, ²³⁹ Pu	0.2 pg l ⁻¹ (solution) 0.04 pg g ⁻¹ (soil)	Boulyga and Becker [125]
Radioactive concrete	LA-ICP-SFMS Element	⁹⁹ Tc, ²³² Th, ²³³ U, ²³⁵ U, ²³⁶ U, ²³⁸ U, ²³⁷ Np	0.02 ng g ⁻¹ (²³⁶ U) 1.4 ng g ⁻¹ (⁹⁹ Tc)	Becker et al. [35]
Spent nuclear fuel	ICP-QMS, ELAN 5000 on-line ion chromatography	²³⁸ U, ²³⁷ Np, ²⁴⁴ Pu, ²⁴³ Am, ²⁴⁸ Cm	0.45 ng ml ⁻¹	Perna et al. [109]

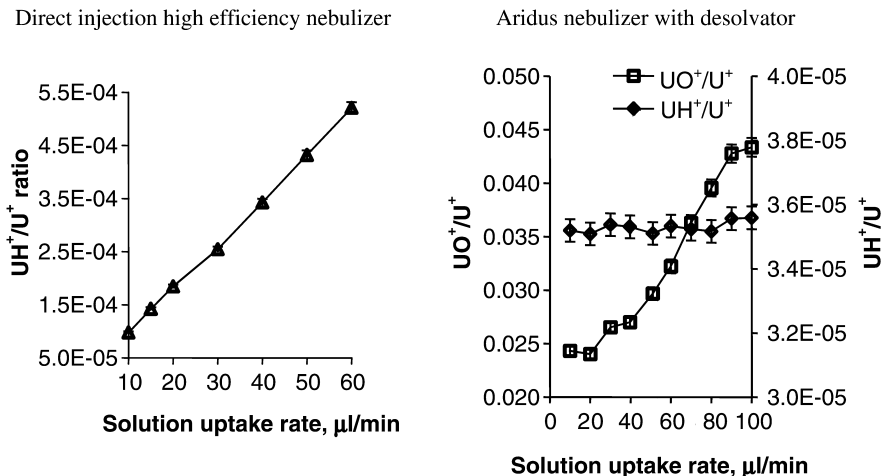


Fig. 3. Comparison of UH^+/U^+ formation rate on solution uptake rate in ICP-SFMS using DIHEN and Aridus microconcentric nebulizers.

MicroMist, Glass Expansion, Australia) [7,124,126] have been increasingly used for determining long-lived radionuclides by solution introduction into the ICP-MS instead of ultrasonic nebulizers, which consume high volumes of solution. Using the direct injection high-efficiency nebulizer (DIHEN, J E Meinhard Associates, USA) [33,90] sample solution is introduced into the inductively coupled plasma with an analyte transport efficiency into the plasma of 100%. By reducing the solution uptake rate and the sample size to the $1 \mu\text{l min}^{-1}$ and fm range, respectively, very sensitive measurements of long-lived radionuclides in aqueous solutions are possible [33,124]. In Fig. 2, the sensitivity (in Mcps/ppm) for ^{238}U determination by ICP-MS using Aridus, Micromist, USN (Cetac Technologies, USA) and DIHEN is compared. For quadrupole-based ICP-MS vs. sector field ICP-MS with a single ion collector (Element, Finnigan MAT) and multiple ion collection (Nu Plasma, Nu Instruments) the lowest ion intensities for $^{238}\text{U}^+$ were observed. The highest sensitivity was observed using USN in sector field ICP-MS but the solution uptake rate of 2 ml min^{-1} for analyzing high-radioactive solutions is relatively high. Considering the different solution uptake rate of several nebulizers, the highest sensitivity for the determination of ^{238}U

($\sim 3000 \text{ cps fg}^{-1}$) was measured using the DIHEN in sector field ICP-MS with a single ion detector due to a low solution uptake rate of 0.01 ml min^{-1} . The problem with the DIHEN is the relatively high molecular ion formation rate, because the DIHEN works without spray chamber and desolvator. So far the Aridus microconcentric nebulizer with desolvator (sensitivity: $\sim 2000 \text{ cps fg}^{-1}$), which works at a solution uptake rate of 0.1 ml min^{-1} , is the micronebulizer of choice especially when disturbing polyatomic ion formation has to be suppressed. Nebulizers with low uranium hydride formation rate are required in particular for ^{239}Pu determination, because due to a large excess of uranium in the presence of an extremely low concentration of plutonium a complete separation of Pu from U is very difficult. A comparison of the uranium hydride formation rate of several nebulizers using different ICP-MS is discussed in Ref. [15]. As demonstrated by these measurements aerosol desolvation (also producing dry aerosol, e.g. by laser ablation, which is not demonstrated here) is advantageous for ^{239}Pu and also ^{236}U analysis. Fig. 3 compares the UH^+/U^+ formation rate on solution uptake rate in ICP-SFMS using DIHEN and Aridus microconcentric nebulizers. The highest hydride formation rate was observed for the DIHEN, whereas using the DIH-

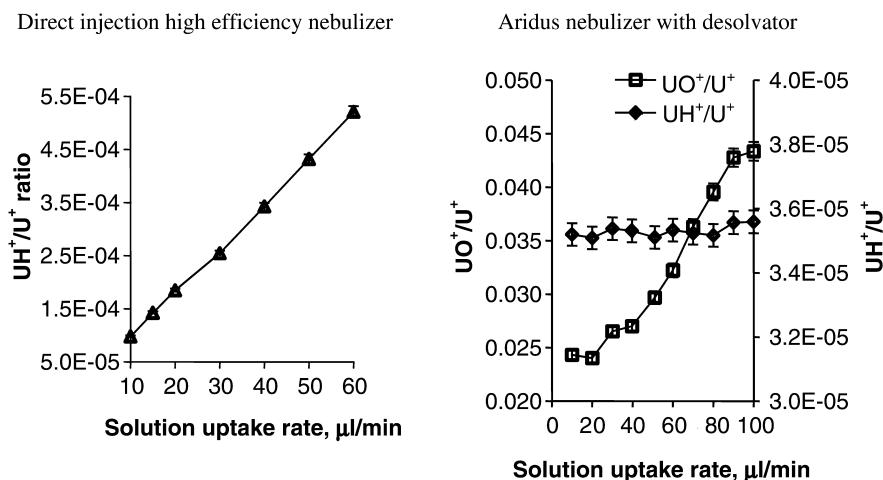


Fig. 3. Comparison of UH^+/U^+ formation rate on solution uptake rate in ICP-SFMS using DIHEN and Aridus microconcentric nebulizers.

EN with decreasing solution uptake rate a decreasing hydride formation rate was observed. With the application of Aridus the hydride formation rate of approximately 3.6×10^{-5} is nearly constant whereas the oxide formation rate increases with increasing solution uptake rate. Characteristics of different ICP-MS instruments are summarized in Table 7 using probably the most useful microconcentric nebulizer with desolvator currently available (Aridus, Cetac Technologies) for the analysis of small volumes of radioactive solutions.

The low-flow microconcentric nebulizer with desolvator (Aridus) coupled to ICP mass spectrometers was successfully applied in our laboratory for environmental monitoring of spent reactor uranium, evaluating origins of contamination with nuclear fuel in Chernobyl samples, studying radionuclide behavior in the environment or for the

analysis of depleted uranium in samples from Kosovo [15].

The application of flow injection, as mentioned before, is extremely helpful for solution introduction of small volumes into the ICP in order to minimize radioactive contamination in the instrument [5,126]. Microliter volumes of an aqueous solution can be handled by a commercial HPLC injection valve which was coupled, e.g. to a microconcentric nebulizer (Micromist, Glass Expansion) for small droplet formation and a minicyclonic spray chamber. It is thus possible to analyze small sample volumes (sample loop: $> 1 \mu\text{l}$) of radioactive waste solution introduced by this HPLC injection valve into a continuous flow of 2% nitric acid. In Fig. 4 an example is given of the application of flow injection ICP-MS (using a quadrupole ICP-MS) for the determination of

Table 7
Characteristics of different ICP-MS instruments using microcentric nebulizer with desolvator (Aridus, Cetac Technologies)

	Absolute sensitivity (counts/atom)	UH^+/U^+	Abundance sensitivity
ICP-QMS ^a	4×10^{-5}	3×10^{-6}	6×10^{-7}
ICP-SFMS	7×10^{-4}	3×10^{-5}	5×10^{-6}
MC-ICP-MS ^b	5×10^{-4}	5×10^{-5}	3×10^{-7}

^a ELAN 6000.

^b Halicz [94].

