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Progress in determination of long-lived radionuclides by inductively coupled plasma mass spectrometry

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ABSTRACT

Mass spectrometric methods [such as inductively coupled plasma mass spectrometry - ICP-MS and laser ablation (LA)-ICP-MS] with their ability to provide a very sensitive multielemental and precise isotopic analysis have become established for the determination of radionuclides in quite different sample materials. The determination of long-lived radionuclides is of increasing interest for the characterization of radioactive waste materials and for the detection of radionuclide contamination in environmental materials in which several radioactive nuclides are present from fallout due to nuclear weapons testing, nuclear power plants or nuclear accidents.

Due to its multielement capability, excellent sensitivity, low detection limits (up to sub pg l⁻¹ range), very good precision, easy sample preparation and simple measurement procedures ICP-MS of aqueous solutions has been increasingly applied for the ultrasensitive determination of long-lived radionuclides such as ⁹⁹Tc, ¹²⁹I, ²³⁰Th, ²³²Th, ²³⁴U, ²³⁵U, ²³⁶U, ²³⁷Np, ²³⁸U, ²³⁹Pu, ²⁴⁰Pu and ²⁴¹Am and precise isotope ratio measurements of U, Th and Pu. The application especially of micro-analytical methods [analysis of some µl by flow injection and on-line coupling techniques such as capillary electrophoresis (CE-ICP-MS) or HPLC-ICP-MS] for the precise determination of nuclide abundances and concentration of long-lived radionuclides at ultratrace concentration levels in radioactive waste and also for controlling contamination from radioactive waste in the environment is a challenging task.

Key words: Isotope ratio measurements / Inductively coupled plasma mass spectrometry/ Long-lived Radionuclides/ Trace analysis.

INTRODUCTION

The determination of long-lived radionuclides in environmental materials (waters, soils, geological, biological and medical materials) is of increasing importance. So is the determination of long-lived radionuclides of special interest for the detection of radionuclide contamination in environmental materials in which several radioactive nuclides (e.g. ⁹⁹Tc, ¹²⁹I, ²³⁶U, ²³⁷Np, ²³⁹Pu, ²⁴⁰Pu, ²⁴¹Am) are present. In particular, isotope ratios of uranium and plutonium can indicate the origin of contaminations in the environment due to nuclear weapons testing, nuclear accidents or fallout from nuclear power plants.⁽¹⁻⁶⁾ Furthermore, very sensitive, correct and precise

determination of long-lived radionuclides is required for characterizing low-radioactive materials from nuclear reactors for recycling and final storage of radioactive waste. The determination of possible isotopic variations in nature due to radioactive decays of unstable nuclides has been applied in geochronology for age determination. For such investigations precise determinations of isotopic ratios are necessary with a relative standard deviation of better than 0.05%. Thermal ionization mass spectrometry (TIMS) with a multiple collector ion detection system is in general the method of choice for high precision (down to 0.002%) isotope abundance ratio measurements of long-lived radionuclides,⁽⁷⁾ whereas the precision achievable with the presently commercially available quadrupole-based ICP-MS (ICP-QMS) is typically limited to 0.1-0.5%. In long-term measurements by ICP-QMS an external precision of about 0.05% for $^{235}\text{U}/^{238}\text{U} \sim 1$ was obtained^(8,9). TIMS, which used to be the dominant analytical technique for precise isotope ratio measurements is being increasingly replaced for precise isotope ratio measurements by ICP-MS due to its excellent sensitivity and good accuracy.

The application of conventional radiochemical methods for the determination of long-lived radionuclides at low concentration levels requires a careful (mostly time-consuming) chemical separation of the analyte and enrichment by extraction or different chromatographic procedures. Compared to radioanalytical methods ICP-MS possesses excellent sensitivity, multielement capability, good precision even at low concentration level, a high isotopic selectivity and the sample preparation is often easier.

In contrast to powerful solid state mass spectrometry such as LA-ICP-MS, TIMS, GDMS (glow discharge mass spectrometry), SSMS (spark source mass spectrometry), SIMS (secondary ion mass spectrometry) and others,^(1,10) inductively coupled plasma mass spectrometry (ICP-MS) is being used for the characterization of long-lived radionuclides in aqueous and solid samples after sample dissolution owing to the simple quantification procedure of the aqueous solution.

