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Laser ablation inductively coupled plasma mass spectrometry for the trace, ultratrace and isotope analysis of long-lived radionuclides in solid samples

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Abstract

The capability of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for determination of long-lived radionuclides in different materials (e.g., in geological samples, high-purity graphite and nonconducting concrete matrix) was investigated. The main problem in the quantification of the analytical results of long-lived radionuclides is that (except for geological samples) no suitable standard reference materials are available. Therefore, synthetic laboratory standards (graphite and concrete matrix doped with long-lived radionuclides, such as ^{99}Tc, ^{232}Th, ^{233}U, ^{235}U, ^{237}Np, ^{238}U) were prepared and used for quantification purposes in LA-ICP-MS. Different calibration procedures—the correction of analytical results with experimentally determined relative sensitivity coefficients (RSCs), the use of calibration curves and solution calibration by coupling LA-ICP-MS with an ultrasonic nebulizer—were applied for the determination of long-lived radionuclides, especially for Th and U in different solid samples. The limits of detection of long-lived radionuclides investigated in concrete matrix are determined in the pg g^{-1} range (e.g., for ^{237}Np-50 pg g^{-1} in quadrupole LA-ICP-MS; for ^{233}U-1.3 pg g^{-1} in double-focusing sector field LA-ICP-MS). Results of isotope ratio measurements of Th and U in synthetic laboratory standards and different solid radioactive waste materials of direct analysis on solid samples using LA-ICP-MS are comparable to measurements using the double-focusing sector field ICP-MS after separation of the analyte, even if no possible interference of atomic ions of analyte and molecular ions are expected. Furthermore, LA-ICP-MS allows precise and accurate isotope ratio measurements of Th and U in solid samples. For example, the isotope ratio $^{234}U/^{238}U = 0.000067$ in radioactive reactor graphite was determined with a precision of 1.1% relative standard deviation (RSD). (Int J Mass Spectrom 202 (2000) 283–297) © 2000 Elsevier Science B.V.

Keywords: Isotope ratio measurements, Laser ablation inductively coupled plasma mass spectrometry, Long-lived radionuclides, Trace analysis

1. Introduction

Laser ablation, inductively coupled plasma mass spectrometry (LA-ICP-MS) has been established as a sensitive multielement analytical solid mass spectrometric technique without any restriction with respect to the chemical and physical properties of the solid sample in widely different application fields in geology, material science and environmental research [1–6]. One of the challenging tasks of analytical chemistry is the determination of long-lived radionu-

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clides in radioactive waste from nuclear reactors, high-purity materials and environmental samples. Conventional radioanalytical methods are well suited for measurements of γ-emitting radionuclides, but for the determination of long-lived α- and β-ray-emitting radionuclides at low concentration levels they are often time-consuming due to the radiochemical separation steps required. Therefore, the development of analytical techniques such as LA-ICP-MS for the direct determination of long-lived radionuclides at ultratrace concentration levels in solid environmental samples and radioactive waste materials with improvement of microanalytical techniques in order to reduce the sample volume, to improve the precision (relative standard deviation) of measurements and the detection limits is required.

The determination of long-lived radionuclides with trace analytical methods in difficult-to-dissolve solid materials (such as soils, ashes, glasses and others) is problematic, especially because no standard reference materials are available. Therefore, developing and applying suitable quantification procedures for analytical measurements in LA-ICP-MS is an important task to obtain more precise and accurate results. Due to lack of suitable standard reference materials (SRMs) a proven technique in different research groups [5,7–9] is the preparation of synthetic laboratory standards with analogous matrix doped with analyte elements of interest at given concentrations. Recently, the implementation of easy solution calibration in LA-ICP-MS well known from ICP-MS could be the method of choice for quantification purposes [10–12].

The primary application for determining long-lived radionuclides by LA-ICP-MS is in environmental monitoring for detecting the results of nuclear weapons tests or contamination from the long-lived radionuclide emission of nuclear power plants. The characterization of radioactive waste materials from nuclear reactors for recycling and final storage of these hazardous materials requires fast, sensitive and precise analytical methods, capable of determining long-lived radionuclidic ultratraces and isotope ratios in a short time. A major application of LA-ICP-MS is the determination of Th and U in minerals and rocks and the dating of geological samples (e.g., U–Pb geochronology [13]). With its the improved sensitivity and accuracy and lower detection limits, LA-ICP-MS will have growing applications in solid-state research and routine measurements, for example for U and Th determination in high-purity materials.

The aim of this article is to discuss the capability of LA-ICP-MS as a solid-state mass spectrometric technique in the trace and ultratrace analysis of long-lived radionuclides in solid samples and the different quantification possibilities using synthetic laboratory standards with graphite and concrete matrix or by solution calibration. Furthermore, LA-ICP-MS can be applied for precise and accurate isotope ratio measurements of long-lived radionuclides in synthetic isotope standards and real radioactive waste materials, so we discuss here some investigations of molecular ion formation in LA-ICP-MS.

2. Experimental

2.1. Instrumentation

The determination of long-lived radionuclides in solid samples was performed by LA-ICP-MS using a commercial laser ablation system LSX 200 from CETAC (CETAC LSX 200, Cetac Technologies, Omaha, NE, USA) coupled to a quadrupole ICP-MS (ICP-QMS, Elan 6000, Perkin Elmer, Sciex Corp., Norwalk, CT, USA). The laser beam is focused on the sample surface in a laser ablation chamber. The ablated material is transported by argon as a carrier gas into the inductively coupled plasma (ICP), where the molecules of evaporated and ablated sample material were dissociated and ionized. The ions formed in the ICP were extracted in the quadrupole mass spectrometer and were separated according to their mass-to-charge ratios. The separated ion beams are detected electrically by a secondary electron multiplier. To demonstrate the increased sensitivity and lower detection limits of long-lived radionuclides, a double-focusing sector field ICP-MS (DF-ICP-MS, ELEMENT, Finnigan MAT, Bremen, Germany) with shielded torch was coupled to the commercial laser ablation system LSX 200 also from CETAC. Table 1