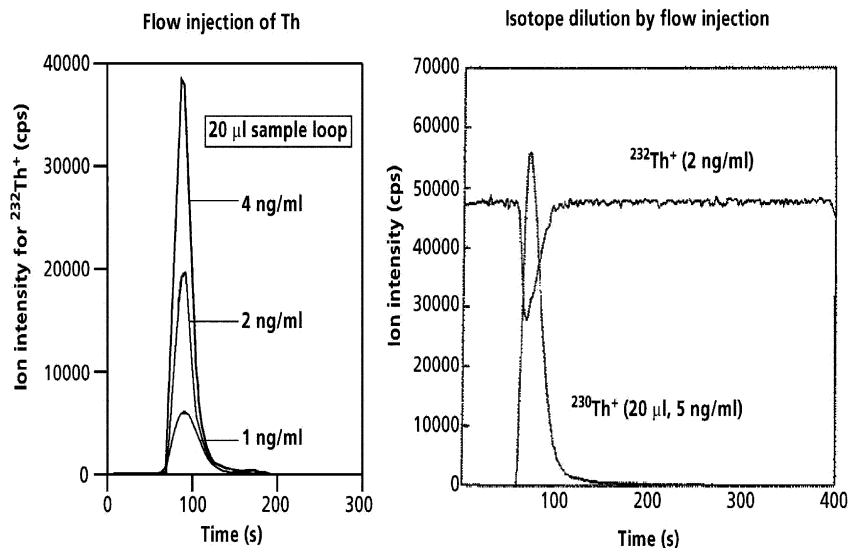


Fig. 4. Application of flow injection ICP-MS for thorium determination in radioactive waste solution (from Ref. [126] with permission).

^{232}Th in small volumes of aqueous solution. In the left part of Fig. 4, transient signals for 1, 2 and 4 ng l^{-1} (at a sample loop of 20 μl) solutions are demonstrated. The flow injection isotope dilution technique (right part of Fig. 4) was developed for the accurate determination of radionuclide concentration. In this experiment a ^{232}Th solution (continuous flow) was spiked with 20 μl of 5 $\mu\text{g l}^{-1}$ high-enriched ^{230}Th (99.85%) for quantitative Th determination in radioactive solutions [126]. Lower analyte concentration in radioactive waste solution can be measured by more sensitive ICP-SFMS. For example, transient signals of a ^{237}Np standard solution (sample loop: 20 μl ; Np concentration: 10 and 100 pg ml^{-1}) were measured with a precision of 2.0 and 1.6% (R.S.D., $N=5$), respectively [5]. Another possibility of analyzing small quantities of sample is the application of electrothermal vaporization-ICP-MS for the determination of long-lived radioisotopes, which is described in Ref. [128].

2.7. Laser ablation inductively coupled plasma mass spectrometry

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 $\lambda/4=266\text{ nm}$) in an inert gas atmosphere (e.g. Ar) under normal pressure and postionization of evaporated and ablated material in an inductively coupled plasma of the ion source of an ICP-MS. 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. In our laboratory a noncommercial and a commercial laser ablation system were coupled to a quadrupole-based ICP-MS ('ELAN 6000', Perkin Elmer SCIEX, Canada), a collision cell ICP-QMS (Platform, Micromass) and a double-focusing sector field mass spectrometer ('ELEMENT', Finnigan MAT, Germany) for the characterization of radionuclides in geological samples and solid radioactive waste materials [11,35,36,41,45]. For example, for the determination of long-lived radionuclides in nonconducting materials a synthetic

Table 8

Estimated limits of quantification of LA-ICP-MS for actinide radionuclides deposited on stainless steel plates after chemical separation [129]

Isotope	Half-life (years)	LOQ (g g^{-1})	
		LA-ICP-MS	Alpha spectrometry
^{230}Th	7.54×10^4	3.8×10^{-15}	2.9×10^{-6}
^{232}Th	1.41×10^{10}	6.8×10^{-15}	2.8×10^{-11}
^{233}U	1.59×10^5	3.8×10^{-15}	1.4×10^{-6}
^{234}U	2.44×10^5	3.8×10^{-15}	8.8×10^{-7}
^{235}U	7.04×10^8	4.9×10^{-15}	3.9×10^{-10}
^{236}U	2.34×10^7	4.0×10^{-15}	9.5×10^{-8}
^{238}U	4.47×10^9	7.1×10^{-15}	8.8×10^{-11}
^{237}Np	2.14×10^6	3.8×10^{-15}	1.0×10^{-7}
^{239}Pu	2.41×10^4	3.9×10^{-15}	9.0×10^{-6}
^{240}Pu	6.56×10^3	3.7×10^{-15}	3.1×10^{-5}
^{241}Pu	1.49×10^1	3.8×10^{-15}	1.4×10^{-2}
^{242}Pu	3.87×10^5	3.6×10^{-15}	5.1×10^{-7}
^{244}Pu	8.26×10^7	3.6×10^{-15}	2.4×10^{-9}
^{241}Am	4.32×10^2	3.7×10^{-15}	4.7×10^{-4}
^{243}Am	7.37×10^3	3.6×10^{-15}	2.7×10^{-5}

laboratory standard with a concrete matrix was doped with low levels of long-lived radionuclides (e.g. ^{99}Tc , ^{129}I , ^{232}Th , ^{233}U , ^{237}Np , ^{238}U). The detection limits determined for Tc, U and Np in a blank concrete sample were in the low picogram per gram concentration range. The detection limits are lower by more than one order of magnitude using double-focusing sector field ICP-MS (Element) in comparison to quadrupole LA-ICP-MS (ELAN 6000) [36]. The capability of LA-ICP-MS for determining long-lived radionuclides for trace, ultratrace and isotope analysis in solid materials is discussed in Ref. [45].

Pu isotope ratios and americium were determined in moss samples which were collected from

the eastern Italian Alps (1500 m a.s.l.). The frozen samples were cut into 1–2 cm sections and analyzed separately to obtain the distribution curves of vertical concentrations. For plutonium and americium isotope analysis 1–2 g of the samples were ashed, leached, separated with respect to analytes and analyzed by alpha spectrometry and LA-ICP-MS after the plutonium or americium had been electroplated on a stainless steel disk [129]. Estimated limits of quantification of LA-ICP-MS for actinide radionuclides deposited on stainless steel plates after chemical separation are summarized in Table 8. For the longest-lived radionuclides in moss samples, lower limits of determination at $10^{-15} \text{ g g}^{-1}$ concentration level

Table 9

Determination of $^{234}\text{U}/^{238}\text{U}$ and $^{236}\text{U}/^{238}\text{U}$ in isotope standard solutions (CCLU-500 and NIST U-020, U concentration = 10 ppb) deposited on stainless steel targets by LA-ICP-SFMS [129]

Isotope standard	Measured IR	R.S.D. (%) ($n=6$)	Certified IR	Accuracy (%)
$^{234}\text{U}/^{238}\text{U}$				
CCLU-500	1.1099×10^{-2}	1.2	1.1122×10^{-2}	-0.21
NIST U-020	1.293×10^{-4}	2.7	1.2756×10^{-4}	1.4
$^{236}\text{U}/^{238}\text{U}$				
CCLU-500	2.77×10^{-3}	1.3	2.789×10^{-3}	-0.67
NIST U-020	1.639×10^{-4}	2.7	1.6856×10^{-4}	-2.8

were found compared to those of alpha spectrometry. The accuracy of LA-ICP-MS measurements was investigated on isotope standard reference materials deposited on steel targets (Table 9). The anthropogenic radionuclide concentrations (^{239}Pu , ^{240}Pu and ^{241}Am) in the samples are extremely low and these mosses appeared to be particularly suitable for investigating atmospheric contamination with actinides and providing a record of the history of atmospheric fallout. The $^{240}\text{Pu}/^{239}\text{Pu}$ 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 sixties. The analysis of vertical distribution of different plutonium nuclides in moss profiles collected in Belluno province yielded a correlation of maximum specific activity of ^{239}Pu and ^{240}Pu with the maximum nuclear fallout from nuclear weapon tests in the 1960s [129].

Further applications of LA-ICP-MS for the trace, ultratrace and isotope analysis of long-lived radionuclides were discussed in Ref. [45].

3. Precise measurements of isotope ratios by ICP-MS

Isotope ratio measurements of radiogenic elements are of great importance in the nuclear industry, where TIMS has occupied a favored position in the last few decades for routine measurements (e.g. quality assurance of fuel material with respect to isotopic composition of U and Pu; also for characterization of nuclear materials from reprocessing plants and radioactive waste control). Callis and Abernathy [52] reported on the development of a rapid high-precision analytical technique for the determination of isotope ratios of uranium and plutonium by total sample volatilization using multiple-filament TIMS with a commercial multicollector instrument (VG-354, VG Isotopes). Run-to-run reproducibilities of $<0.02\%$ R.S.D. have been obtained for isotope ratios of U and Pu. At present TIMS is being increasingly replaced for precise isotope ratio measurements by ICP-MS due to its excellent sensitivity and good R.S.D. [9,53,61,130,131]. In particular, ICP-MS

has been applied more and more frequently in recent years for environmental monitoring of actinides and evaluation of the contamination sources (nuclear weapons tests, nuclear power or reprocessing plants accidents).