The principle of ICP-MS can be described as follows. The chemical compounds contained in the sample solution are decomposed into their atomic constituents in an inductively coupled argon plasma 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.

For determination of long-lived radionuclides different commercial double-focusing sector field ICP-MS, e.g., "ELEMENT" (Finnigan MAT, Bremen, Germany), "PlasmaTrace 2" (Micromass Ltd, UK), "AXIOM" (VG Elemental, UK) and "JMS-Plasma X2" (Joel, Japan), and quadrupole-based ICP-mass spectrometers (e.g. Perkin Elmer Sciex, Hewlett Packard, VG Elemental, Varian GmbH analytical instruments, Spectro Analytical Instruments, Micromass) are available on the international market. 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- pg l^{-1} concentration range.⁽⁶⁾

DETECTION LIMITS OF LONG-LIVED RADIONUCLIDES IN ICP-MS

In Table 1 the detection limits for quadrupole-based ICP-MS (ICP-QMS) "Elan 6000", Perkin Elmer, Sciex and double-focusing ICP-MS "ELEMENT", Finnigan MAT, Germany (DF-ICP-MS) with ultrasonic nebulizer for selected long-lived radionuclides are summarized.

Extremely low detection limits for long-lived radionuclides in the sub-ppq (pg l^{-1}) range were observed due to the low background (< 0.1 cps) and the high sensitivity of double-focusing sector field ICP-MS at low mass resolution. The detection limits are several orders of magnitude higher

for the determination of the long-lived radionuclides by DF-ICP-MS at higher mass resolution where isobaric interferences with molecular or atomic ions would be expected, as demonstrated for the determination of ^{79}Se or ^{129}I , where mass spectrometric interferences of analyte ions with $^{38}\text{Ar}^{40}\text{ArH}^+$ molecular ions¹¹ or $^{129}\text{Xe}^+$ atomic ions of plasma gas contaminant¹², were observed.

Table 1: Comparison of detection limits for several actinides in high-purity water by double-focusing sector field ICP-MS (DF-ICP-MS) and quadrupole-based ICP-MS (ICP-QMS) using the ultrasonic nebulization

Nuclide	Half-life [years]	DF-ICP-MS		ICP-QMS [pg l ⁻¹]
		[pg l ⁻¹]	[kBq l ⁻¹]	
^{230}Th	$7.5 \cdot 10^4$	0.08	6.2×10^{-8}	11
^{232}Th	$1.4 \cdot 10^{10}$	0.1	2.2×10^{-13}	15
^{233}U	$1.6 \cdot 10^5$	0.07	2.3×10^{-8}	12
^{238}U	$4.5 \cdot 10^9$	0.2	2.4×10^{-12}	26
^{237}Np	$2.1 \cdot 10^{16}$	0.05	1.3×10^{-9}	186
^{239}Pu	$2.4 \cdot 10^4$	0.04	9.4×10^{-8}	63
^{241}Am	$7.3 \cdot 10^3$	0.05	3.6×10^{-7}	89

One of the serious problems in ICP mass spectrometry for the determination of long-lived radionuclides is that different isobaric interferences with analyte ions appear. A large number of molecular ions [e.g., $^{79}\text{Se}^+$ and $^{38}\text{Ar}^{40}\text{ArH}^+$: $R(m/\Delta m) \approx 5000$, $^{239}\text{Pu}^+$ and $^{238}\text{UH}^+$: $R(m/\Delta m) \approx 3100$] can often be separated using double-focusing sector field ICP-MS with a maximum mass resolution of 12 000. However, the application of mass spectrometers at high mass resolution yielded a significant loss of intensity of analyte ions and an increase of detection limits. Therefore another possible way of solving the interference problem with disturbing molecular ions for some analytical applications is the application of collision cells in ICP-MS.