Table 1
Experimental parameters of LA-ICP-MS

ICP-QMS Elan 6000, Perkin Elmer and DF-ICP-MS ELEMENT, Finnigan MAT	
Rf power	1000 W
Coolant gas flow rate	14 L min^{-1}
Auxiliary gas flow rate	0.8 L min^{-1}
Carrier gas flow rate	0.6 L min^{-1}
Mass resolution m/Δm	300
Acquisition mode	Peak hopping
Detector mode	Dual (Elan 6000); counting (ELEMENT)
Dwell time	10 ms
No. of sweeps	10
No. of replicates	6
Sampling cone	Nickel with a 1.1 mm orifice
Skimmer cone	Nickel with a 0.9 mm orifice
Laser ablation	
Laser ablation system	CETAC LSX 200
Wavelength	266 (4th harmonic of Nd:YAG laser)
Pulse duration	5 ns
Repetition frequency	20 Hz
Pulse energy	5 mJ
Laser power density	1,1*10^9 W cm^{-2}
Spot diameter	340 μm
Pre-ablation time	10 s
Ablation method	Single line scan

summarizes the experimental parameters used for LA-ICP-QMS and DF-LA-ICP-MS for the determination of long-lived radionuclides in different types of solid materials.

2.2. Optimization procedure

The optimization of experimental parameters in LA-ICP-MS is performed with respect to laser parameters (such as wavelength, pulse length and laser power density), carrier gas flow rate and radiofrequency (rf) power of ICP in order to obtain maximum ion intensities of long-lived radionuclides for the trace element analysis and the best precision for $^{235}U/^{238}U$ isotope ratios.

The optimization curves for $^{238}U^+$ and $^{232}Th^+$ for the determination of uranium and thorium concentration in a concrete matrix as a function of a carrier gas flow rate at an ICP-rf power of 950 W measured by LA-ICP-QMS are shown in Figure 1. The maximum ion intensity for $^{238}U^+$ and $^{232}Th^+$ was observed at a carrier gas flow rate of ~0.9 L min^{-1}. Figure 2 demonstrates the ion intensities for $^{238}U^+$ and $^{232}Th^+$ in concrete matrix as a function of rf power of the inductively coupled plasma. A maximum ion intensity in LA-ICP-QMS was observed at 950 W measured at a carrier gas flow rate of 0.9 L min^{-1}. In contrast, maximum ion intensities for $^{232}Th^+$ and $^{238}U^+$ were observed in DF-LA-ICP-MS without (and with) a shielded torch at an ICP-rf power of 730 W (and of 710 W) and a carrier gas flow rate of ~1.2 L min^{-1}.

Whereas the optimization of uranium for the determination of concentration was performed with respect to maximum ion intensity of analytes, for isotope ratio measurements the optimization of experimental parameters was performed with respect to a good precision and the accuracy of the isotope ratios. Optimization procedure for uranium isotope ratio measurements in a graphite target doped with U (uranium concentration: 10 μg g^{-1}) yielded the best precision of $^{235}U/^{238}U$ at a carrier gas flow rate of 1.0 L min^{-1} and ICP-rf power at 1000 W.

2.3. Samples and standards

For the comparison of different calibration procedures used in the present work uranium and thorium were determined in selected geological samples (basalt KL2-G, andesite StHs6/80-G using BCR-2G—basaltic glass prepared from reference material BCR-2—for the determination of RSCs) and in zeolite TSM 180 (using the NIM-L standard from National Institute for Metallurgy, South Africa for quantification).

Furthermore, synthetic concrete and graphite laboratory standards were prepared for the quantification procedure of long-lived radionuclides in these matrices. The synthetic concrete standard was prepared from a commercial cement powder (with thorium concentration: 1.8 μg g^{-1} and uranium concentration: 0.73 μg g^{-1}) which was mixed with ^{99}Tc, ^{233}U and ^{237}Np as aqueous solutions at the concentrations given in Table 2. The mixture was carefully homogenized and dried in the atmosphere. A solid compact concrete piece (diameter 10 mm, thickness 5 mm) of the laboratory standard was investigated directly by

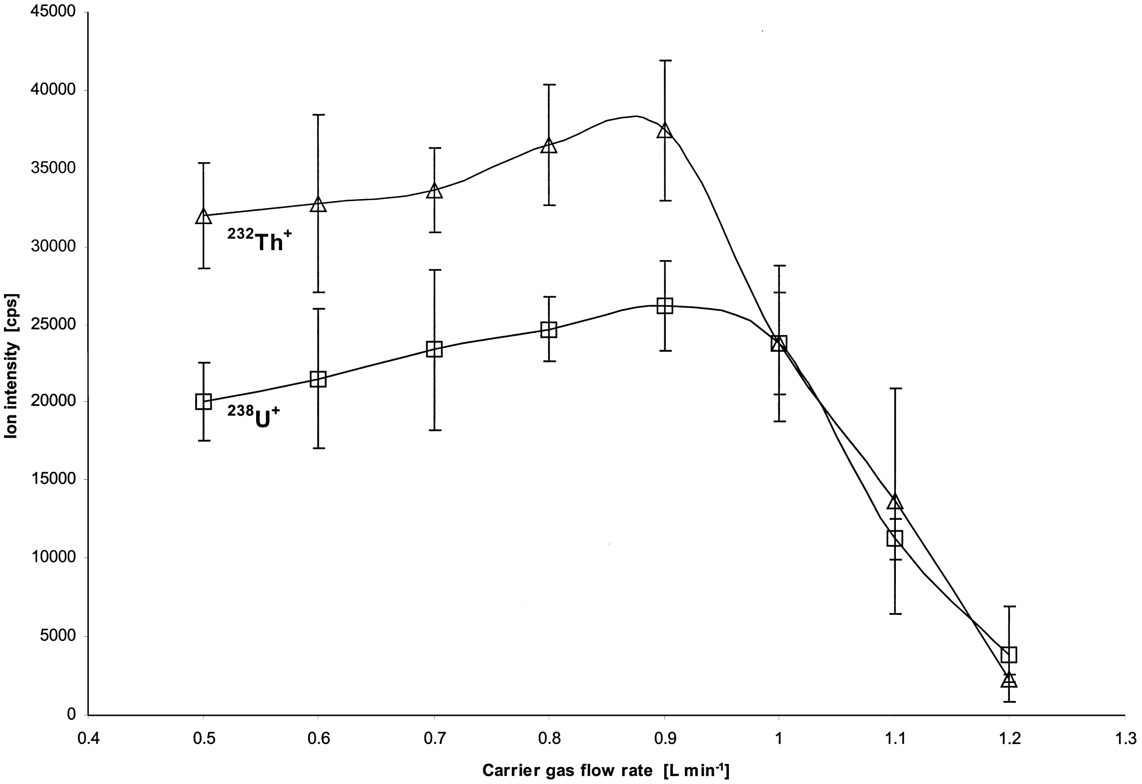

Fig. 1. Ion intensity of thorium and uranium as a function of carrier gas flow rate in LA-ICP-QMS (concrete matrix), rf power: 950 W; concentration of U = 0.725 μg g^{-1} and Th = 1.8 μg g^{-1}.