The state of the art in precise and accurate isotope ratio measurements by ICP-MS and LA-ICP-MS was reviewed recently in Ref. [11]. ICP-MS allows the determination of uranium and plutonium isotope ratios including $^{236}\text{U}/^{238}\text{U}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ at the ultratrace level in small amounts of soil samples or hot particles [13,15,16]. Depleted uranium ($^{235}\text{U}/^{238}\text{U}=0.00202$) was determined in penetrator samples and contaminated soil samples from Kosovo by ICP-SFMS and α -spectrometry (after analyte separation) in good agreement. ^{236}U ($3.1 \times 10^{-5} \text{ g g}^{-1}$) and ^{241}Am ($1.7 \times 10^{-12} \text{ g g}^{-1}$) have also been detected in penetrator samples, which indicates the previous existence of neutron-related processes and points to a possible presence of spent reactor uranium in munitions [15,132]. Isotope analysis of depleted uranium in uranium ammunitions and contaminated soil samples collected during the Kosovo conflict was described also in Refs. [132,133]. The result of Pu isotope analysis [$^{240}\text{Pu}/^{239}\text{Pu}=0.35 \pm 0.1$ at Pu concentration of $(5.5 \pm 1.1) \times 10^{-13} \text{ g g}^{-1}$] on a soil sample from Kosovo indicates a mixed fallout including spent reactor fuel due to the Chernobyl nuclear power plant accident in 1986 and plutonium due to nuclear weapons test in the 1960s [15]. Isotope analysis of uranium and plutonium can also be used for estimating the burn-up of spent uranium in contaminated environmental samples as described in Ref. [125]. Table 10 summarizes the results of calculating the percentage of spent uranium (%) in spent/natural uranium mixture in soil samples for different depths on the basis of ICP-MS measurements using instruments with single ion detection and multiple ion collectors. The maximum level of contamination of soil samples with spent uranium on the soil surface is demonstrated. With increasing depth the contamination of soil samples with spent uranium decreases.

$^{240}\text{Pu}/^{239}\text{Pu}$ isotope ratios in marine samples from areas affected by nuclear weapon tests or nuclear reprocessing plants and in surface soils from Marshall Island measured by ICP-MS has

Table 10
Results of calculation of spent uranium portion (%) in spent/natural uranium mixture in soil samples

Depth (cm)	Calculated from results of							
	Single ion detector ICP-SFMS				MC-ICP-MS			
	Via $^{235}\text{U}/^{238}\text{U}$ (R.S.D., %)		Via $^{236}\text{U}/^{238}\text{U}$ (R.S.D., %)		Via $^{235}\text{U}/^{238}\text{U}$ (R.S.D., %)		Via $^{236}\text{U}/^{238}\text{U}$ (R.S.D., %)	
0–5	61.2	(5.0)	67.5	(1.8)	61.7	(0.4)	67.5	(0.3)
5–10	4.0	(64)	5.3	(5.7)	4.4	(7.9)	5.4	(0.6)
10–15	2.0	(120)	1.64	(6.2)	–		1.63	(0.6)

been reported in Refs. [134,135], respectively. A wide range of $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratios of 0.065 (weapon grade Pu collected on Runit Island)–0.306 (contamination of BRAVO thermonuclear test, 1954, Bikini atoll) were found. The variation can be related to specific events during the nuclear weapon testing program [135].

Ketterer et al. [136] investigated naturally occurring radioactive material of ^{238}U , ^{235}U and ^{232}Th which is released into the environment from many anthropogenic sources by quadrupole ICP-MS after uranium and thorium separation and enrichment by selective extraction. $^{234}\text{U}/^{238}\text{U}$ was determined in natural waters after two stage extraction with Chelex 20 and UTEVA (sample amount: 15–25 μgU) with a precision of 0.3–0.5%. A correlation of $^{241}\text{Pu}/^{239}\text{Pu}$ and $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio was found by the study of nuclear fallout in environmental samples. Low isotope ratios are evidence of global fallout, higher ratios were detected in Chernobyl-derived Pu ($^{240}\text{Pu}/^{239}\text{Pu} \approx 0.3\text{--}0.35$) in forest soils from Poland [137].

Characterization of airborne uranium and thorium contamination in Northern England was described by Bellis et al. [24,138]. The authors measured significant enrichments of the natural $^{235}\text{U}/^{238}\text{U}$ ratio in tree barks near the nuclear installations after bark digestion using quadrupole ICP-MS. Howe et al. [113] found a contamination of sediments (Rivacre Brook) from the vicinity of a uranium enrichment plant with ^{235}U enriched uranium, via isotope ratio measurements in sequential extracts using ICP-MS.

Mass spectrometric techniques are also increasingly being applied for the precise and accurate determination of $^{235}\text{U}/^{238}\text{U}$ isotope ratios at the

trace and ultratrace level in medical samples, such as urine, in order to demonstrate possible contamination with uranium [25,28,139–143]. Inkret et al. [130] discussed applications of TIMS to the sensitive detection of ^{239}Pu and ^{240}Pu intakes. The determination of Pu concentration in urine samples yielded an average measurement uncertainty of 3.8 $\mu\text{Bq } 24 \text{ h}^{-1}$, a 40-fold improvement over the measurement uncertainties associated with radiochemistry and α -spectroscopy analytical methods. In order to reduce possible contamination problems during sample preparation an analytical method using LA-ICP-MS was developed in our laboratory for sensitive isotope ratio measurements on urine samples after deposition on a quartz substrate [144].

A determination of Pu isotope ratios at the femtogram to nanogram level by multicollector ICP-MS with hexapole collision cell (Isoprobe, Micromass) using the $^{236}\text{U} + ^{233}\text{U}$ double spike technique in order to correct for instrumental mass bias and instrumental drift was described by Taylor et al. [9]. The results of isotope ratio measurements are compared with those of TIMS in Fig. 5 and demonstrate the capability of powerful ICP-MS techniques for extreme analysis.

Thorium and uranium isotope ratios in low concentration geological materials ($< 0.1 \mu\text{g g}^{-1}$) by MC-ICP-MS ('Nu Plasma' from Nu Instruments using an Aridus microconcentric nebulizer with desolvator) were determined by Turner et al. [145]. Isotope ratio measurements of $^{230}\text{Th}/^{232}\text{Th}$ — 6×10^{-6} (at Th concentration: $5 \mu\text{g l}^{-1}$) were performed with a precision of 1.1%.

Stirling et al. [146] discussed the application of laser ablation multicollector ICP-MS to certified

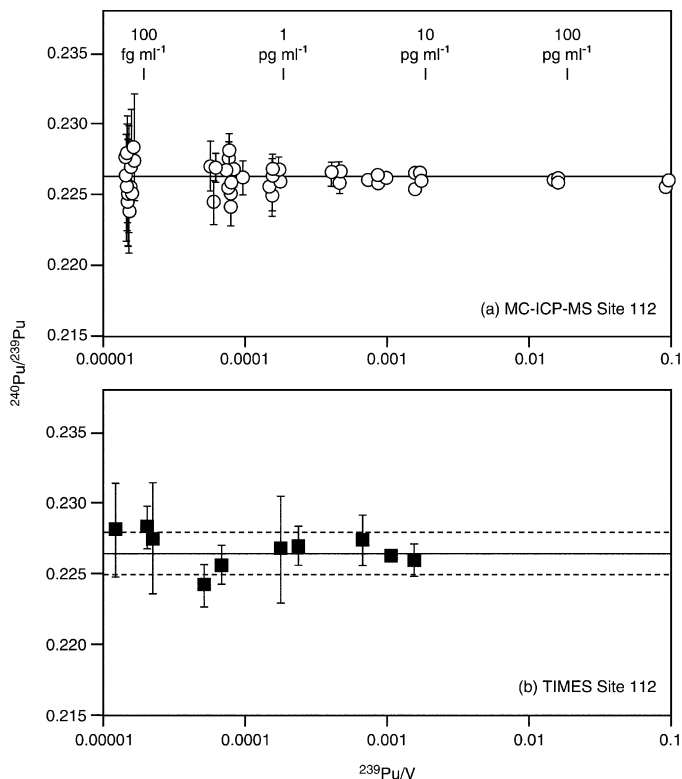


Fig. 5. Plutonium isotope ratio analysis at femtogram to nanogram levels by MC-ICP-CC-MS vs. TIMS (from Ref. [9] with permission).

glass standards and naturally occurring opal for in situ uranium and thorium isotopic analysis. The precision of isotope ratio measurements of long-lived radionuclides obtained by ICP-QMS and double-focusing sector field ICP-MS with single ion collector and MC-ICP-MS together with different applications has been demonstrated in several papers [11,87,147–156]. Recently, the monthly plutonium deposition fallout collected in Tsukuba (Japan) was analyzed using the sector field ICP-MS ‘PlasmaTrace’ by Hirose et al. [157].

Selected applications of mass spectrometry for the determination of isotope ratios are summarized in Table 11.