INSTRUMENTAL DEVELOPMENTS

The application of the collision cell - which is an old, well-known principle in organic mass spectrometry for controlled collision-induced fragmentation of organic molecules in structure analysis - in inorganic mass spectrometers represents important progress in ICP-MS instrumentation which is relevant for improving the precise determination of isotope ratios. Initial experiments to reduce the molecular ion interferences in ICP-MS were described by Douglas⁽¹³⁾. The collision cell was introduced in ICP-MS by the mass spectrometric company Micromass Ltd (Manchester, UK) using a hexapole collision cell (Platform-ICP-MS) to thermalize the ions and to dissociate disturbing molecular ions⁽¹⁴⁾. The hexapole collision cell - which works as an ion optical lens system - is inserted between the interface and the quadrupole mass analyser. There is no photon stop in the Platform instrument. In order to reduce the background in mass spectra arising by photons from the ICP, the hexapole is mounted off-axis in the collision cell chamber. In the collision cell, collision-induced reactions, such as charge transfer and proton transfer

reactions take place, causing the dissociation of some argon molecular ions (especially the argon based molecular ions such as ArO^+ , ArC^+ , ArN^+ , ArH^+ and Ar_2^+ and others), and the neutralization of Ar^+ . Furthermore, a decrease of initial energy of ions of up to 0.1 eV results in an improved sensitivity of elements and precision in the determination of isotope ratios.

With Platform ICP-MS using a mixture of hydrogen and helium as the reaction gas a significant increase in ion intensity was observed, for example, a maximum sensitivity of $\approx 12\,500$ MHz/ppm for ^{238}U was measured in our laboratory using the Platform ICP-MS with an ultrasonic nebulizer (USN) for solution introduction. This sensitivity achieved with the platform ICP-MS and USN is comparable to the sensitivity of DF-ICP-MS with shielded torch. In contrast, the sensitivity of Platform ICP-MS with a commercial Meinhard nebulizer for ^{238}U was 400 MHz/ppm. By measurements of isotope ratio measurements of $10\ \mu\text{g L}^{-1}$ uranium by collision cell ICP-MS using the Platform ICP-MS (see Table 2) and a commercial Meinhard nebulizer for solution introduction we yielded a short-term precision of 0.07% RSD. Of interest is the good accuracy of 0.42%, which does not require a correction of mass discrimination in this experiment. ⁽¹⁵⁾

Table 2: Uranium Isotope Ratios by Collision Cell ICP-QMS
("Platform" quadrupole ICP-MS with hexapole collision cell, Micromass)

$^{234}\text{U}/^{238}\text{U}$	RSD (%)	$^{235}\text{U}/^{238}\text{U}$	RSD (%)	$^{236}\text{U}/^{238}\text{U}$	RSD (%)
0.00638	1.5	0.9967	0.16	0.00219	0.8
0.00629	0.8	0.9954	0.20	0.00219	1.2
0.00620	1.0	0.9951	0.17	0.00213	1.2
0.00611	1.0	0.9953	0.09	0.00208	1.1
0.00597	1.9	0.9959	0.23	0.00202	2.3
0.00619	2.6	0.9957	0.07	0.00212	3.5

Perkin Elmer developed the ICP-MS Elan 6100 DRC with a quadrupole collision cell (on the basis of the Elan 6000) which is inserted between the ion optic lens system and the quadrupole-based analyser. NH_3 , CH_4 , H_2 and He were successfully used as the collision gas for different applications, e.g., in microelectronics. ⁽¹⁶⁻¹⁸⁾ The application of the dynamic reaction cell results in an improvement of the precision of isotope ratio measurements as demonstrated for lead by Bandura and Tanner. ⁽¹⁹⁾

Important progress in the instrumental improvement of ICP-MS in order to obtain a better precision of isotope ratio measurements was achieved by the introduction of the multi-ion collector device. Using double-focusing sector field ICP-MS with multiple ion collector, for example the Plasma 54 ⁽²⁰⁻²²⁾ with nine Faraday cups and the Axiom from VG Elemental, a precision of up to 0.005% was achieved in isotope ratio analysis but the concentration of analyte in the mg L^{-1} concentration range was significantly higher compared to ICP-MS with ion counting detector.