LA-ICP-MS. The laboratory standard for the graphite matrix was prepared from high-purity graphite powder (SGL Carbon GmbH, Werk Ringsdorff, Bonn, Germany) doped with U of natural isotope composition, ^{99}Tc, ^{233}U, ^{230}Th, ^{232}Th and ^{237}Np (1 μg g^{-1} each) by careful mixing and homogenizing, then the mixture was dried and pressed to form compact targets (2 mm × 2 mm × 5 mm) for LA-ICP-MS experiments. The concentrations of long-lived radionuclides in concrete and graphite laboratory standards are summarized in Table 2.

To check the performance of LA-ICP-MS for precise and accurate isotope ratio measurements, high-purity graphite was doped with different synthetic isotope mixtures for ^{235}U/^{238}U and ^{230}Th/^{232}Th with isotope ratios from 1 to $\approx 10^{-3}$ (uranium and thorium concentration was 1 μg g^{-1} of each). For mass bias correction, an isotope laboratory standard (CCLU 500 isotope standard reference material with a ^{235}U/^{238}U isotope ratio of $\sim$1; uranium concentration in graphite: 1 μg g^{-1}) was prepared. The isotopic composition of the CCLU 500 isotope standard and mass bias correction for the precise determination of uranium isotope ratio is described in Ref. 14.

Furthermore, real radioactive solid waste samples (filter, silt and glass) were studied by LA-ICP-MS.

2.4. Sample preparation by lithium borate fusion of powdered materials

Sample preparation for the determination of long-lived radionuclides in LA-ICP-MS is important for inhomogeneous compact and powdered geological and radioactive waste samples. To prepare a homogeneous target the powdered and homogenized sample was mixed with a lithium borate mixture (90% $Li_2B_4O_7$, 10% $LiBO_2$). Iron oxide was added for a better absorption of laser photons during the ablation

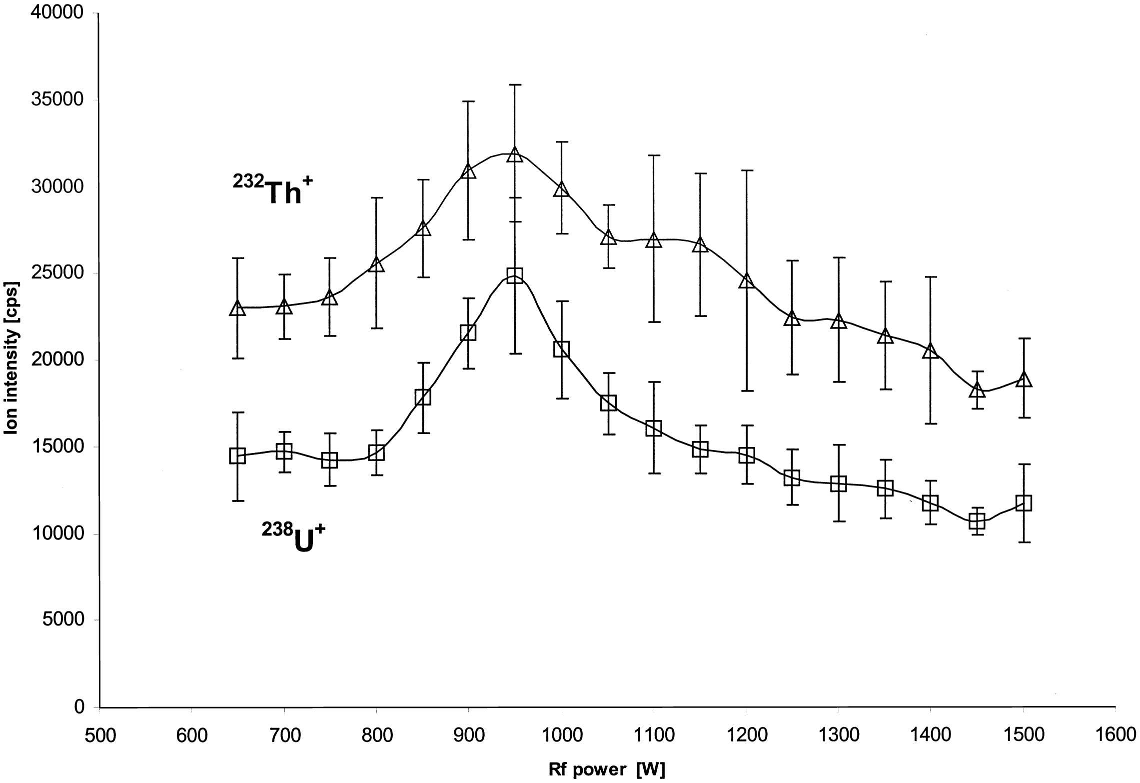

Fig. 2. Ion intensity of thorium and uranium as a function of ICP-rf power in LA-ICP-QMS (concrete matrix). Carrier gas flow rate: 0.8 L min^{-1}; concentration of U = 0.725 μg g^{-1} and Th = 1.8 μg g^{-1}.

process. The homogeneous mixture was fused in a muffle furnace at 1050°C. The target was inverted and fused again. The blank targets were prepared by the same procedure. Details of the preparation of homogeneous lithium-borate fused targets for LA-ICP-MS measurements are described in a recent publication [15].

