ICP-MS: determination of long-lived radionuclides

J. Sabine Becker

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

Inductively coupled plasma mass spectrometry (ICP-MS), with its ability to provide a very sensitive multielemental determination of long-lived radionuclides at trace and ultra-trace concentration and precise isotopic analysis, has been increasingly established for several years, especially for environmental materials such as waters, geological, biological and medical samples, nuclear materials and radioactive waste.[1–4]

The determination of the radionuclide concentration (e.g. ^{238}U, ^{234}U, ^{235}U, ^{230}Th, ^{232}Th and the decay nuclides) and/or precise isotope abundances of natural radioactive elements as terrestrial sources of radioactivity is a main application field for environmental research. Geochronology (age dating) is based on the decay of ^{238}U, ^{235}U and ^{232}Th to stable ^{206}Pb, ^{207}Pb and ^{206}Pb isotopes, respectively. The U-series geochronometers have traditionally been based on measuring the activity ratios of the radiometric pairs by counting techniques.[5] Nowadays, ICP-MS yields an improvement with respect to fewer sample preparation steps together with greater precision by measuring the amount of accumulated decay products. In order to detect the isotope variation of long-lived radionuclides in natural samples (for example of ^{234}U or ^{230}Th to determine U–Th non-equilibrium) very precise and accurate isotope analysis is required. Small isotope variations of uranium in nature were determined by ICP-MS with single and multi-ion collectors, e.g. in water samples from the Sea of Galilee. For the ^{234}U/^{238}U isotope ratio a significant enrichment by a factor of 1.5 using ICP-MS was found as a result of the a decay of ^{238}U ($t_{1/2} = 4450$ Ma) via short-lived ^{234}Th and ^{234}Pa nuclides in ^{234}U.[3]

The analysis of long-lived radionuclides plays a role in health and safety control (analysis of tissues, body fluids or foods and beverages) or in high-purity materials and ceramics for microelectronic purposes,[6,7] where, in particlar, the natural a-emitting radionuclides of U and Th can disturb
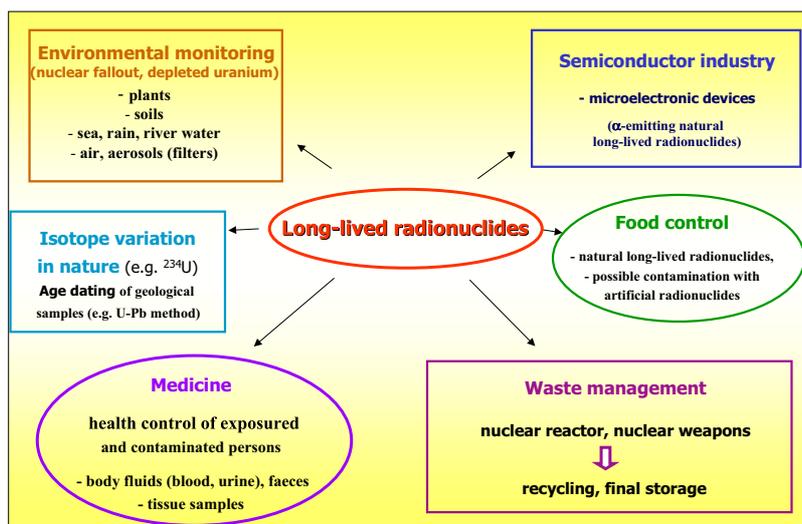
Figure 1. Application of inductively coupled plasma mass spectrometry for determination of long-lived radionuclides.

the microelectronic properties of devices.

The determination of long-lived radionuclides is, however, also of increasing importance for radioactive waste control and management of radioactive waste for final storage. Long-lived radionuclides can be used as environmental monitors in order to identify nuclear contamination or nuclear fallout.

The measurement of the contamination and enrichment of selected radioactive nuclides (e.g. ^{129}I as an environmental indicator of nuclear accidents, ^{99}Tc or ^{79}Se as fission products, ^{237}Np, ^{239}Pu, ^{240}Pu, ^{241}Am) at ultra-low concentration levels is therefore of great importance for environmental monitoring due to fallout from nuclear weapons testing, nuclear power plants (NPP) or nuclear accidents. For example, during the nuclear power plant accident at Chernobyl in 1986 about 10 tonnes of spent nuclear fuel was released into the atmosphere. Artificial actinides have contaminated the environment worldwide. The average ^{239}Pu concentration in the soil on the Earth's surface (northern hemisphere) is ~10^{-13} g g^{-1}.[8] Recently, ^{239}Pu

and ^{240}Pu were also detected in quantities of 4–5×10^{-13} g g^{-1} in Kosovo soil samples. The measured isotope ratio of ^{240}Pu/^{239}Pu = 0.35 is characteristic, thus proving the source of Pu contamination to be nuclear fallout from the NPP accident in Chernobyl. In contrast, the ^{240}Pu/^{239}Pu isotope ratio of fallout in the environment from nuclear weapons tests is 0.2 or less.[4]