4. Conclusions

Inorganic mass spectrometric techniques of solid samples allow the direct determination of long-

lived radionuclides in the picogram per gram range with a minimum of sample preparation. ICP-MS is an excellent tool for the analysis of aqueous solutions, especially with on-line coupling techniques (ETV, HPLC, ion chromatography, flow injection) achieving detection limits in the sub-femtogram per milliliter range. A wide variety of applications demonstrates the excellent capability of inorganic mass spectrometry techniques for determining very low levels of radioactive nuclides, due to their low detection limits, for evidence of contamination from radioactive waste in the environment (in biological and medical samples, waters or geological materials).

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.

Table 11
Application of mass spectrometry in isotopic measurements

Samples	Method and Equipment	Isotopic ratios	Precision of isotopic analysis (at concentration)	References
Standard solutions	ICP-SFMS 'Plasma 54' prototype	$^{235}\text{U}/^{238}\text{U}$	0.03 % (1 mg l ⁻¹)	Taylor et al. [147]
Standard solutions Waste samples	ICP-SFMS 'ELEMENT'	$^{240}\text{Pu}/^{239}\text{Pu}$ $^{230}\text{Th}/^{232}\text{Th} = 10^{-3}$	2.0 % (Pu: 0.1 ng l ⁻¹ , 50 fg) 0.34% (5 ng l ⁻¹)	Becker and Dietze [7]
Nuclear samples	ICP-QMS, 'ELAN 5000' on-line ion chromatography	$^{135}\text{Cs}/^{138}\text{Cs}$ $^{136}\text{Cs}/^{138}\text{Cs}$	0.92% (50 µg l ⁻¹) 0.94% (50 µg l ⁻¹)	Barrero Moreno et al. [150]
Standard solutions	ICP-SFMS, 'Plasma 54'	$^{235}\text{U}/^{238}\text{U}$	0.014% (U: 1 mg l ⁻¹)	Walder and Freedmann [151]
Geological samples	ICP-SFMS 'Plasma 54'	$^{230}\text{Th}/^{232}\text{Th}$ $^{234}\text{U}/^{238}\text{U}$ (0.000054)	0.04% 0.12%	Luo et al. [152]
Environmental samples (sediments, soil, needles)	ICP-MS, 'HP 4500' 'PMS-2000'	$^{240}\text{Pu}/^{239}\text{Pu}$	4.1% (at pg ml ⁻¹ level)	Momoshima et al. [153]
Environmental samples	ICP-SFMS 'PlasmaTrace 2'	$^{240}\text{Pu}/^{239}\text{Pu}$	2%	Stürup et al. [154]
Soil samples (Chernobyl fallout)	ICP-SFMS 'ELEMENT' after extraction	$^{236}\text{U}/^{238}\text{U}$, $^{240}\text{Pu}/^{239}\text{Pu}$, $^{234}\text{U}/^{238}\text{U}$, $^{235}\text{U}/^{238}\text{U}$	3.5% (Pu: $\approx 10^{-13}$ g g ⁻¹)	Boulyga and Becker [125]
Tree barks (nuclear fuel fabrication plant)	ICP-QMS 'HP 4500'	$^{235}\text{U}/^{238}\text{U}$	<1%	Bellis et al. [24,138]
Moss (environmental monitor for nuclear fallout)	LA-ICP-SFMS after separation and electrolytic deposition	$^{240}\text{Pu}/^{239}\text{Pu}$	1.4% (Pu: $\approx 10^{-13}$ g g ⁻¹)	Boulyga et al. [129]

List of abbreviation

AMS	accelerator mass spectrometry
CE	capillary electrophoresis
DIHEN	direct injection high-efficiency nebulizer
ETV	electrothermal vaporization
GDMS	glow discharge mass spectrometry
d.c. GDMS	direct current glow discharge mass spectrometry
r.f. GDMS	radio frequency glow discharge mass spectrometry
HPLC	high-performance liquid chromatography
ICP-MS	inductively coupled plasma mass spectrometry
ICP-QMS	quadrupole based inductively coupled plasma mass spectrometry
ICP-SFMS	sector field inductively coupled plasma mass spectrometry
MC-ICP-MS	multiple ion collectors inductively coupled plasma mass spectrometry
LA-ICP-MS	laser ablation inductively coupled plasma mass spectrometry
LLRW	long-lived radioactive waste
MCN	microconcentric nebulizer
RIMS	resonance ionization mass spectrometry
SIMS	secondary ion mass spectrometry
SNMS	secondary neutral mass spectrometry
TIMS	thermal ionization mass spectrometry
TOF	time of flight
USN	ultrasonic nebulizer

References

- [1] J.S. Becker, H.-J. Dietze, Mass spectrometry of long-lived radionuclides, in: A. Meyers (Ed.), *Encyclopedia Analytical Chemistry*, Wiley, 2000, pp. 12947–12961.
- [2] R. Henry, D. Koller, M. Liezers, O.T. Farmer, C. Barinaga, D.W. Koopenaal, J. Wacker, New advances in inductively coupled plasma mass spectrometry (ICP-MS) for routine measurements in the nuclear industry, *J. Radioanal. Nucl. Chem.* 249 (2001) 103–108.
- [3] J.S. Becker, ICP-MS: determination of long-lived radionuclides, *Spectrosc. Europe* 14 (6) (2002) 8–16.
- [4] J.S. Crain, Applications of inductively coupled plasma mass spectrometry in environmental radiochemistry, *Atom. Spectrosc. Perspect.* 11 (1996) 30–39.
- [5] J.S. Becker, H.-J. Dietze, Determination of long-lived radionuclides by double-focusing sector field ICP mass spectrometry, *Adv. Mass Spectrom.* 14 (1998) 681–689.
- [6] C.K. Kim, R. Seki, S. Morita, S. Yamasaki, A. Tsumura, Y. Igarashi, M. Yamamoto, Application of high-resolution inductively coupled plasma mass spectrometry to the measurements of long-lived radionuclides, *J. Anal. Atom. Spectrom.* 6 (1991) 205–209.
- [7] J.S. Becker, H.-J. Dietze, Application of double-focusing sector field ICP mass spectrometry with shielded torch using different nebulizers for ultratrace and precise isotope analysis of long-lived radionuclides, *J. Anal. Atom. Spectrom.* 14 (1999) 1403–1500.
- [8] J.S. Becker, H.-J. Dietze, Precise isotope ratio measurements for uranium, thorium and plutonium by quadrupole-based inductively coupled plasma mass spectrometry, *Fresen. J. Anal. Chem.* 364 (6) (1999) 482–488.
- [9] R.N. Taylor, T. Warneke, J.A. Milton, I.W. Croudace, P.E. Warwick, R. Nesbitt, Plutonium isotope ratio analysis at femtogram to nanogram levels by multicollector ICP-MS, *J. Anal. Atom. Spectrom.* 16 (2001) 279–284.
- [10] H. Geckeis, Th. Ngo Manh, M. Bouby, J.I. Kim, Aquatic colloids relevant to radionuclide migration: characterization by size fractionation and ICP-mass spectrometric detection, *Colloids Surf. A: Physicochem. Eng. Aspects* 217 (2003) 101–108.
- [11] J.S. Becker, State of the art in isotope ratio measurements by inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 17 (2002) 1172–1185.
- [12] A.G. Adriaens, J.D. Fassett, W.R. Kelly, D.S. Simons, F.C. Adams, Determination of uranium and thorium concentrations in soils: comparison of isotope dilution-secondary ion mass spectrometry and isotope dilution-thermal ionization mass spectrometry, *Anal. Chem.* 64 (1992) 2945–2950.
- [13] S.F. Boulyga, J.S. Becker, Determination of uranium isotopic composition and ^{236}U content in soil samples and hot particles using inductively coupled plasma mass spectrometry, *Fresen. J. Anal. Chem.* 370 (2001) 612–617.
- [14] M. Betti, Environmental monitoring of radioisotopes by mass spectrometry and radiochemical methods in urban areas, *Microchem. J.* 67 (2000) 363–373.
- [15] S.F. Boulyga, C. Testa, D. Desideri, J.S. Becker, Optimization and application of ICP-MS and alpha spectrometry for determination of isotopic ratio of depleted uranium and plutonium in samples collected in Kosovo, *J. Anal. Atom. Spectrosc.* 16 (2001) 1283–1289.
- [16] S.F. Boulyga, J.L. Matusevich, V.P. Mironov, V.P. Kudrjashov, L. Halicz, I. Segal, J.A. McLean, A. Montaser, J.S. Becker, Determination of $^{236}\text{U}/^{238}\text{U}$ isotope ratio in contaminated environmental samples using different ICP-MS instruments, *J. Anal. Atom. Spectrom.* 17 (2003) 958–964.
- [17] E.H. Bailey, A.J. Kemp, V. Ragnarsdottir, Determination of uranium and thorium in basalts and uranium in aqueous solution by inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 8 (1993) 551–556.
- [18] N.E. Bibler, W.F. Kinard, W.T. Boyce, C.J. Coleman, Determination of long-lived fission and actinides in Savannah river site HLW sludge and glass for waste acceptance, *J. Radioanal. Nucl. Chem.* 234 (1998) 159–163.
- [19] A.E. Eroglu, C.W. McLeod, K.S. Leonard, D. McCubbin, Determination of technetium in sea-water using ion exchange and inductively coupled plasma mass