Table 2
Comparison of concrete and graphite synthetic laboratory standards in respect with long-lived radionuclides

Nuclide	Half life [years]	Concentration [μg g^{-1}]	
		Concrete	Graphite
^{99}Tc	2.1×10^5	0.0285 ± 0.0010	1.00 ± 0.01
^{232}Th	1.4×10^{10}	1.80 ± 0.18	1.00 ± 0.01
^{233}U	1.6×10^5	0.051 ± 0.001	1.00 ± 0.01
^{235}U	7.0×10^8	0.0050 ± 0.0005	0.0070 ± 0.0001
^{237}Np	2.1×10^6	0.628 ± 0.015	1.00 ± 0.01
^{238}U	5.4×10^9	0.725 ± 0.073	0.9930 ± 0.0099

2.5. Quantification procedures

2.5.1. Correction of analytical results by relative sensitivity coefficients

The quantification of analytical results in LA-ICP-MS similar to other solid-state mass spectrometric techniques is mostly carried out using relative sensitivity coefficients as the correction factor [2]. For the determination of relative sensitivity coefficients (RSCs)

$$\text{RSC} = \text{measured value/certified (true) value}$$

as correction factors of measured values one standard reference material (SRM) with the same or similar matrix composition and certified concentrations of the elements of interest is required. The RSC of an element is a function of the matrix composition of sample, chemical and physical properties of the element and the experimental parameters used.

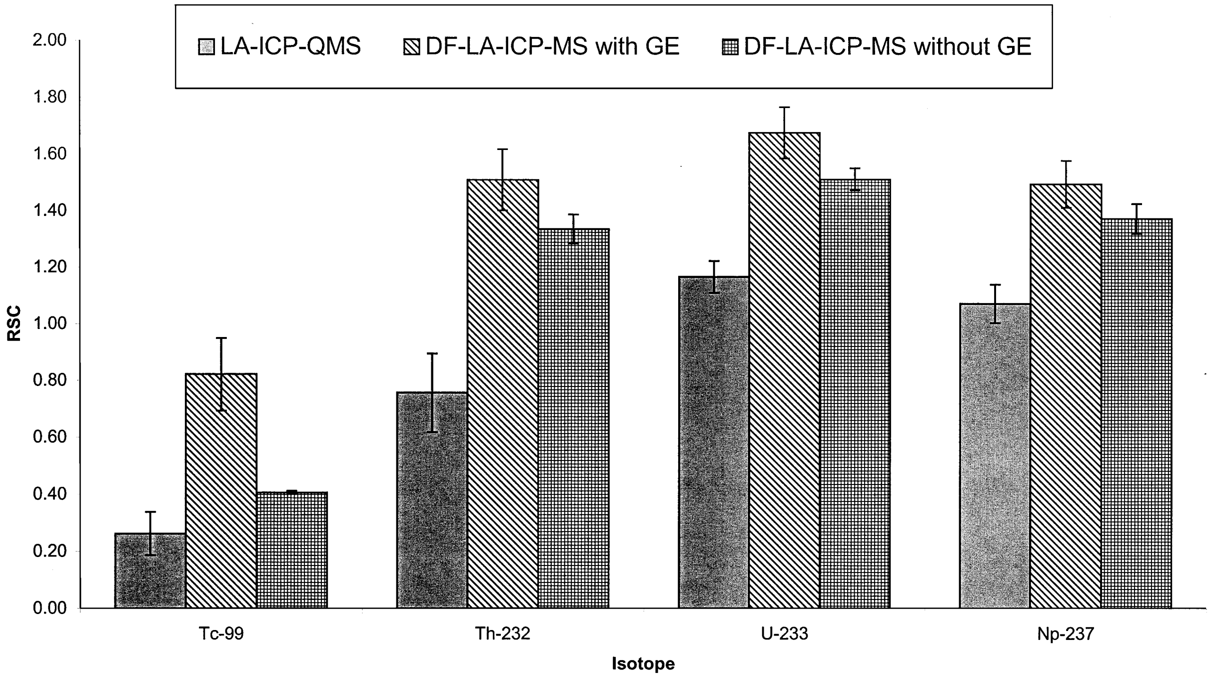

Fig. 3. Relative sensitivity coefficients of long-lived radionuclides in a concrete matrix in quadrupole-based LA-ICP-QMS (Elan 6000) and double-focusing sector field DF-LA-ICP-MS [ELEMENT without and with shielded torch (GE, guard electrode)].

Relative sensitivity coefficients of Th and U are determined in geological glass (BCR-2G) as 2.92±0.06 and 3.07±0.08, respectively and in lithium-borate-fused geological reference material granite GM as 2.30±0.11 and 3.20±0.19 (GM from former Central Institute of Geology, Berlin), respectively (Sr was used as internal standard element). Furthermore, synthetic laboratory standards with known concentrations of selected long-lived radionuclides were used for determination of RSCs of long-lived radionuclides in a concrete and graphite matrix. Figure 3 compares the RSCs of long-lived radionuclides in a concrete matrix measured by LA-ICP-QMS (Elan 6000) and double-focusing sector field LA-ICP-MS [DF-LA-ICP-MS without and with shielded torch (guard electrode-GE)]. These DF-LA-ICP-MS measurements were performed with optimized parameters concerning the maximum ion intensity of $^{232}Th^+$. The lowest RSC caused by low element sensitivity was observed for Tc (0.26±0.08 in LA-ICP-QMS versus 0.82±0.13 in DF-LA-ICP-MS with shielded torch and 0.41±0.006 without shielded torch). An increase of RSC with an increasing mass of measured radionuclide was observed, which is in agreement with the findings recently reported that the RSC for heavy elements in geological materials are higher than for lighter ones [15]. This result can be explained by instrumental mass-discrimination effects. Furthermore, in agreement with our results, Appelblad et al. described different mass-dependent ion intensities for elements in DF-ICP-MS (on aqueous solution) with and without shielded torch [16]. The RSCs of the other radionuclides investigated varied between 0.75±0.13 and 1.16±0.06 in LA-ICP-QMS ($N=3$) and between 1.33±0.05 and 1.68±0.04 in DF-LA-ICP-MS ($N=3$). The experimentally determined RSCs in different matrices measured by quadrupole-based and double-focusing sector field LA-ICP-MS were used as correction factors.