In Figure 1 some important application fields for the determination of natural and artificial long-lived radionuclides are summarised. The aim of this article is to discuss the figures of merit and selected applications of ICP-MS for the determination of long-lived radionuclides in different materials.

Capability of ICP-MS

Today ICP-MS is one of the most powerful analytical methods in trace and ultra-trace analysis and has been increasingly used for the determination of long-lived radionuclides with extremely low activity, which are difficult to measure by radioanalytical methods or which require a great effort

for sample preparation. ICP-MS is used for the characterisation of long-lived radionuclides in aqueous solutions and solid samples after sample dissolution because of the simple quantification procedure via external calibration, standard addition or the isotope dilution technique in an aqueous solution. Direct determination of long-lived radionuclides in solid samples can be performed without any chemical sample preparation steps, mainly by laser ablation ICP-MS (LA-ICP-MS). For the determination of long-lived radionuclides, the multi-element capability is used as the main advantage of powerful ICP-MS and LA-ICP-MS; that means the actinides are determined quasi-simultaneously. If isobaric interferences of long-lived radionuclides with stable isotopes of impurities (e.g. ^{79}Se and ^{79}Br) or molecular ion formation ($^{238}UH^+$ and $^{239}Pu^+$) are expected, a special sample introduction system (e.g. hydride generation), matrix separation and/or a chemical enrichment of long-lived radionuclides after dissolution of solid sample is mostly required.[1,9]

At present different commercial double-focusing sector field ICP mass spectrometers with single (DF-ICP-MS) and multiple ion collection (MC-ICP-MS), e.g. "Element" (DF-ICP-MS, Finnigan MAT, Bremen, Germany), Nu Plasma from Nu Instruments (MC-ICP-MS), Neptune from Finnigan MAT (MC-ICP-MS) and quadrupole-based ICP mass spectrometers (ICP-QMS from PerkinElmer Sciex, Agilent, Thermo Elemental, Varian, Micromass) without and with collision cell are available on the analytical market. In Figure 2, a schematic of a quadrupole ICP mass spectrometer with hexapole collision cell from Micromass is shown. The advantage of this equipment is the very high sensitivity for long-lived radionuclides in the mass range >200 u (up to 27×10^9 cps ppb^{-1} using an ultrasonic nebuliser) and an improved precision in comparison to ICP-QMS without collision cell. ICP-MS with collision cell is well suited for the sensitive determination of rare long-lived radionuclides such as ^{129}I and ^{79}Se. For example, using He and H$_2$ as the collision gases in ICP-MS with a hexapole collision cell an efficient reduction of the disturbing background intensity of ^{129}Xe$^+$ ions was observed,[3] which results in a decrease of the detection limit for ^{129}I down to 3 ng L^{-1}. The determination of ^{129}I ($t_{1/2} \gg 1.6 \times 10^7$ a) is of great interest for environmental monitoring of nuclear fallout, for monitoring of radioactive emissions from nuclear facilities and for thyroid dose recon-
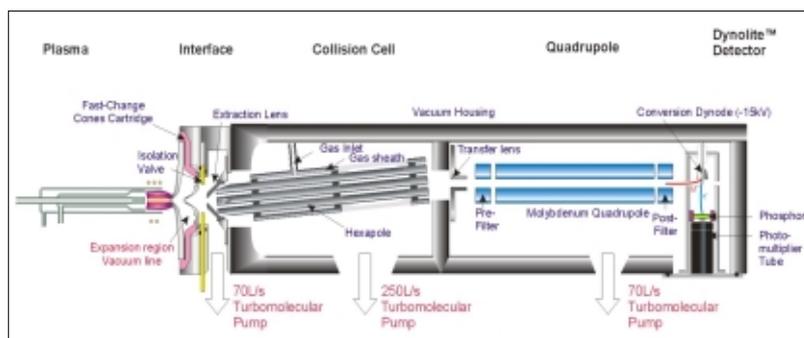
Figure 2. Schematic of a quadrupole ICP-MS with hexapole collision cell (Platform, Micromass).