The first multiple collector sector field ICP-MS with a hexapole collision cell available on the

analytical market is the IsoProbe from Micromass.⁽²³⁾ The collision cell is used mainly for the thermalization of ions from the eV up to the 0.1 eV energy of ions, therefore in this instrument just a single magnetic sector field is sufficient for the mass/charge separation of ions. Ten Faraday channels are arranged for simultaneous multi-ion collection. High-precision isotope ratio measurements using the Faraday cups were performed, mostly at the 1 mg L⁻¹ level. In a special arrangement, but in a more expensive sector field ICP-MS, eight ion counting channels can be used for precise isotope ratio measurement at the ultratrace level. The application of the hexapole collision cell, which works effectively with a hydrogen / helium gas mixture, is used for the thermalization of ions and for the dissociation of argon-based molecular ions.⁽²³⁾ So far a precision for the determination of the ⁸²Se/⁸⁰Se isotope ratio of 0.0015 % has been achieved. By collision-induced reactions in the hexapole cell, the Ar⁺ ion intensity was reduced by some orders of magnitude using the neutralization reaction. This allows the determination of ⁴⁰Ca by ICP-MS. Using the multi-ion collector IsoProbe ICP-MS with a collision cell, the ⁴²Ca/⁴⁰Ca isotope ratio of 0.0067 was determined with a precision of 0.009% RSD (at 1mg L⁻¹ Ca) in aqueous solution. ⁶Li/⁷Li and ¹¹B/¹⁰B isotope ratios were measured at the 0.5 mg L⁻¹ and 1 mg L⁻¹ concentration level as 0.027% RSD and 0.008% RSD, respectively. This precision of isotope ratios in MC-ICP-MS are comparable to those of TIMS.^(23,24)

Recently, Finnigan MAT constructed a multiple ion collector, ICP-MS NEPTUNE, on the basis of a double-focusing sector field with Nier-Johnson geometry.⁽²⁵⁾ Eight Faraday cups are interchangeable with ion counting detectors in order to measure isotope ratios at very low concentration levels. In contrast to the DF-ICP-MS with single ion collector (ELEMENT from Finnigan MAT), flat-top peaks were observed at a mass resolution of $R(m/\Delta m) = 4000$, which are important for the precise determination of isotope ratios.

These ICP mass spectrometers with multiple ion collector systems will have increasing importance for precise isotope ratio measurements especially age dating in the future.

DETERMINATION OF LONG-LIVED RADIONUCLIDES IN SMALL SAMPLE VOLUMES

The development of micro-analytical methods for the precise determination of nuclide abundances and concentration of long-lived radionuclides at ultratrace concentration levels in radioactive wastes and also for controlling contamination from radioactive waste in the environment is a challenging task. In order to analyze small sample volumes, micronebulizers (MCN-100, Cetac Technologies, USA and MicroMist, Glass Expansion, Australia) and the direct injection high-efficiency nebulizer (DIHEN, J E Meinhard Associates, USA)^(26,27) have been increasingly used instead of high solution volume consuming ultrasonic nebulizers for determining long-lived radionuclides by the solution introduction into the inductively coupled plasma of an ICP-MS. Due to direct nebulization of the sample solution in the inductively coupled plasma with the DIHEN (with an analyte transport efficiency into the plasma of 100%), and the reduction of the solution uptake rate and the sample size to the 1 μ l min⁻¹ and fg range, respectively, very sensitive measurements of long-lived radionuclides in aqueous solutions are possible⁽²⁶⁾.

Microanalytical techniques such as μ -FI-ICP-MS (μ -FI microflow injection) is of special interest in radioactive waste and environmental research where very small sample volumes have to be characterized. In order to inject small sample volumes (>1 μ L) of aqueous solution in a continuous flow of 2% nitric acid a HPLC injection valve was coupled to the microconcentric nebulizer for small droplet formation. The application of μ -FI-ICP-MS using a quadrupole based instrument for the Th determination in aqueous solution by isotope dilution techniques was described in⁽²⁸⁾. The ²³²Th (in 2% nitric acid continuous flow) solution was spiked with 20 μ L of

a 4 µg/L ²³⁰Th solution and the ²³²Th concentration can be calculated using the known formula for isotope dilution analysis.