2.5.2. External calibration using calibration curves

If at least three standard reference materials or synthetic matrix-matched laboratory standards with different concentrations of trace elements exist,

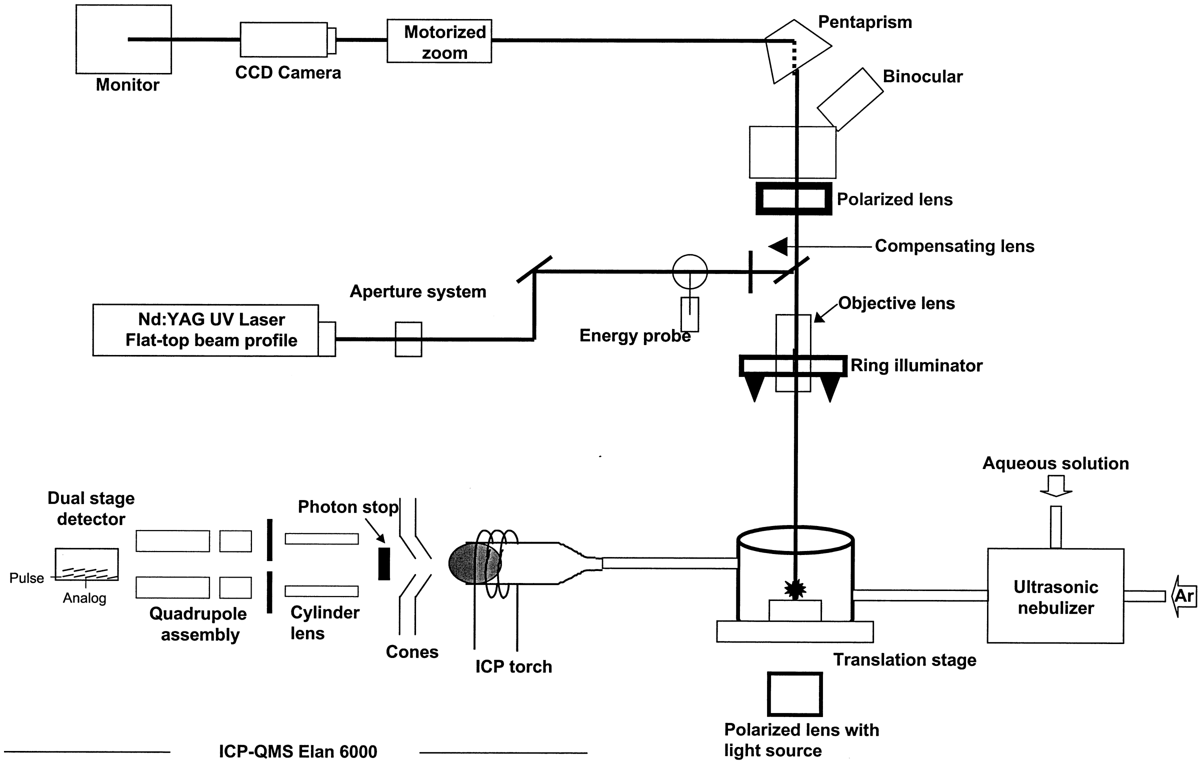

Fig. 4. Experimental arrangement for solution calibration in LA-ICP-QMS.

quantification was performed using calibration curves. Some calibration curves for trace elements in fused lithium borate targets of geological reference materials and further details are described elsewhere [17].

2.5.3 Quantification of analytical results by solution calibration

Solution calibration is of special interest not only if quantification procedures with the other described techniques are not possible because of the lack of suitable matrix-matched standard reference materials but also if the preparation of synthetic laboratory standards is too time consuming.

A possible arrangement for solution calibration in LA-ICP-MS is the direct coupling of the ultrasonic nebulizer (to produce a dry aerosol of standard solutions) with a laser ablation chamber as demonstrated in Figure 4. The proposed experimental arrangement allows an ideal mixing of the nebulized calibration solutions (2% HNO_3) with laser-ablated material in the laser ablation chamber using argon as the nebulizer and carrier gas. Furthermore, the matrix-matched standard addition as a calibration procedure considers matrix effects inherent in LA-ICP-MS. The solution calibration should be applied for uranium and thorium determination in fused lithium borate targets of geological samples and in geological glasses. During solution calibration with standard solution using the ultrasonic nebulizer a blank lithium borate target is ablated by Nd-YAG laser simultaneously. The nebulizer gas flow rate for USN (0.88 L/min), which is used for the transport of dry aerosol from the USN into the laser ablation chamber, is the same (carrier gas flow rate) for the transport of laser ablated material mixed with dry aerosol from the USN into the ICP. The dry mixed aerosol is atomized and ionized in the inductively coupled plasma at an rf power of 1150 W. A detailed description of the analytical procedure for solution calibration in LA-ICP-MS is given elsewhere [12].

Table 3
Results of determination of Th and U in geological glasses using RSCs (standard reference materials: BCR-2G)

	Basalt (KL2-G)		Andesite (StHs6/80-G)	
	Measured value	Recommended value [18]	Measured value	Recommended value [18]
Th	0.93 ± 0.07	1.08 ± 0.16	1.90 ± 0.03	2.23 ± 0.22
U	0.54 ± 0.04	0.56 ± 0.07	1.01 ± 0.03	1.05 ± 0.16

Table 4
Comparison of U and Th determination on zeolite TSM 180 by LA-ICP-QMS and NAA (concentration in μg g^{-1})

	LA-ICP-MS		
Element	RSC/NIM-L	Calibration curve	NAA
Th	15.0 ± 0.4	14.2 ± 0.4	15.0 ± 1.5
U	8.0 ± 0.1	8.2 ± 0.1	9.0 ± 0.9

3. Results and Discussion

3.1. Results of thorium and uranium determination in geological samples by different quantification procedures

The most important application of LA-ICP-MS for the determination of long-lived radionuclides is the measurement of naturally occurring thorium and uranium in geological samples. Within the framework of a measurement comparison to prepare reference materials for geological work [18] the radiogenic elements thorium and uranium were determined by LA-ICP-QMS on a number of geological glasses. Quantification of analytical results was performed using RSCs measured on BCR-2G standard reference material (three measurements on different sample areas). The results of Th and U measurements on geological reference glasses basalt (KL2-G) and an andesite (StHs6/80-G) sample are summarized in Table 3. The measured concentration of these investigated radiogenic elements are in agreement with the recommended values (averaged concentration using different mircoanalytical techniques) summarized in Ref. 18. In a recent article, the multielement determination by LA-ICP-QMS of trace elements in zeolite samples, which were used for clean-up processes in the nuclear industry, is discussed [17]. Table 4 demonstrates the comparison of different quantification procedures in LA-ICP-QMS ($N=5$, Th and U determination in a zeolite using RSCs and calibration curves) with results of neutron activation analysis (NAA). LA-ICP-QMS and NAA on a zeolite sample yielded a good agreement of results, considering that LA-ICP-MS is an easy and fast analytical method whereas NAA requires powerful irradiation facilities, a specially equipped laboratory, more time, a higher amount of sample-producing radioactive waste and a far more expensive cost.