- spectrometry with ultrasonic nebulization, *J. Anal. Atom. Spectrom.* 13 (1998) 875–878.
- [20] A.E. Eroglu, C.W. McLeod, K.S. Leonard, D. McCubbin, Determination of plutonium in seawater using co-precipitation and inductively coupled plasma mass spectrometry with ultrasonic nebulization, *Spectrochim. Acta, Part B* 53 (1998) 1221–1233.
- [21] H.N. Edmonds, S.B. Moran, J.A. Hoff, J.N. Smith, R.L. Edwards, Protactinium-231 and thorium-230 abundances and high scavenging rates in the Western Arctic Ocean, *Science* 280 (1998) 405–407.
- [22] M. Nunnemann, N. Erdmann, H.-U. Hasse, G. Huber, J.V. Kratz, P. Kunz, A. Mansel, G. Passler, O. Stetzer, N. Trautmann, A. Waldek, Trace analysis of plutonium in environmental samples by resonance ionization mass spectroscopy (RIMS), *J. Alloys Comp.* 271–273 (1998) 45–48.
- [23] L.L. Crain, J.S. Smith, J.A. Yaeger, J.A. Alvarado, Determination of long-lived actinides in soil leachates by inductively coupled plasma mass spectrometry, *J. Radioanal. Nucl. Chem.* 194 (1995) 133–139.
- [24] D. Bellis, R. Ma, N. Bramall, C.W. McLeod, N. Chapman, K. Satake, Airborne uranium contamination—as revealed through elemental and isotopic analysis of tree bark, *Environ. Pollut.* 114 (2001) 383–387.
- [25] J.S. Becker, M. Burow, S.F. Boulyga, C. Pickhardt, P. Hille, P. Ostapczuk, Determination of uranium and thorium concentration and isotope ratios at trace and ultratrace level in urine by ICP-MS, *Atom. Spectrosc.* 25 (2002) 177–180.
- [26] A. Amaral, C. Cossonnet, P. Galle, The use of secondary ion mass spectrometry in radiotoxicology, *Radiat. Prot. Dosimet.* 79 (1998) 137–140.
- [27] P. Roth, W. Werner, I. Wendler, P. Schramel, Variation of natural ^{232}Th excretion in non-exposed persons, *J. Radioanal. Nucl. Chem.* 226 (1997) 285–287.
- [28] M. Halidman, M. Baduraux, A. Eastgate, P. Froidvaux, S. O'Donovan, D. Von Gunten, O. Zoller, Determining picogram quantities of uranium in urine by isotope dilution inductively coupled plasma mass spectrometry. Comparison with α -spectrometry, *J. Anal. Atom. Spectrom.* 16 (2001) 1364–1369.
- [29] F. Chartier, M. Aubert, M. Pilier, Determination of Am and Cm in spent nuclear fuels by isotope dilution inductively coupled plasma mass spectrometry and isotope dilution thermal ionization mass spectrometry after separation by high-performance liquid chromatography, *Fresen. J. Anal. Chem.* 364 (1999) 320–327.
- [30] M. Betti, Use of ion chromatography (ICP-MS) for the determination of fission products and actinides in nuclear applications, *J. Chromatogr. A* 789 (1997) 369–379.
- [31] W. Kerl, J.S. Becker, W. Dannecker, H.-J. Dietze, Application of on-line HPLC-ICP-MS for the determination of the nuclide abundances of lanthanides produced via spallation reactions in an irradiated tantalum target of a spallation neutron source, *Fresen. J. Anal. Chem.* 362 (1998) 433–439.
- [32] J.I. Garcia Alonso, Determination of fission products and actinides by inductively coupled plasma mass spectrometry using isotope dilution analysis: a study of random and systematic errors, *Anal. Chim. Acta* 312 (1995) 57–78.
- [33] J.S. Becker, H.-J. Dietze, J.A. McLean, A. Montaser, Ultratrace and isotope analysis of long-lived radionuclides by inductively coupled quadrupole mass spectrometry using a direct injection high efficiency nebulizer, *Anal. Chem.* 71 (1999) 3077–3084.
- [34] J.I. Garcia Alonso, D. Thoby-Schultendorff, B. Giovanonne, J.-P. Glatz, G. Pagliosa, L. Koch, Characterization of spent nuclear fuel dissolver solutions and dissolution residues by inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 9 (1994) 1209–1215.
- [35] J.S. Becker, M. Gastel, D. Tenzler, H.-J. Dietze, LA-ICP-MS for trace analysis of long-lived radionuclides in solid non-conducting radioactive waste samples, *Adv. Mass Spectrom.* 14, MoPo141 (1998).
- [36] M. Gastel, J.S. Becker, H.-J. Dietze, Determination of long-lived radionuclides in solid non-conducting radioactive waste materials by LA-ICP-MS, *Spectrochim. Acta B* 52 (1997) 2051–2059.
- [37] B. Beer, K.G. Heumann, Trace analyses of U, Th and other heavy metals in high purity aluminium with isotope dilution mass spectrometry, *Fresen. J. Anal. Chem.* 343 (1992) 741–745.
- [38] P. Herzner, K.G. Heumann, Ultratrace analysis of U, Th, Ca and selected heavy metals in high-purity refractory metals with isotope dilution mass spectrometry, *Microchim. Acta* 106 (1992) 127–135.
- [39] M. Fukuda, Y. Sayama, Determination of traces of uranium and thorium in (Ba, Sr)TiO₃ ferroelectrics by inductively coupled plasma mass spectrometry, *Fresen. J. Anal. Chem.* 357 (1997) 647–651.
- [40] J.S. Becker, Applications of inductively coupled plasma mass spectrometry and laser ablation inductively coupled plasma mass spectrometry in material science, *Spectrochim. Acta Part B* 57 (2002) 1805–1820.
- [41] J.S. Becker, H.-J. Dietze, State of the art in inorganic mass spectrometry for analysis of high-purity materials', *Int. J. Mass Spectrom.* 228 (2003) 127–150.
- [42] U. Rohr, L. Meckel, H.M. Ortner, Ultratrace analysis of uranium and thorium in glass; Part I: ICP-MS, classical photometry and chelate-GC, *Fresen. J. Anal. Chem.* 348 (1994) 356–363.
- [43] R.A. Kerr, Yucca mountain panel says DOE lacks data, *Science* 283 (1999) 1235–1237, (detailed report in: www.ymp.gov).
- [44] T. Hirata, Soft ablation technique for laser ablation inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 12 (1997) 1337–1342.
- [45] J.S. Becker, C. Pickhardt, H.-J. Dietze, Laser ablation inductively coupled plasma mass spectrometry for the trace, ultratrace and isotope analysis of long-lived radionuclides, *Int. J. Mass Spectrom.* 203 (2000) 283–297.