Furthermore, small sample volume (sample loop: > 1 µl) of standard or radioactive waste solution was introduced by this HPLC injection valve into a continuous flow of 2 % nitric acid. For example, a ²³⁷Np 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. ⁽⁶⁾

HPLC-ICP-MS AND CE-ICP-MS FOR DETERMINATION OF SPALLATION NUCLIDES

The most important problem in determining long-lived radionuclides in radioactive waste or environmental samples is the appearance of isobars of radioactive and stable nuclides at the same mass with a different atomic number, causing interferences in mass spectra. In order to separate isobars, such as long-lived ¹⁷³Lu from stable ¹⁷³Yb, on-line high performance liquid chromatography (HPLC - for a chromatographic separation of a lanthanide mixture into the individual elements) coupled to an inductively coupled plasma mass spectrometer (ICP-MS - for the mass spectrometric determination of the nuclides from each of the previously separated elements as a function of their mass) is a possible analytical method. In past years on-line ion chromatography ICP-MS has been increasingly used for the characterization of radioactive materials and environmental samples using quadrupole-based ICP-MS. ⁽²⁹⁾ The use of ion chromatography for the determination of fission products and actinides in nuclear applications is reviewed by Betti. ⁽³⁰⁾

An important task in our institute is the nuclide analysis of an irradiated tantalum target. Tantalum was used as the target material in a spallation neutron source where the neutrons are produced via spallation reactions between a highly energetic proton beam, with 800 MeV protons.

HPLC-ICP-MS was developed at the Central Department of Analytical Chemistry, Research Centre Juelich (see schematic in Figure 1) for the separation of long-lived from the stable rare earth elements spallation nuclides in an irradiated tantalum target of a spallation neutron source. ^(31,32)

For the determination of spallation nuclides in irradiated tantalum, double-focusing sector field ICP-MS will be used after liquid-liquid extraction of the tantalum matrix in order to reduce the high ¹⁸²Ta activity. Small pieces of tantalum were dissolved in a HNO₃/HF mixture and the tantalum matrix was separated by liquid-liquid extraction so that only the spallation nuclides were left in the sample solutions.

If the sample solutions of spallation nuclides were determined using only ICP-MS without any preceding chromatographic separation technique, we found an increasing amount of spallation nuclides for lanthanides in the mass spectra of the tantalum sample. According to the theoretical prediction the concentration of the spallation nuclides in the higher mass range increases with increasing mass (see Figure 2).