Table 1. Figures of merit of different ICP mass spectrometers for determination of long-lived radionuclides.

	Detection limits ng L^{-1}	Precision for isotope Ratio measurement (RSD)
ICP-QMS	0.01–0.6	0.1–0.5%
DF-ICP-MS ($m/D\,m - 300$)	0.00004–0.005	0.02–0.1%
ICP-QMS with collision cell	0.003–0.01	0.07–0.1%
MC-ICP-MS	0.0001–0.0002	0.002–0.02%

struction in contaminated regions after the accident at Chernobyl NPP or for radioactive waste control. The application of collision cell ICP-MS allows ^{79}Se to be measured at a very low concentration level (detection limit: 5 ng L^{-1}—this is a factor of 20 better than DF-ICP-MS) because, after separation of Se analyte using hydride generation for solution introduction, disturbing argon hydride molecular ions ($^{38}Ar^{40}Ar^1H^+$) are additionally suppressed in the collision cell.

Furthermore, a single-focusing sector field ICP mass spectrometer with collision cell, e.g. Isoprobe from Micromass with multiple ion collectors, is advantageous for precise isotope ratio measurements of long-lived radionuclides.[4]

Table 1 summarises the figures of merit for the determination of uranium concentration and isotope ratios using different ICP mass spectrometers. In the low-resolution mode, the element sensitivity of commercial double-focusing sector field ICP mass spectrometers is significantly higher than conventional quadrupole ICP mass spectrometers without collision cell. The high element sensitivity and especially the low background (0.3 cps) of double-focusing sector field ICP mass spectrometers in the mass range >200 u permits ultra-trace analysis down to the sub-fg mL^{-1} concentration range.[10] Whereas with a quadrupole-based ICP mass spectrometer using a micronebuliser the detection limits of long-lived radionuclides

(^{230}Th, ^{237}Np, ^{238}U, ^{239}Pu and ^{241}Am) in aqueous solutions varied from 0.012 to 0.11 ng L^{-1}, in double-focusing sector field ICP-MS with a shielded torch the detection limits are determined down to 0.00004 ng L^{-1}.[10,11]

Table 2 summarises selected applications of ICP-MS for the determination of long-lived radionuclides in different matrices.

Microanalytical techniques

The development of microanalytical methods for the precise determination of nuclide abundances and concentrations of long-lived radionuclides at ultra-trace concentration levels in radioactive wastes and also for checking contamination in the environment is a challenging task. In order to reduce the dose to the operator and contamination of the ICP-MS instruments, microanalytical methods for the determination of long-lived radionuclides (especially in radioactive waste solution or if the environmental sample volume is extremely low) have been developed at our laboratory. For the analysis of small sample volumes, micronebulisers (Micromist, Glass Expansion, Australia),[10,11] the direct injection high efficiency nebuliser (DIHEN)[12] and the Aridus (Cetac Technologies)[9] have been increasingly used instead of highly sensitive ultrasonic nebulisers (USN),

10

Table 2. Application of mass spectrometry in trace and ultra-trace analysis of long-lived radionuclides in different samples.

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)	13
Sediments, fish samples	DF-ICP-MS 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)	14
Irradiated tantalum target of spallation neutron source	DF-ICP-MS, Element on-line with capillary electrophoresis	spallation nuclides, all lanthanides	0.72–3.9 µg L^{-1} (35 nL sample size)	15
Radioactive waste	DF-ICP-MS Element	^{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)	10
Soil samples (Kosovo)	DF-ICP-MS Element	^{236}U, ^{234}U, ^{235}U, ^{239}Pu, ^{240}Pu	1.3 × 10^{-13} g g^{-1} (^{240}Pu)	9
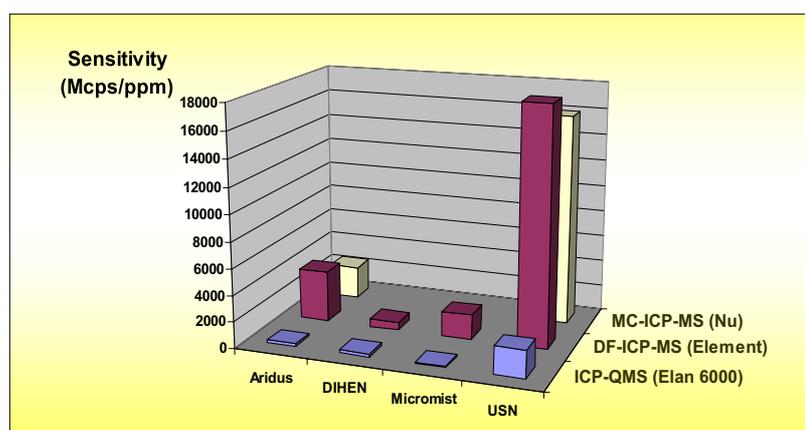
Figure 3. Comparison of different solution introduction systems using Aridus, a direct injection high efficiency nebuliser (DIHEN), Micromist, and ultrasonic nebuliser in ICP-QMS (Elan 6000), DF-ICP-MS (Element, ThermoFinnigan), Nu Plasma (Nu Instruments).