- [46] C. Pickhardt, I.B. Brenner, J.S. Becker, H.-J. Dietze, Determination of trace elements in zeolites by laser ablation ICP-MS, *Fresen. J. Anal. Chem.* 368 (2000) 79–87.
- [47] M. Betti, S. Giannarelli, T. Hiernaut, G. Rasmussen, L. Koch, Detection of trace radioisotopes in soils, sediments and vegetations by glow discharge mass spectrometry, *Fresen. Z. Anal. Chem.* 355 (1996) 642–646.
- [48] L. Aldave de las Heras, E. Hmecek, O. Bildstein, M. Betti, Neptunium determination by dc glow discharge mass spectrometry (dc.-GDMS) in Irish Sea sediment samples, *J. Anal. Atom. Spectrom.* 17 (2002) 1011–1014.
- [49] M. Betti, Use of a direct current glow discharge mass spectrometer for the chemical characterization of samples of nuclear concern, *J. Anal. Atom. Spectrom.* 11 (1996) 855–860.
- [50] M. Betti, G. Rasmussen, L. Koch, Isotopic abundance measurements on solid nuclear-type samples by glow discharge mass spectrometry, *Fresen. J. Anal. Chem.* 355 (1996) 808–812.
- [51] A. Amaral, P. Galle, C. Cossonnet, D. Franck, P. Pihet, M. Carrier, O. Stephan, Perspectives of uranium and plutonium analysis in urine samples by secondary ion mass spectrometry, *J. Radioanal. Nucl. Chem.* 226 (1997) 41–45.
- [52] E.L. Callis, R.M. Abernathy, High-precision isotopic analyses of uranium and plutonium by total sample volatilization and signal integration, *Int. J. Mass Spectrom. Ion Proc.* 103 (1991) 93–105.
- [53] I.T. Platzer, *Modern isotope ratio mass spectrometry*, vol. 145 in *Chem. Anal.*, John Wiley, Chichester, 1997, pp. 1–530.
- [54] J. Rucklidge, Accelerator mass spectrometry in environmental geoscience, *Analyst* 120 (1995) 1283–1290.
- [55] C. Vockenhuber, I. Ahmad, R. Golser, W. Kutschera, V. Liechtenstein, A. Priller, P. Steier, S. Winkler, Accelerator mass spectrometry of heavy long-lived radionuclides, *Int. J. Mass Spectrom.* 223–224 (2003) 713–732.
- [56] K. Wendt, J.V. Kratz, J. Lantzsch, P. Müller, W. Northershäuser, A. Seibert, N. Trautmann, W. Waldek, K. Zimmer, Rapid ultratrace determination of $^{89,90}\text{Sr}$ in environmental samples by collinear laser resonance ionization spectrometry, *Kerntechnik* 62 (1997) 2–3.
- [57] J.S. Becker, H.-J. Dietze, Inorganic trace analysis by mass spectrometry, *Spectrochim. Acta, Part B* 53 (1998) 1475–1506.
- [58] K. Habfast, Fractionation correction and multiple collectors in thermal ionisation isotope ratio mass spectrometry, *Int. J. Mass Spectrom. Ion Proc.* 176 (1998) 133–148.
- [59] P. Herzner, K.G. Heumann, Trace determination of uranium, thorium, calcium, and other heavy metals in high-purity refractory metal silicides, niobium and silicon dioxide with isotope dilution mass spectrometry, *Anal. Chem.* 64 (1992) 2942–2944.
- [60] K.G. Heumann, Isotope dilution mass spectrometry (IDMS) of the elements, *Mass Spectrom. Rev.* 11 (1992) 41–67.
- [61] S.K. Aggarwal, H.C. Crain, Thermal ionization mass spectrometry, in: S.K. Aggarwal, H.C. Crain (Eds.), *Introduction to Mass Spectrometry*, Indian Society for Mass Spectrometry (ISMAS), 1997.
- [62] S. Grazhulene, V. Karandashev, L. Zadnepruk, V. Orlova, AAS-ETA, ICP-AES and ICP-MS analysis of high purity indium using matrix separation by analytical autoclaves of a special design, *Fresen. J. Anal. Chem.* 355 (1996) 297–299.
- [63] J.S. Becker, C. Pickhardt, H.-J. Dietze, Determination of trace elements in high-purity platinum by laser ablation inductively coupled plasma mass spectrometry using solution calibration, *J. Anal. Atom. Spectrosc.* 16 (2001) 603–606.
- [64] B. Beer, K.G. Heumann, Trace analysis of microelectronically relevant heavy metals in high-purity titanium with isotope dilution mass spectrometry, *Anal. Chem.* 65 (1993) 3199–3203.
- [65] B. Beer, K.G. Heumann, Isotope dilution mass spectrometry of microelectronically relevant heavy metal traces in high-purity cobalt, *Fresen. J. Anal. Chem.* 347 (1993) 351–355.
- [66] V.K. Panday, J.S. Becker, H.-J. Dietze, Determination of trace impurities in tantalum by inductively coupled plasma mass spectrometry after removal of the matrix by liquid–liquid extraction, *Anal. Chim. Acta* 329 (1996) 153–159.
- [67] V.K. Panday, J.S. Becker, H.-J. Dietze, Trace impurities in zircalloys by inductively coupled plasma mass spectrometry after removal of the matrix by liquid–liquid extraction, *Atom. Spectrom.* May/June (1995) 97–100.
- [68] J.S. Becker, C. Pickhardt, N. Hoffmann, H. Höcker, J.S. Becker, Multielement analysis of alkaline-resistant glass and basalt glass fibres using laser ablation ICP-MS: a useful tool in technical textile quality control, *Atom. Spectrom.* 23 (2002) 1–6.
- [69] M. Betti, New developments for the exploitation of GDMS in nuclear and environmental samples, 2003 European Conference on Plasma Spectrochemistry, Garmisch, January 12–17, 2003, Book of abstracts, p. 125.
- [70] K. Shinotsuka, M. Ebihara, Precise determination of rare earth elements, thorium and uranium in Chondritic meteorites by inductively coupled plasma mass spectrometry a comparative study with radiochemical neutron activation analysis, *Anal. Chim. Acta* 338 (1997) 237–246.
- [71] J.B. Truscott, L. Bromley, P. Jones, E.H. Evans, J. Turner, B. Fairman, Determination of natural uranium and thorium in environmental samples by ETV-ICP-MS after matrix removal by on-line solid phase extraction, *J. Anal. Atom. Spectrom.* 14 (1999) 627–631.
- [72] R. Chiappini, J.-M. Taillade, S. Brébion, Development of a high-sensitivity inductively coupled plasma mass

- spectrometer for actinide measurement in the femtogram range, *J. Anal. Atom. Spectrom.* 11 (1996) 497–503.
- [73] S. Joannon, C. Pin, Ultra-trace determination of ^{226}Ra in thermal waters by high sensitivity quadrupole ICP-mass spectrometry following selective extraction and concentration using radium-specific membrane disks, *J. Anal. Atom. Spectrom.* 16 (2001) 32–36.
- [74] P. Evans, S. Elahi, K. Lee, B. Fairman, A rapid and accurate method for the determination of plutonium in food using magnetic sector ICP-MS with an ultra-sonic nebuliser and ion chromatography, *J. Environ. Monit.* 5 (2003) 175–179.
- [75] K. Wendt, G.K. Bhomwick, B.A. Busha, G. Herrmann, J.V. Kratz, J. Lantsch, P. Müller, W. Nörtershäuser, E.W. Otten, R. Schwalbach, U.-A. Seibert, N. Trautmann, *Radiochim. Acta* 79 (1997) 183.
- [76] K. Wendt, N. Trautmann, B.A. Bushaw, Resonant laser ionisation mass spectrometry: an alternative to AMS?, *Nucl. Inst. Meth. Phys. Rev. B* 172 (2000) 162.
- [77] P. Müller, B.A. Bushaw, K. Blaum, S. Diel, Ch. Geppert, A. Nähler, N. Trautmann, W. Nörtershäuser, K. Wendt, ^{41}Ca ultratrace determination with isotopic selectivity $< 10^{12}$ by diode-based-RIMS, *Fresen. J. Anal. Chem.* 370 (2001) 508–513.
- [78] N. Erdmann, G. Herrmann, G. Huber, S. Köhler, J.V. Kratz, A. Mansel, M. Nunnemann, G. Passler, N. Trautmann, A. Turchin, A. Waldek, Resonance ionization mass spectroscopy for trace determination of plutonium in environmental samples, *Fresen. J. Anal. Chem.* 359 (1997) 378–381.
- [79] N. Trautmann, Ultratrace analysis of long-lived radioisotopes by laser resonance ionisation mass spectrometry (RIMS), in: S.K. Aggarwal (Ed.), ISMAS Silver Jubilee Symposium on Mass Spectrometry ISMAS-SJ-2003, Indian Society for Mass Spectrometry, Goa, India, January 27–31, 2003, pp. 439–451.
- [80] A.E. Litherland, *Ann. Rev. Nucl. Part. Sci.* 30 (1989) 437.
- [81] W. Kutschera, VERA, a dedicated AMS facility for ‘all’ isotopes, Proceedings of ISMAS Silver Jubilee Symposium on Mass Spectrometry, Goa, India, January 28–31, 2003, pp. 193–194.
- [82] W. Kutschera, W. Müller, ‘Isotope language’ of the Alpine iceman investigated with AMS and MS, *Nucl. Instr. Meth. B* 204 (2003) 705–719.
- [83] X.L. Zhao, L.R. Kilius, A.E. Litherland, T. Beasley, AMS measurement of environmental U-236 preliminary results and perspectives, *Nucl. Instrum. Meth. B* 126 (1997) 297–300.
- [84] L.K. Fifield, R.G. Cresswell, M.L. di Tada, T.R. Ophel, J.P. Day, A.P. Clacher, S.J. King, N.D. Priest, Accelerator mass spectrometry of plutonium isotopes, *Nucl. Instrum. Meth. B* 117 (1996) 295–303.
- [85] J.C. Vickerman, *Surface Analysis—The Principal Techniques*, Wiley, Chichester, 1998, pp. 135–214.
- [86] H. Jenett, *Sekundärneutralteilchen-Massenspektrometrie (Plasma-SNMS)*, Analytikertaschenbuch, vol. 16, Springer, Berlin, 1997, pp. 43–117.
- [87] G. Tamborini, M. Betti, V. Forcina, T. Hiernaut, B. Giovannone, L. Koch, Application of secondary ion mass spectrometry to the identification of single particles of uranium and their isotope ratio measurement, *Spectrochim. Acta Part B* 53 (1998) 1289–1302.
- [88] M. Betti, G. Tamborini, L. Koch, Use of secondary ion mass spectrometry in nuclear forensic analysis for the characterization of plutonium and highly enriched uranium particles, *Anal. Chem.* 71 (1999) 2616–2622.
- [89] N. Erdmann, M. Betti, O. Stetzer, G. Tamborini, J.V. Kratz, N. Trautmann, J. van Geel, Production of monodisperse uranium oxide particles and their characterization by scanning electron microscopy and secondary ion mass spectrometry, *Spectrochim. Acta Part B* 55 (2000) 1565–1575.
- [90] A. Montaser (Ed.), *Inductively Coupled Plasma Source Mass Spectrometry*, VCH Publishers, New York, 1998, pp. 1–950.
- [91] M. Yamamoto, K. Syarbaini, K. Kofuji, A. Tsumura, K. Komura, K. Ueno, D.J. Assinder, Determination of low-level ^{99}Tc environmental samples by high resolution ICP-MS, *J. Radioanal. Nucl. Chem.* 197 (1995) 185.
- [92] I. Platzner, S. Ehrlich, L. Halicz, Isotope ratio measurements of lead in NIST standard reference materials by multiple-collector inductively coupled plasma mass spectrometry, *Fresen. J. Anal. Chem.* 370 (2001) 624–628.
- [93] S. Ehrlich, I. Gavrieli, L.-B. Dor, L. Halicz, Direct high-precision measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in natural water, carbonates and related materials by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS), *J. Anal. Atom. Spectrom.* 16 (2001) 1389–1392.
- [94] L. Halicz, personal communication.
- [95] J.S. Becker, H.-J. Dietze, Oxide ion formation of long-lived radionuclides in double-focusing sector field ICP-MS and their analytical application, *Int. J. Mass Spectrom.* 202 (2000) 69–79.
- [96] P. Turner, T. Merren, J. Speakman, M. Haines, in: G. Holland, S.D. Tanner (Eds.), Special Publication (No. 202) of the Royal Chemical Society, Cambridge, 1997, p. 28.
- [97] I. Feldmann, N. Jakubowski, C. Thomas, D. Stüwer, Application of a hexapole collision and reaction cell in ICP-MS: analytical figures of merit and first applications, *Fresen. J. Anal. Chem.* 365 (1999) 422–428.
- [98] D.R. Bandura, V.L. Baranov, S.D. Tanner, Reaction chemistry and collisional processes in multipole devices for resolving isobaric interferences in ICP-MS, *Fresen. J. Anal. Chem.* 370 (2001) 454–470.
- [99] D.R. Bandura, V.I. Baranov, S.D. Tanner, Direct high-precision measurements of the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio in natural water, carbonates and related materials by multiple collector inductively coupled plasma mass spec-