The results of the trace analysis of uranium on geological samples using different quantification procedures for the analytical results, including solution calibration on lithium-borate-fused targets and geological glasses, are summarized with the results of measurements using RSC and the reference values in Table 5. The application of solution calibration on lithium-borate-fused targets yielded values that agree with the reference values for uranium. In addition, thorium was determined by solution calibration in the lithium-borate-fused andesite StHs6/80 with an excellent agreement with the reference value (Th: 2.27±0.14 μg g^{-1} measured versus 2.25±0.11 μg g^{-1}). However, the results for uranium and thorium (measured Th concentration on geological glass of

Table 5
Results of determination of uranium in geological samples by solution calibration by LA-ICP-QMS (concentration in μg g^{-1})

	Solution calibration			
	Lithium borate fused target	Geological glass	Using RSC (BCR-2G)	Recommended value [18]
Basalt AH83ML3B	0.42 ± 0.04	0.36 ± 0.04	0.39 ± 0.04	0.44 ± 0.044
Andesite StHs6/80	0.84 ± 0.06	(1.58 ± 0.11)	1.01 ± 0.03	1.05 ± 0.10

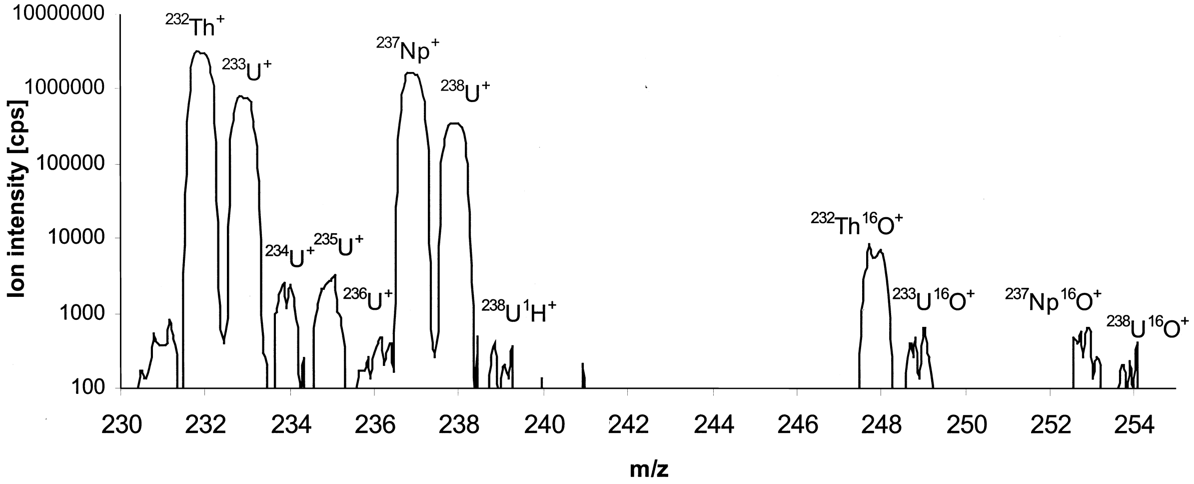

Fig. 5. Part of DF-LA-ICP-MS mass spectrum of long-lived radionuclides in concrete matrix.

andesite StHs6/80: 1.25±0.09) do not agree very well on geological glasses because no matrix matching (no suitable blank target was available) in solution calibration was performed. Further applications of solution calibration for multielement determination in geological samples is described elsewhere [12].

3.2. Results of determination of long-lived radionuclides on concrete and graphite matrix

Part of the mass spectrum of the laboratory concrete standard using DF-LA-ICP-MS in the mass range of 230–254 u is shown in Figure 5. Besides the atomic ions of long-lived radionuclides (for composition see Table 2), hydride ions and oxide ions as shown in this figure are observed in DF-LA-ICP-MS. Therefore, a careful study of molecular ion formation is necessary for an accurate determination of long-lived radionuclide concentrations and their isotope ratios.

The sensitivities of selected long-lived radionuclides and detection limits in a concrete matrix measured by LA-ICP-QMS using the quadrupole-based ICP-MS Elan 6000 and the double-focusing sector field ICP-MS ELEMENT (DF-LA-ICP-MS) are summarized in Table 6. The sensitivities for long-lived radionuclides in a concrete matrix varied between 33000 cps/ppm (for ^{99}Tc) and 170 000 cps/ppm (for ^{233}U) in LA-ICP-QMS and between 180000 cps/ppm (for ^{99}Tc) and 720000 cps/ppm (for ^{233}U) in DF-LA-

Table 6
Sensitivity and detection limits [ng g^{-1}] for long-lived radionuclides in a concrete matrix using LA-ICP-QMS (Elan 6000) and maximum allowed concentration in radioactive waste for final storage in Germany (Morsleben)

	Sensitivity [cps/ppm]		Detection limit[a] [ng g^{-1}]		
Nuclide	LA-ICP-QMS	DF-LA-ICP-MS	LA-ICP-QMS	DF-LA-ICP-MS	Max. allowed conc. [ng g^{-1}][b]
^{99}Tc	33 000	180 000	0.18	0.025	70
^{232}Th	93 000	490 000	0.10	0.002	720 000
^{233}U	170 000	720 000	0.06	0.0013	0.05
^{235}U	114 000	506 000	0.07	0.002	900
^{238}U	95 000	470 000	0.10	0.020	1 000
^{237}Np	162 000	670 000	0.05	0.0015	1.5

[a] Gas blank.