which consume high solution volumes, for determining long-lived radionuclides by solution introduction into the inductively coupled plasma of an ICP mass spectrometer. Figure 3 compares the sensitivity (Mcps ppm^{-1}) of different micronebulisers vs USN together with an ICP-QMS (Elan 6000), DF-ICP-MS with single ion collector and multicollector ICP-MS (Nu Plasma, Nu Instruments). In quadrupole ICP-MS, the sensitivity for ^{238}U$^+$ determination is about one order of magnitude lower than in sector field ICP-MS. The highest sensitivity (Mcps ppm^{-1}) was observed using the USN in double-focusing sector field ICP-MS (DF-ICP-MS). Considering the solution uptake rate for the different nebulisers used [Aridus: 0.1 mL min^{-1}; DIHEN: 0.01 mL min^{-1}, Micromist: 0.2 mL min^{-1} and USN 2 mL min^{-1} (MC-ICP-MS: 0.6 mL min^{-1})] micronebulis-

ers (DIHEN and Aridus) are advantageous. However, using the DIHEN a significantly higher uranium hydride formation rate (UH$^+$/U$^+$ ~ 1 × 10^{-4}–5 × 10^{-4} vs 3.2 × 10^{-5} using the Aridus) was observed, which can disturb the ^{236}U and ^{239}Pu determination in many samples. For the determination of ^{236}U and ^{239}Pu the Aridus micronebuliser with desolvator is the best solution introduction system at present due to high sensitivity and especially to the low hydride formation rate.[9] The application of flow injection is useful for sample introduction to measure small sample volumes of environmental samples or radioactive waste solutions in order to minimise radioactive contamination in the ICP mass spectrometer.[10,11] To handle microlitre amounts of an aqueous solution of long-lived radionuclides a commercial HPLC injection valve was coupled to a

micronebuliser (for small droplet formation) and a minicyclonic spray chamber. The small sample volume (sample loop: >1 µL) of the standard or radioactive waste solution is introduced by this HPLC injection valve into a continuous flow of 2% nitric acid. For example, a ^{237}Np standard solution (sample loop: 20 µL; Np concentration: 10 ng L^{-1} and 100 ng L^{-1}) was measured with a precision of 2.0% and 1.6% (RSD, N = 5), respectively.[10] Due to the high sensitivity of ICP-MS, the radioactive solution can be measured in an extremely high dilution at a small sample size thus minimising the dose and possibility of contamination. Compared to radiometric methods, mass spectrometric techniques offer the best detection limits for the determination of long-lived radionuclides.[1,16]