- trometry (MC-ICP-MS), *J. Anal. Atom. Spectrom.* 15 (2000) 921–928.
- [100] S.D. Tanner, V.I. Baranov, D.R. Bandura, Reaction cells and collision cells for ICP-MS—tutorial review, *Spectrochim. Acta B* 57 (2002) 1361–1452.
- [101] S.F. Boulyga, J.S. Becker, H.-J. Dietze, Performance of ICP-MS with hexapole collision cell for determination of trace elements in bio-assays, *Mikrochim. Acta* 137 (2001) 93–103.
- [102] S.F. Boulyga, J.S. Becker, ICP-MS with hexapole collision cell for isotope ratio measurements of Ca, Fe and Se, *Fresen. J. Anal. Chem.* 370 (2001) 618–623.
- [103] J.S. Becker, H.-J. Dietze, Grundlagen und Anwendung von Gastargets zur Empfindlichkeitssteigerung massenspektrometrischer Methoden, *Isotopenpraxis* 19 (1983) 105–112.
- [104] W. Kerl, J.S. Becker, H.-J. Dietze, W. Dannecker, Determination of iodine using a special sample introduction system coupled to a double focusing sector field inductively coupled plasma mass spectrometer, *J. Anal. Atom. Spectrom.* 11 (1996) 723–726.
- [105] A. Izmer, S.F. Boulyga, J.S. Becker, Determination of ^{129}I in environmental samples by ICP-MS, European Winter Conference on Plasma Spectrochemistry, Garmisch, January 12–17, 2003, P-IS-035, Book of abstracts, p. 363.
- [106] K. Hoppstock, J.S. Becker, H.-J. Dietze, Assessment of the determination of ^{79}Se using double focusing sector field ICP-MS after hydride generation, *Atom. Spectrom.* 18 (6) (1997) 180–185.
- [107] S.F. Boulyga, J. Dombovari, J.S. Becker, H.-J. Dietze, Determination of Se in ICP-QMS, *Atom. Spectrosc.* 21 (2000) 149–155.
- [108] J.M. Barrero Moreno, M. Betti, J.I. Garcia Alonso, Determination of neptunium and plutonium in the presence of high concentrations of uranium by ion chromatography-inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 12 (1997) 355–361.
- [109] L. Perna, P. Bocci, L. Aldave de las Heras, J. De Pablo, M. Betti, Studies on simultaneous separation and determination of lanthanides and actinides by ion chromatography inductively coupled plasma mass spectrometry combined with isotope dilution technique, *J. Anal. Atom. Spectrom.* 17 (2002) 1166–1171.
- [110] J.M. Barrero Moreno, J.I.G. Alonso, P. Arbore, G. Nicolaou, L. Koch, Characterization of spent nuclear fuels by ion chromatography-inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 11 (1996) 929–935.
- [111] Y. Marumatsu, S. Uchida, K. Tagami, S. Yoshida, T. Fujikawa, Determination of plutonium concentration and its isotopic ratio in environmental materials by ICP-MS after separation using ion-exchange and extraction chromatography, *J. Anal. Atom. Spectrom.* 14 (1999) 859–865.
- [112] D. Larivière, V.N. Epov, R.D. Evans, R.J. Cornett, Determination of radium-226 in environmental samples by inductively coupled plasma mass spectrometry after sequential selective extraction, *J. Anal. Atom. Spectrom.* 18 (2003) 338–343.
- [113] S.E. Howe, C.M. Davidson, M. McCartney, Determination of uranium concentration and isotopic composition by means of ICP-MS in sequential extracts of sediment from the vicinity of uranium enrichment plants, *J. Anal. Atom. Spectrom.* 17 (2002) 407–501.
- [114] W. Kerl, *Ultrasparen- und Isotopenanalyse langlebiger Radionuklide mittels doppel-fokussierender Sektorfeld-ICP-Massenspektrometrie*, Berichte des Forschungszentrum Jülich 3605 (1998) 1–103.
- [115] J.S. Becker, G. Küppers, F. Carsugi, W. Kerl, H. Schaal, H. Ullmaier, H.-J. Dietze, Application of mass and γ spectrometry for the nuclide analysis of an irradiated tantalum target of a spallation neutron source, *Berichte des Forschungszentrum Jülich* 3272 (1997) 143–159.
- [116] W. Kerl, J.S. Becker, H.-J. Dietze, W. Dannecker, Application of on-line HPLC-ICP-MS for the determination of the nuclide abundances of lanthanides produced via spallation reactions in an irradiated tantalum target of a spallation neutron source, *Fresen. J. Anal. Chem.* 362 (1998) 433–439.
- [117] J.B. Truscott, P. Jones, B.E. Fairman, E.H. Evans, Determination of actinides in environmental and biological samples using high-performance chelation ion chromatography coupled to sector field inductively coupled plasma mass spectrometry, *J. Chromatogr. A* 928 (2001) 1–98.
- [118] E. Hertendi, Z. Szücs, J. Csongor, J. Gulyás, E. Svingor, P. Ormai, A. Fritz, J. Solymosi, I. Gresitis, N. Vajda, Z. Molnar, Proceedings of Third Regional Meeting: Nuclear Energy in Central Europe, Portoroz, Slovenia, September 16–19, 1996.
- [119] J.S. Becker, W. Kerl, H.-J. Dietze, Nuclide analysis of an irradiated tantalum target of a spallation neutron source using high performance ion chromatography and inductively coupled plasma mass spectrometry, *Anal. Chim. Acta* 387 (1999) 145–154.
- [120] J.A. Day, J.A. Caruso, J.S. Becker, H.-J. Dietze, Application of capillary electrophoresis interfaced to double focusing sector field ICP-MS for nuclide abundance determination of lanthanides produced via spallation reactions in an irradiated tantalum target, *J. Anal. Atom. Spectrom.* 15 (2000) 1343–1348.
- [121] M. Betti, L. Menichetti, J.M. Barrero Moreno, R. Fuoco, A preliminary study for the determination of long-lived radionuclides (second transition group 4-d) in environmental samples by ion chromatography inductively coupled plasma-mass spectrometry (IC-ICP-MS), *Microchem. J.* 67 (2000) 285–290.
- [122] S. Dadfarnia, C. McLeod, On-line trace enrichment and determination of uranium in waters by flow injection inductively coupled plasma mass spectrometry, *Appl. Spectrosc.* 48 (1994) 1331–1335.