[b] Conditions for final storage of radioactive waste in Germany (Morsleben).

Table 7
Sensitivity and detection limits [ng g^{-1}] for long-lived radionuclides in graphite matrix using LA-ICP-QMS (Elan 6000)

Nuclide	Sensitivity [cps/ppm]	Detection limit [ng g^{-1}]
^{99}Tc	22 000	1.3
^{232}Th	45 000	0.8
^{233}U	47 000	0.5
^{235}U	51 000	0.7
^{238}U	56 000	2.1[a]
^{237}Np	38 000	0.5

[a] Possible contamination.

ICP-MS. The detection limits in LA-ICP-QMS in concrete were determined to be between 0.05 ng g^{-1} for ^{237}Np and 0.18 ng g^{-1} for ^{99}Tc and in DF-LA-ICP-MS between 0.0013 ng g^{-1} for ^{233}U and 0.025 ng g^{-1} for ^{99}Tc. The detection limits in DF-LA-ICP-MS are about one order of magnitude lower than in LA-ICP-QMS due to higher sensitivity and lower background. Comparing these detection limits in LA-ICP-MS with the maximum allowed concentrations for final storage of radioactive waste in Germany, the LA-ICP-MS is well suited for characterizing unknown concrete radioactive waste materials.

Lower sensitivity for long-lived radionuclides (from 22000 cps/ppm for ^{99}Tc to 56000 cps/ppm for ^{238}U) and higher detection limits (between 0.5 and 2 ng g^{-1}) in LA-ICP-QMS were observed for graphite compared to the concrete matrix because of different physical and chemical properties (e.g., absorption and reflectivity of photon energy). The sensitivities and the detection limits of long-lived radionuclides measured by LA-ICP-QMS in a graphite matrix are summarized in Table 7.

In contrast, the sensitivity of long-lived radionuclides in ICP-QMS and DF-ICP-MS (using micronebulization) of aqueous solutions are significantly higher compared to the sensitivity in LA-ICP-MS (e.g., ^{238}U-45*10^6 cps/ppm in ICP-QMS [19] and 2110*10^6 cps/ppm in DF-ICP-MS [20], respectively). The detection limits of long-lived radionuclides in high-purity aqueous solutions using ICP-QMS and DF-ICP-MS are in the sub ng L^{-1} and pg L^{-1} range, respectively [19,20]. Such very low detection limits cannot be achieved in a digested solution of solid samples, because the long-lived radionuclides were determined after a dilution of digested solution by a factor of 500 to 1000. Matrix effects occurring at higher matrix concentrations represent an important limit for ICP-MS. A trace/matrix separation is required to reduce matrix effects in such complicated concrete samples and interference by molecular ion formation (e.g., oxides, hydride and argon molecular ions with matrix elements) which disturb the sensitive trace analysis. Nevertheless, a direct solid analytical method has the advantage of avoiding the contamination problems that occur during sample preparation.

3.3. Results of isotope ratio measurements

An important application of LA-ICP-MS on radioactive waste materials is isotope ratio measurements. To check the performance of LA-ICP-MS for precise and accurate isotope ratio measurements, high-purity graphite targets doped with different isotope mixtures for ^{235}U/^{238}U and ^{230}Th/^{232}Th with isotope ratios from 1 to 10^{-3} were analyzed by LA-ICP-QMS. The results of eight isotope ratio measurements of ^{235}U/^{238}U on NIST U020 isotope standard reference material mixed with high-purity graphite are summarized in Figure 6 (each data point represents the averaged isotope ratio of six single measurements). The ^{235}U/^{238}U isotope ratio (mean value of the eight independent measurements given in Figure 6) on the NIST U020 isotope standard reference material in graphite matrix was determined with a precision of 1.2% RSD and an accuracy of 0.43%. The mass bias was corrected using CCLU 500 isotope standard reference material in graphite with a ^{235}U/^{238}U = 1 as described elsewhere [14].

To verify the accuracy and precision of the Th isotope ratio, measurements in LA-ICP-QMS on two synthetic isotope mixtures with a ^{230}Th/^{232}Th ratio of about 1 and 0.019, respectively in graphite matrix were performed (Table 8). The isotope ratio was calculated as the average of five independent measurements where each measurement is given by a mean value of six replicates. For both mixtures we observed an excellent accuracy of 0.19% and 0.3%. The precision of isotope ratio measurements by LA-

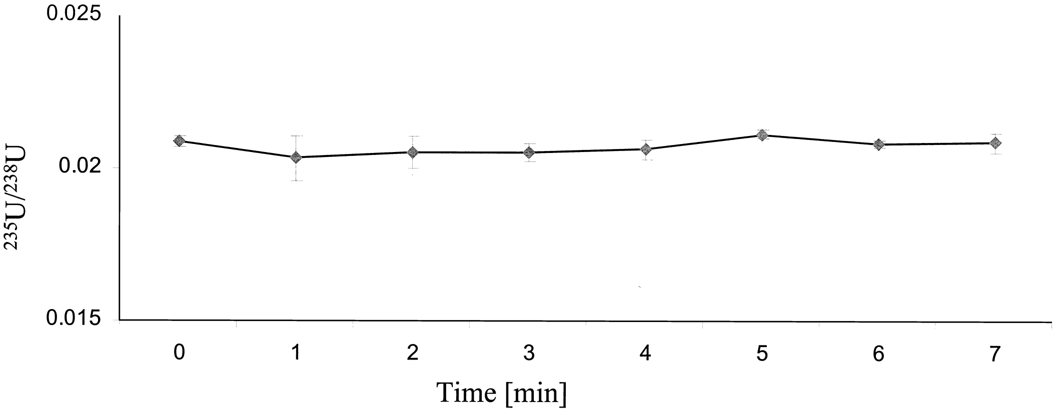

Fig. 6. Isotope ratio measurements of uranium isotope standard (NIST U020) in graphite (rf power, 1100 W; carrier gas flow rate, 0.84 L min^{-1}) measured by LA-ICP-QMS.

ICP-QMS was 1.1% and 6.2% for $^{230}Th/^{232}Th \approx 1$ and 0.019, respectively. The Th concentration for both isotope mixtures in graphite was 1 μg g^{-1} only.