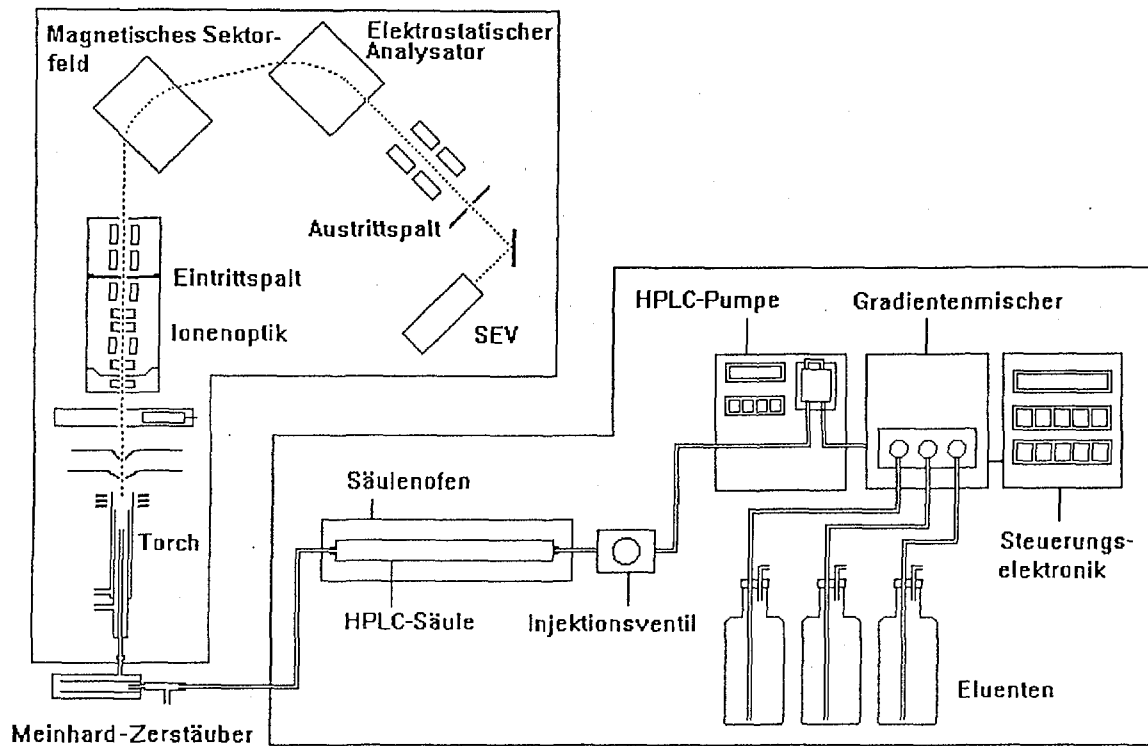


Figure 1: Scheme of HPLC-ICP-MS

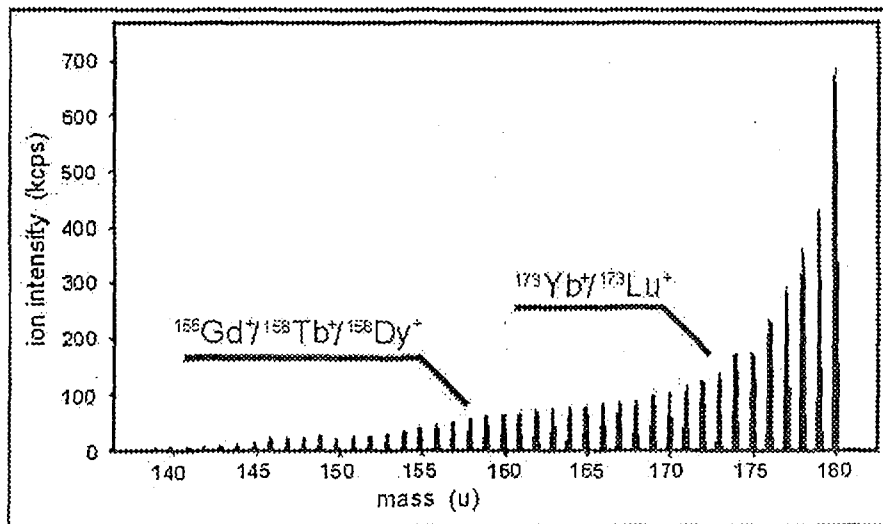


Figure 2: Mass spectrum of spallation nuclides in an irradiated tantalum target after matrix separation

The separation of rare earth elements with natural isotope composition using a strong acid cation exchanger is shown in Figure 3.