The most important problem in determining long-lived radionuclides in environmental samples (or in radioactive waste) is the appearance of isobars of radioactive and stable nuclides at the same mass with a different atomic number, causing interferences in mass spectra. Therefore a chemical separation, e.g. by high performance liquid chromatography (HPLC—for a chromatographic separation of a lanthanide mixture into the individual elements) or capillary electrophoresis (CE), before mass spectrometric measurement is the method of choice.[16–18] For example, on-line coupling of HPLC and CE together with DF-ICP-MS has been applied for the separation of lanthanides in an irradiated tantalum target from a spallation neutron source in our laboratory.[17,15] Figure 4 shows the experimental arrangement of the coupling of capillary electrophoresis with a double-focusing sector field ICP mass spectrometer and a mass spectrum of lan-
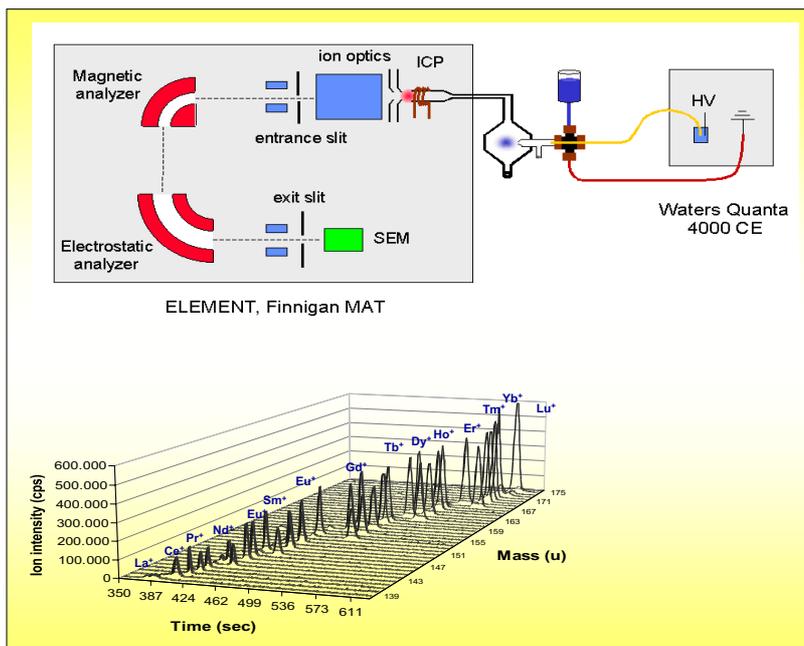
Figure 4. Schematic of coupling of CE with DF-ICP-MS Element (Finnigan, MAT) and mass spectrum of lanthanides in an irradiated tantalum target measured by CE-ICP-MS.[15]

thanides in an irradiated tantalum target measured by CE-ICP-MS. Only 35 nL of a radioactive solution (detection limits for lanthanides varied from 0.72 to 3.9 ppb) was separated in this experiment.[15]

In recent years, on-line ion chromatography ICP-MS has been increasingly used for the characterisation of radioactive materials and environmental samples using ICP-MS. Perna *et al.* reported recently the separation and determination of lanthanides and actinides in spent nuclear fuel samples by ion chromatography ICP-MS using the isotope dilution technique.[16] A further application of the isotope dilution technique—as an absolute quantification technique—in the determination of long-lived radionuclides using flow injection ICP-MS is described in Reference 11.

Precise measurements of isotope ratios

Whereas thermal ionisation mass spectrometry (TIMS) has occupied a favoured position in the last few decades for routine isotope analyses of radiogenic elements, nowadays mea-

Table 3. Isotope variation of long-lived radionuclides in different samples.

Samples	Method	Radionuclides	Isotope ratio	References
Tree bark Airborne contamination	ICP-QMS HP 4500	$^{235}U/^{238}U$	Isotope variation 0.0055–0.0097	22
Depleted uranium (DU) ammunitions	DF-ICP-MS, Element extraction chromatography a-spectrometry	$^{235}U/^{238}U$ $^{234}U/^{238}U$ $^{236}U/^{238}U$ $^{240}Pu/^{239}Pu$	0.00202 8.0×10^{-6} 3.1×10^{-5} 0.12	23
Soil samples (Kosovo) contaminated by DU	DF-ICP-MS, Element extraction chromatography a-spectrometry	$^{235}U/^{238}U$ $^{234}U/^{238}U$	0.00202 7.9×10^{-6}	9
Moss samples nuclear weapon fallout	DF-ICP-MS, Element laser ablation of electroplated Pu	$^{240}Pu/^{239}Pu$	0.2	24
Soil samples Chernobyl nuclear fallout	DF-ICP-MS, Element ICP-CC-QMS, Platform	$^{235}U/^{238}U$ $^{236}U/^{238}U$ $^{234}U/^{238}U$	0.0075–0.01 5.6×10^{-5}–9.8×10^{-4} $6.4 - 10^{-5}$–1.2×10^{-4}	25

surements by ICP-MS have been increasingly performed in the nuclear industry (e.g. quality assurance of fuel material; isotopic composition of U and Pu, reprocessing plant, nuclear material accounting and radioactive waste control). For the determination of isotope ratios within the framework of environmental monitoring, in order to identify the source of radioactive contamination, ICP-MS is the best analytical technique at present due to the high accuracy of the analytical data and excellent detection limits. Sources of radioactive contamination, e.g. as a result of nuclear fallout due to the emission of radionuclides from a nuclear power plant or NPP accident, nuclear weapons tests from the 1960s or any other contamination, e.g. in connection with the use of depleted uranium in ammunition during the Gulf War or Kosovo conflict or as passenger luggage in aircraft etc., can be detected and differentiated by accurate isotope ratio measurements.