- [123] M. Hollenbach, J. Grohs, S. Mamich, M. Kroft, E.R. Denoyer, Determination of technetium-99, thorium-230 and uranium-234 in soils by inductively coupled plasma mass spectrometry using flow injection preconcentration, *J. Anal. Atom. Spectrom.* 9 (1994) 927–933.
- [124] A. McLean, J.S. Becker, S.F. Boulyga, H.-J. Dietze, A. Montaser, Ultratrace analysis of long-lived radionuclides by double-focusing sector field inductively coupled plasma mass spectrometry using direct liquid introduction, *Int. J. Mass Spectrom.* 208 (2001) 193–204.
- [125] S.F. Boulyga, J.S. Becker, Isotope analysis of uranium and plutonium using ICP-MS and estimation of burn-up of spent uranium contaminated environmental samples, *J. Anal. Atom. Spectrom.* 17 (2002) 1143–1147.
- [126] J.S. Becker, R.S. Soman, K.L. Sutton, J. Caruso, H.-J. Dietze, Determination of long-lived radionuclides by inductively coupled plasma mass spectrometry using different nebulizers, *J. Anal. Atom. Spectrom.* 14 (1999) 933–937.
- [127] J.S. Becker, Determination of trace elements in small amounts of environmental samples by ICP-MS, *Can. J. Mass Spectrom.* 47 (2002) 98–108.
- [128] J.S. Alvarado, M.D. Erickson, Determination of long-lived radioisotopes using electrothermal vaporization-inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 11 (1996) 923–928.
- [129] S.F. Boulyga, D. Desideri, M.A. Meli, C. Testa, J.S. Becker, Plutonium and americium determination in mosses by laser ablation ICP-MS combined with isotope dilution technique', *Int. J. Mass Spectrom.* 226 (2003) 329–339.
- [130] W.C. Inkret, D.W. Efurud, G. Miller, D.J. Rokop, T.M. Benjamin, Application of thermal ionization mass spectrometry to the detection of ^{239}Pu and ^{240}Pu intakes, *Int. J. Mass Spectrom.* 178 (1998) 113–120.
- [131] M. Agarande, K. Mayer, P. De Bièvre, Verification of the long term stability of uranium reference solutions of low concentration, *J. Radioanal. Nucl. Chem.* 207 (1996) 395–400.
- [132] D. Desideri, M.A. Meli, C. Roselli, C. Testa, S.F. Boulyga, J.S. Becker, Determination of ^{236}U and trans-uranium elements in depleted uranium ammunition by α -spectrometry and ICP-MS, *Anal. Bioanal. Chem.* 374 (2002) 1091–1095.
- [133] U. Sansone, P.R. Danesi, S. Barbizzi, M. Belli, M. Campbell, S. Gaudino, G. Jia, R. Ocone, A. Pati, S. Rosamilia, L. Stellato, Radioecological survey at selected sites hit by depleted uranium ammunitions during the 1999 Kosovo conflict, *Sci. Total Environ.* 281 (2001) 23–35.
- [134] S.H. Lee, J. Gastaud, J.J. La Rosa, L.L.W. Kwong, P.P. Provinec, W. Wyse, L.K. Fifield, P.A. Hausladen, L.M. Di Tada, G.M. Santos, *J. Radioanal. Nucl. Chem.* 248 (2001) 757.
- [135] Y. Muramatsu, T. Hamilton, S. Uchida, K. Tagami, S. Yoshida, W. Robinson, Measurement of $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratios in soils from Marshall Islands using ICP-MS, *Sci. Total Environ.* 278 (2001) 151–159.
- [136] M.E. Ketterer, J.A. Jordan, S.C. Szechenyi, D.D. Hudson, R.R. Layman, Envirogeochemical 'NORM' wastes; quadrupole inductively coupled plasma mass spectrometric measurements of thorium and uranium isotopes, *J. Anal. Atom. Spectrom.* 15 (2000) 1573–1596.
- [137] M.E. Ketterer, K. Hafer, C. Royden, C. Link, C. Hartsock, Resolving global vs. local/regional Pu sources in the environment by sector ICP-MS, P-IS-20, European Winter Conference on Plasma Spectrochemistry, Garmisch-Partenkirchen, Germany, January 12–17, 2003, Book of abstracts, p. 348.
- [138] D. Bellis, R. Ma, C. McLeod, Characterization of airborne uranium and thorium contamination in Northern England through measurement of U, Th and $^{235}\text{U}/^{238}\text{U}$ in tree bark, *J. Environ. Monit.* 3 (2001) 198–201.
- [139] P. Krystek, R. Ritsema, Determination of uranium in urine—measurement of isotope ratios and quantification by use of inductively coupled plasma mass spectrometry, *Anal. Bioanal. Chem.* 374 (2002) 226–229.
- [140] R.S. Pappas, B.G. Ting, J.M. Jarett, D.C. Paschal, S.P. Caudill, D.T. Miller, Determination of uranium-235, uranium-238 and thorium-232 in urine by magnetic sector coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 17 (2002) 131–134.
- [141] L. Moens, F. Vanhaecke, Recent developments in and applications of precise isotope ratio measurements, European Winter Conference on Plasma Spectrochemistry, Garmisch, January 12–17, 2003, P-Is-035, Book of abstracts, p. 106.
- [142] E.A. Ough, B.J. Lewis, W. Andrews, L.G.I. Bennett, R.G.V. Hanock, K. Scott, *Health Phys.* 82 (2002) 527.
- [143] O.V. Protasova, I.A. Maksimova, V.Y. Cheprasov, A.M. Nikiforov, *Biol. Bull.* 28 (2001) 344.
- [144] J.S. Becker, M. Burow, C. Pickhardt, in preparation.
- [145] S. Turner, P. van Calsteren, N. Vigier, L. Thomas, Determination of thorium and uranium in low concentration geological materials using fixed multicollector ICPMS, *J. Anal. Atom. Spectrom.* 16 (2001) 612–615.
- [146] C.H. Stirling, J.N. Christensen, A.N. Halliday, In situ ^{238}U – ^{234}U – ^{230}Th isotopic analysis by laser ablation multiple collector ICP-MS, *Mineral. Mag., Part A* 62 (1998) 1462–1463.
- [147] P.D.P. Taylor, P. De Bievre, A.J. Walder, A. Entwistle, Validation of the analytical linearity and mass discrimination correction model exhibited by a multiple collector inductively coupled plasma mass spectrometry by means of a set of synthetic uranium isotope mixtures, *J. Anal. Atom. Spectrom.* 10 (1995) 395–398.
- [148] I.T. Platzner, J.S. Becker, H.-J. Dietze, Stability study of isotope ratio measurements for uranium and thorium by ICP-QMS, *Atom. Spectrosc.* 20 (1) (1999) 6–12.
- [149] S. Richter, A. Alonso, R. Wellum, P.D.P. Taylor, The isotopic composition of commercially available uranium

- chemical reagents, *J. Anal. Atom. Spectrom.* 14 (1999) 889–891.
- [150] J.M. Barrero Moreno, M. Betti, G. Nicolaou, Determination of caesium and its isotopic composition in nuclear samples using isotope dilution—ion chromatography-inductively coupled plasma mass spectrometry, *J. Anal. Atom. Spectrom.* 14 (1999) 875–879.
- [151] A.J. Walder, P.A. Freedman, Isotopic ratio measurement using a double-focusing magnetic sector mass analyser with an inductively coupled plasma as an ion source, *J. Anal. Atom. Spectrom.* 7 (1992) 571–575.
- [152] X. Luo, M. Rehkämper, D.-Ch. Lee, A.N. Halliday, High precision $^{230}\text{Th}/^{232}\text{Th}$ and $^{234}\text{U}/^{238}\text{U}$ measurements using energy-filtered ICP magnetic sector multiple collector mass spectrometry, *Int. J. Mass Spectrom. Ion Proc.* 171 (1997) 105–117.
- [153] N. Momoshima, H. Kakiuchi, Y. Maeda, E. Hirai, T. Ono, Identification of the contamination source of plutonium in environmental samples with isotopic ratios determined by inductively coupled plasma mass spectrometry and alpha-spectrometry, *J. Radioanal. Nucl. Chem.* 221 (1–2) (1997) 213–217.
- [154] S. Stürup, H. Dahlgard, S.C. Nielsen, High Resolution inductively coupled plasma mass spectrometry for the trace determination of plutonium isotopes and isotope ratios in environmental samples, *J. Anal. Atom. Spectrom.* 13 (1998) 1321–1326.
- [155] E.J. Wyse, S.H. Lee, J. La Rosa, P. Povined, S.J. de Mora, ICP-sector field mass spectrometry analysis of plutonium isotopes: recognizing and resolving potential interferences, *J. Anal. Atom. Spectrom.* 16 (2001) 1107.
- [156] C. Mahan, S. Bonchin, D. Figg, D. Gerth, C. Collier, Chromatographic extraction of plutonium and inorganic impurity analysis using ICP-MS and ICP-AES, *J. Anal. Atom. Spectrom.* 15 (2000) 929–935.
- [157] K. Hirose, Y. Igarashi, M. Aoyama, C.K. Kim, C.S. Kim, B.W. Chang, Recent trends of plutonium fallout observed in Japan: plutonium as a proxy for desertification, *J. Environ. Monit.* 5 (2003) 307–310.