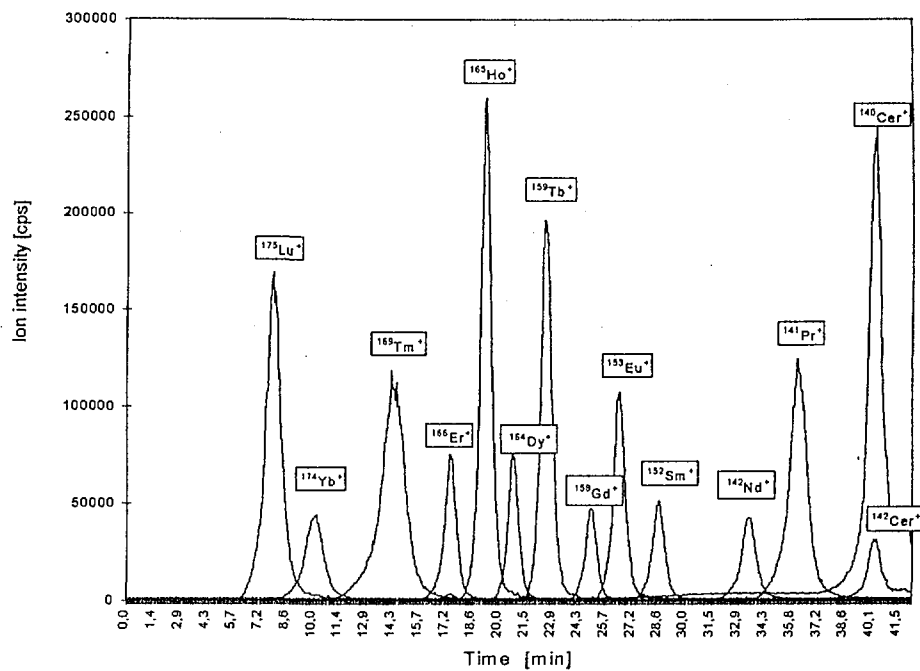


Figure 3: Chromatogram of separated (natural) rare earth elements by HPLC-ICP-MS

The lanthanide metals were predicted in the irradiated tantalum target as a major fraction of spallation nuclides with quite significantly different nuclide abundances in comparison to the natural isotopic composition (see e.g, for gadolinium Table 3).

In order to reduce the high radioactive solution volume of the digested irradiated tantalum target the capillary electrophoresis system (Waters Quanta 4000) was coupled to the DF-ICP-MS ELEMENT. The optimization of coupling technique and the analysis of spallation nuclides in the irradiated tantalum target is described by Day et al. ⁽³³⁾ In Figure 3 a mass spectrum of all rare earth elements in the irradiated tantalum target separated and measured by CE-ICP-MS is shown. In agreement with the theoretical prediction for the rare earth elements, an increase of ion intensity was found with increasing mass, the highest ion intensity being for $^{175}\text{Lu}^+$. All REE were well separated with respect to the analytes by capillary electrophoresis using a sample volume of 30 nl only at the $800 \mu\text{g L}^{-1}$ concentration level of each lanthanide element. In Table 3 the nuclide abundances of gadolinium produced via a spallation reaction in an irradiated tantalum target separated and measured by HPLC-ICP-MS of 10 μl of highly radioactive digested and diluted solution and CE-ICP-MS of 30 nl sample volume are compared. It is shown, that the abundance distribution of spallation nuclides of gadolinium is quite different from the gadolinium isotopes which were measured in the natural samples (left column). With respect to the small sample volume used, the agreement of analytical results is excellent and the theory is confirmed. The precision of isotope abundances measured using both techniques is in the low % range.

Table 3: Nuclide abundances of gadolinium (%) produced via spallation reactions in an irradiated tantalum target

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	26	<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	-	-	-

Our experiments with HPLC-ICP-MS and CE-ICP-MS demonstrated for all investigated lanthanides a good agreement of measured nuclide abundances with those calculated. ⁽³¹⁻³³⁾

CONCLUSIONS

Inductively coupled plasma mass spectrometry with detection limits in the sub fg ml⁻¹ range is an excellent tool for the analysis of long-lived radionuclides in aqueous solutions. Due to the excellent sensitivity and very low detection limits, isotope ratio measurements are possible with very small sample amounts of analyte and for solid samples mostly only simple preparation steps are required (compared to the time-consuming TIMS).

The insertion of the collision cell in ICP-MS results in new interesting applications for precise isotope ratio measurements of long-lived radionuclides.

CE- and HPLC-ICP-MS are important for isotope ratio measurements on small sample solutions and if the separation of analytes is required.

Numerous, quite different applications demonstrate the excellent capability of ICP-MS in determining of radioactive nuclides for the evidence of contamination from radioactive waste in the environment (in biological and medical samples, waters or geological materials).

REFERENCES

- (1) J.S. Becker and H.-J. Dietze, "Mass Spectrometry of Long-Lived Radionuclides", Encyclopedia Anal. Chem. ed. by R.A. Meyers, John Wiley Sons, (in press).
- (2) J.S. Crain, Spectroscopy 11 (1996) 31.
- (3) J.S. Becker and H.-J. Dietze, Adv. Mass Spectrom. 14 (1998) 681.
- (4) C.K. Kim, R. Seki, S. Morita, S. Yamasaki, T. Tsumura, Y. Igarashi, M. Yamamoto, J. Anal. At. Spectrom. 6 (1991) 205.
- (5) J.S. Becker, H.-J. Dietze, Spectrochim. Acta 53B (1998) 1475.