Recently, together with C. Testa (University Urbino, Italy), we analysed depleted uranium in uranium ammunition (in penetrator samples as well as in Kosovo soil) with respect to the isotope composition of uranium and plutonium and the content of other transuranic radionuclides. In these investigations the same uranium isotope composition with respect to the $^{235}U/^{238}U$ and $^{236}U/^{238}U$ isotope ratio [with $^{235}U/^{238}U = (2.02 \pm 0.01) \times 10^{-3}$ and $^{236}U/^{238}U = (3.14 \pm 0.40) \times 10^{-6}$] was detected in both the soil and penetrator samples.[9] Furthermore, Pu and Am were found. It was surprising that the Pu detected in Kosovo soil samples (both contaminated and uncontaminated with depleted uranium) was a result of nuclear fallout from the Chernobyl

accident as demonstrated by the measured isotope ratio [$^{240}Pu/^{239}Pu$ (measured) 0.35 ± 0.10 vs Chernobyl fallout: $^{240}Pu/^{239}Pu \sim 0.39$].[9,19]

Recently, Amselfelder red wine from Kosovo was investigated in our laboratory with respect to uranium concentration and to contamination with depleted uranium by DF-ICP-MS using the microconcentric nebuliser Aridus with desolvator for solution introduction. In different red wine samples a uranium concentration of 0.145 ± 0.011 µg L^{-1} was found, which is, however, the normal background concentration. Furthermore, depleted uranium and plutonium ($<10^{-5}$ µg L^{-1}) were not detectable.[3]

Boulyga *et al*. determined uranium isotope ratios, especially of ^{236}U content in hot particles and in a multitude of soil samples from the Chernobyl

area.[20,21] The determination of ^{236}U content, which is as a result of nuclear fallout from the reactor accident in Chernobyl in 1986, was used to monitor nuclear contamination in the environment and to study the behaviour of long-lived nuclides. In all investigated soil samples collected close to Chernobyl, non-natural ^{236}U was detected—with an abundance of between 0.0972% and 0.00017%. Also for ^{234}U and ^{235}U, deviations in abundances from the table value were found. $^{234}U/^{238}U$ in Chernobyl soil samples thus varied between 0.000068 and 0.000117 (nature: 0.00006) and ^{235}U was also enriched ($^{235}U/^{238}U$: 0.00739–0.01006; table value: 0.00725). The highest contamination with nuclear spent uranium was detected on the soil surface in the neighbourhood of the NPP. We found in many

Table 4. Isotope ratio measurements of long-lived radionuclides using different ICP-MS methods.

Isotope ratio	Method	Precision (%)	Conc. (µg L^{-1})	Reference
$^{230}Th/^{232}Th \sim 0.2$	ICP-QMS	0.031[a]	10	29
$^{234}U/^{238}U \sim 0.0001$	LA-ICP-QMS	0.7	1000	27
$^{235}U/^{238}U \sim 1$	DF-ICP-MS	0.028	1	10
$^{235}U/^{238}U \sim 1$	ICP-CC-QMS	0.07	10	30
$^{232}Th/^{232}Th \sim 0.001$	DF-ICP-MS	0.35	0.005	10
$^{239}Pu/^{240}Pu \sim 0.17$	DF-ICP-MS	13	0.00001	10
$^{233}U/^{235}U \sim 1$	MC-ICP-MS	0.002	1000	31
$^{240}Pu/^{236}U \sim 10^{-7}$	MC-ICP-CC-MS	4	2230	4
$^{230}Th/^{232}Th \sim 6 \times 10^{-6}$	MC-ICP-MS	1.1	100	26

[a]long-term stability

14

experiments that the contamination of the soil sample decreased with increasing depth due to radionuclide migration in soils in the vicinity of Chernobyl. By comparing isotope ratio measurements on Chernobyl soil samples using single ion and multiple ion collection an agreement of isotope ratios was observed, whereby MC-ICP-MS demonstrated better precision by one order of magnitude in comparison to DF-ICP-MS with single ion collection. Table 3 summarises some isotope variations of long-lived radionuclides in different sample types.

The capability of isotope ratio measurements of long-lived radionuclides by ICP-QMS (without and with collision cell) and double-focusing sector field ICP-MS with single ion collector has been demonstrated in various investigations in our laboratory.[1,3,9–11,15,17,19–21,23–25]

Recently, plutonium isotope analysis at the femtogram to nanogram level was described by Taylor and co-workers[4] using MC-ICP-CC-MS (single-sector field ICP-MS with a hexapole collision cell, Isoprobe, Micromass). The authors applied the double-spike technique using a synthetic isotope mixture $^{236}U/^{233}U$ (~1) to correct instrumental mass bias and instrumental drifts. Very small $^{239}Pu/^{236}U$ and $^{240}Pu/^{236}U$ ratios down to 10^{-7} were determined with a precision of 2 and 4%, respectively. With decreasing analyte concentration the standard deviation of the isotope ratios measured by MC-ICP-CC-MS increases.[4]

In order to study small isotope ratios, the $^{230}Th/^{232}Th$ isotope ratios down to 6×10^{-6} were measured by DF-ICP-MS in our laboratory. Whereas the accuracy of small isotope ratios is sufficient, the relative standard deviation (RSD) increases with decreasing isotope ratio.[3] In our experiment for the isotope ratio of 6×10^{-6} at a Th concentration of $1\ ng\ L^{-1}$ using an ICP-SFMS with a single ion collector a precision of about 15% was observed. Turner et al.[26] reported a precision of 1.1% for MC-ICP-MS measurements of $5\ ng\ L^{-1}$ solution using the Nu Plasma.

In comparison to ICP-MS, where for solid samples a dissolution step is required, LA-ICP-MS allows a direct isotope analysis of solid samples without chemical sample preparation. Nevertheless, in spite of the advantages of LA-ICP-MS this technique was only used in a few percent of papers published on the determination of isotope ratios. Most studies were performed in geological research (e.g. for microlocal analysis or age dating). Apart from inhomogeneity problems,

fractionation effects at laser power density $<10^9$ W cm^{-2} could occur resulting in incorrect data.[27] One other problem could be possible interferences with molecular ions as demonstrated by LA-ICP-MS measurements of $^{230}Th/^{232}Th$ isotope ratios in solid radioactive waste samples in comparison to ICP-MS measurements after digestion and Th separation.[14] Where no interference problems were observed, a good agreement of isotope ratios measured by LA-ICP-MS and ICP-MS after analyte separation was found, as demonstrated for $^{235}U/^{238}U$ determination in the radioactive silt,

filter and ash samples investigated.[10] The precise isotope analysis of uranium was demonstrated in radioactive waste graphite using double-focusing sector field LA-ICP-MS. The $^{236}U/^{238}U$ isotope ratio of 10^{-4} was determined with a precision of 0.7%,[27] where the detection limit for ^{233}U in graphite matrix was found to be 1.3 pg g^{-1}.

The application of laser ablation multicollector ICP-MS for *in situ* uranium and thorium isotopic analysis to certified glass standards and naturally occurring opal is described by Stirling *et al.*[28]

Some selected applications of ICP-MS for the determination of isotope ratios of long-lived radionuclides are summarised in Table 4. The most precise isotope ratio measurements were performed by MC-ICP-MS. In contrast, DF-ICP-MS allows the smallest samples sizes to be measured with excellent detection limits in the fg mL^{-1} range and below.

Conclusions

Inductively coupled plasma mass spectrometry with detection limits in the sub-fg mL^{-1} range is an excellent tool for the determination of long-lived radionuclides in environmental and radioactive waste samples. Numerous, quite different applications demonstrate the excellent capability of ICP-MS for determining very low radioactive nuclides due to their low detection limits for the 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 ultra-trace levels is increasing, especially when multicollector and/or double-focusing sector field instruments are used.