- (6) J.S. Becker, H.-J. Dietze, *J. Anal. At. Spectrom.* 14 (1999) 1493.
- (7) T.I. Platzner, *Modern Isotope Ratio Mass Spectrometry*, John Wiley and Sons, 1997.
- (8) T.I. Platzner, J.S. Becker, H.-J. Dietze (1999) *Atom Spectrom.* 20: 6
- (9) J.S. Becker, H.-J. Dietze, *Fresenius J. Anal. Chem.* 364 (1999) 482.
- (10) J.S. Becker, H.-J. Dietze, *Int. J. Mass Spectrom.* 197 (2000) 1.
- (11) K. Hoppstock, J.S. Becker, H.-J. Dietze, *At. Spectrom. Atomic Spectroscopy*, 18, 1997, 180.
- (12) W. Kerl, J.S. Becker, H.-J. Dietze, W. Dannecker, W., *J. Anal. At. Spectrom.*, 10 (1996) 723 .
- (13) D.J. Douglas *Can J Spectrosc* 34 (1989) 38.
- (14) P. Turner, T. Merren, J. Speakman, M. Haines (ed. by Holland G, Tanner SD), *Special Publication (No. 202) of the Royal Chemical Society, Cambridge* (1997) 28.
- (15) J.S. Becker, H.-J. Dietze, H.-J., *Fresenius J. Anal. Chem.* (in press).
- (16) E.R. Denoyer, S.D. Tanner, U. Völlkopf, *Spectroscopy* 14 (1999) 2.
- (17) S.D. Tanner, V.L. Baranov, *Atom. Spectr.* 20 (1999) 45.
- (18) V.I. Baranov, S.D. Tanner, *Anal. At. Spectrom.* 14 (1999) 1133.
- (19) D.R. Bandura, S.D. Tanner, *Atom. Spectr.* 20 (1999) 69.
- (20) D.C. Lee, A.N. Halliday, *Int. J. Mass Spectrom. Ion Proc.* 146/147 (1995) 35.
- (21) A.J. Walder, D. Koller, N.M. Reed, R.C. Hutton, P.A. Freedman, *J. Anal. At. Spectrom.* 8 (1993) 1037.
- (22) M. Rehkämper, A.N. Halliday, *Intern. J. Mass Spectrom.* 181 (1998) 123.
- (23) Z. Palacz, P.J. Turner, C. Haines, F. Abou-Sahakra, A.N. Eaton, *Mineral Mag* 62A, Part 2 (1998) 1126.
- (24) S. Meffan-Main, Z. Palacz, *Application Briefs AB 11 and 12 Micromass* (1999).
- (25) M. Hamester, G. Jung, R. Pesch, L. Rottman, D. Tuttas, J. Wills, 2000 Winter Conference on Plasma Spectrochemistry, 10 –15 January 2000, Fort Lauderdale, Book of Abstracts, 2000, p. 372
- (26) McLean, J.A.; Zhang, H.; Montaser, A. *Anal. Chem.* 1998, 70, 1012-1020.
- (27) J.S. Becker, H.-J. Dietze, J.A. McLean and A. Montaser, *Anal. Chem.* (1999) in press.
- (28) J.S. Becker, R.S. Soman, K. L. Sutton, J. Caruso, H.-J. Dietze, *J. Anal. At. Spectrom.*, 14, (1999) 933.
- (29) Y. Marumatsu, S. Uchida, K. Tagami, S. Yoshida and T. Fujikawa, *J. Anal. Atom. Spectrom.*, 14 (1999) 859.
- (30) M. Betti, *J. Chromatogr. A*, 789 (1997) 369.
- (31) W. Kerl, J.S. Becker, H.-J. Dietze, W. Dannecker, *Fresenius J. Anal. Chem.* 362 (1998) 433.
- (32) J.S. Becker, W. Kerl, H.-J. Dietze, *Anal. Chim. Acta* 387 (1999) 145.
- (33) J. Day, J. Caruso, J.S. Becker, H.-J. Dietze, *J. Anal. At. Spectrom.* (submitted).