Acknowledgements

References

1. J.S. Becker and H.-J. Dietze, "Mass spectrometry of long-lived radionuclides", in *Encyclopedia of Analytical Chemistry*, Ed by A. Meyers. John Wiley & Sons, 12947 (2000).
2. R. Henry, D. Koller, M. Liezers, O.T. Farmer, C. Barinaga, D.W. Koopenaal and J. Wacker, *J. Radioanal. Nucl. Chem.* **249,** 103 (2001).
3. J.S. Becker, *J. Anal. At. Spectrom.* **17,** 1172 (2002).
4. R.N. Taylor, T. Warneke, J.A. Milton, I.W. Croudace, P.E. Warwick and R. Nesbitt, *J. Anal. At. Spectrom.* **16,** 279 (2001).
5. J.R. De Laeter, *Applications of Inorganic Mass Spectrometry*. Wiley, New York (2001).
6. M. Fukuda and Sayama, *Fresenius J. Anal. Chem.* **357,** 647 (1997).
7. J.S. Becker, *Spectrochim. Acta B*, Special issue of the Seventh Rio Symposium on Atomic Spectrometry, 7–12 April 2002, Florianopolis – SC, Brazil, in press.
8. S.N. Begichev, A.A. Borovoj, E.B. Burlakov, A.J. Gagarinsky, V.F. Demin, A.A. Khrulev and I.L. Khodakovsky, "Radioactive release due to the Chernobyl Accident", in *Fission Product Transport Processes in Reactor Accidents*, Ed by J.T. Rogers. Hemisphere, New York, USA, p. 717 (1990).
9. S.F. Boulyga, C. Testa, D. Desideri and J.S. Becker, *J. Anal. At. Spectrom.* **16,** 1283 (2001).
10. J.S. Becker and H.-J. Dietze, *J. Anal. At. Spectrom.* **14,** 1493 (1999).
11. J.S. Becker, R.S. Soman, K. L. Sutton, J. Caruso and H.-J. Dietze, *J. Anal. At. Spectrom.* **14,** 933 (1999).
12. J.A. McLean, J.S. Becker, S.F. Boulyga and H.-J. Dietze, A. Montaser, *Int. J. Mass Spectrom.* **208,** 193 (2001).
13. J.M. Barrero Moreno, M. Betti and J.I. Garcio Alonso, *J. Anal. At. Spectrom.* **12,** 355 (1997).
14. R. Chiappini, J.-M. Taillade and S. Brébion, *J. Anal. At. Spectrom.* **11,** 497 (1996).
15. J. Day, J. Caruso, J.S. Becker and H.-J. Dietze, *J. Anal. At. Spectrom.* **15,** 1343 (2000).
16. L. Perna, F. Bocci, L. Aldave de las Heras, J. De Pablo and M. Betti, *J. Anal. At. Spectrom.* **17,** 1166 (2002)
17. W. Kerl J.S. Becker, W. Dannecker and H.-J. Dietze, *Fresenius J. Anal. Chem.* **362,** 433 (1998).
18. M. Betti, *Microchem. J.* **67,** 363 (2000).
19. S.F. Boulyga and J.S. Becker, *J. Anal. At. Spectrom.* **17,** 1143 (2002).
20. S.F. Boulyga, J.L. Matusevich, V.P. Mironov, V.P. Kudrjashov, L. Halicz, I. Segal, J.A. McLean, A. Montaser and J.S. Becker, *J. Anal. At. Spectrom.* **17,** 958 (2002).
21. S.F. Boulyga and J.S. Becker, *Fresenius J. Anal. Chem.* **370,** 612 (2001).
22. D. Bellis, R. Ma, N. Bramall, C.W. McLeod, N. Chapmana and K. Satake, *Environmental Pollution* **114,** 383 (2001).
23. D. Desideri, M.A. Meli, C. Roselli, C. Testa, S.F. Boulyga and J.S. Becker, *Anal. Bioanal. Chem.*, published as an advanced article on 16 October 2002, DOI: 10.1007/s00216-002-1575-5.
24. C. Testa, S.F. Boulyga, D. Desideri and J.S. Becker, *Int. J. Mass Spectrom.*, submitted.
25. S.F. Boulyga, J.S. Becker, J. L.Matusevitch and H.-J. Dietze, *Int. J. Mass Spectrom.* **203,** 143 (2000).
26. S. Turner, P. van Calssteren, N. Vigier and L. Thomas, *J. Anal. At. Spectrom.* **16,** 612 (2001).
27. J.S. Becker, C. Pickhardt and H.-J. Dietze, *Int. J. Mass Spectrom.* **292,** 283 (2001).
28. C.H. Stirling, J.N. Christensen and A.N. Halliday, *Mineralogical Magazine* **62A,** 1462 (1998).
29. I.T. Platzner, J.S. Becker and H.-J. Dietze, *Atom. Spectrosc.* **20,** 6 (1999).
30. J.S. Becker and H.-J. Dietze, *Fresenius J. Anal. Chem.* **364,** 482 (1999).
31. C.R. Quétel, J. Vogl, T. Prohaska, S. Nelms, P.D.P. Taylor and P. De Bievre, *Fresenius J. Anal. Chem.* **368,** 148 (2000).