LA-ICP-QMS was used for the characterization of real radioactive waste with graphite matrix (Figure 7). With respect to measured isotope ratios of uranium (10 measurements using averaged isotope ratio of six replicates were performed on the sample), the investigated waste sample shows a significant variation in $^{235}U/^{238}U$ and $^{234}U/^{238}U$ isotope ratios compared to the table values that are typical of natural samples [21]. A significant enrichment of ^{235}U in the reactor graphite was found by LA-ICP-QMS. The $^{235}U/^{238}U$ isotope ratio in radioactive graphite was determined as 0.009264 (RSD, 0.4%) versus the isotope ratio of 0.00725 in natural samples [21]. Furthermore, non-natural ^{236}U was detected and the $^{236}U/^{238}U$ isotope ratio was determined to be 0.000113 (RSD, 0.7%). In this radioactive graphite target $^{234}U/^{238}U$ was measured as 0.000067 (RSD, 1.1%). Because of the very homogeneous distribution of uranium, good precision, as demonstrated for $^{235}U/^{238}U$ isotope ratio in Figure 7, was observed even for small isotope ratios.

Table 8
Thorium isotope ratio measurements ($^{230}Th/^{232}Th$) on synthetic isotope mixtures in graphite matrix by LA-ICP-MS

	$^{230}Th/^{232}Th$		
	Measured ratio	Isotope mixture	Accuracy
Mixture 1	1.0473 ± 0.0199	1.0453 ± 0.0105	0.19%
Mixture 2	0.01907 ± 0.00119	0.01913 ± 0.00019	0.31%

Table 9 compares the results of isotope ratio measurements of U and Th in different solid radioactive waste materials (filter and silt sample) obtained by direct measurements by LA-ICP-QMS and by DF-ICP-MS after the digestion and separation of the uranium by liquid–liquid extraction and Th by ion exchange [22]. For LA-ICP-QMS measurements homogeneous fused, lithium borate targets were prepared from powdered radioactive waste samples. The results of uranium isotope ratios by LA-ICP-QMS (five measurements were performed on the sample) were verified by ICP-QMS measurements on digested solution of the filter and silt powder and uranium separation by liquid–liquid extraction. The natural isotope ratio for $^{235}U/^{238}U$ was confirmed by comparing the results obtained by LA-ICP-QMS and the ICP-QMS measurements. The precision of $^{235}U/^{238}U$ determination on the radioactive silt and filter sample by LA-ICP-QMS was about 2% (versus 0.4% RSD by ICP-QMS on digested radioactive waste sample with uranium separation). Whereas the $^{235}U/^{238}U$ isotope ratios measured in radioactive filter and silt samples are close to the isotope ratio in nature ($^{235}U/^{238}U = 0.00725$ [21]) an enrichment of ^{235}U by a factor of ≈ 4 was detected in a radioactive ash sample (e.g., $^{235}U/^{238}U = 0.0317 \pm 0.0008$ in LA-ICP-MS versus $^{235}U/^{238}U = 0.0314 \pm 0.0002$ in ICP-QMS after uranium extraction).

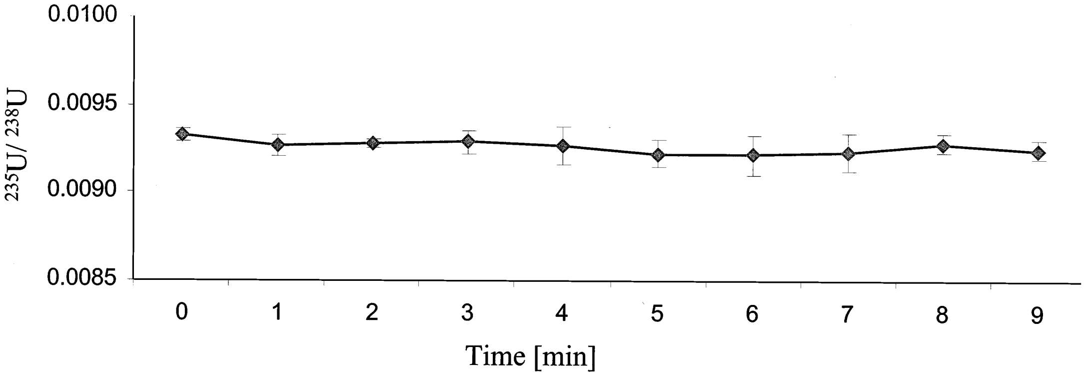

Fig. 7. Isotope ratio measurements of uranium in radioactive waste graphite (rf power, 1100 W; carrier gas flow rate, 0.84 L min^{-1}) measured by LA-ICP-QMS.

The comparison of results of thorium isotope ratio measurements using LA-ICP-QMS and DF-ICP-MS on digested solution after Th separation by ion exchange [22] demonstrates the limits of direct solid analysis. In different radioactive solid samples the $^{230}Th/^{232}Th$ isotope ratios varied between 0.0015 (radioactive glass sample) and 0.003 (radioactive silt sample). LA-ICP-QMS yielded lower thorium isotope ratios for silt and filter samples compared to DF-ICP-MS after Th separation. This difference can be explained by possible interference with molecular ions in LA-ICP-QMS at a mass of 232 u (e.g., $^{24}Mg^{208}Pb^+$, $^{206}Pb^{12}C^{14}N^+$ or $^{208}Pb^{12}C^{2+}$).

3.4. Molecular ion formation of long-lived radionuclides in LA-ICP-MS

A limiting factor for the precision and accuracy of analytical results by LA-ICP-MS is the molecular ions formed, which lead to isobaric interference with the atomic ion of the analytes.

Figure 8 shows the oxide ion formation for uranium, thorium and neptunium as a function of ICP-rf power measured by LA-ICP-QMS. For lower ICP-rf power, higher oxide rates were measured because of incomplete dissociation of the original oxides. By studying the oxide ion formation for uranium, thorium and neptunium as a function of the carrier gas flow rate, it was found that the oxide formation for long-lived radionuclides increased with increasing carrier gas flow rate in LA-ICP-MS (Figure 9). At higher carrier gas flow rate the resistance time of ablated original oxides is lower, therefore the compounds were not completely dissociated in the ICP. Analogous behavior for the formation of oxide ions of long-lived radionuclides as a function of rf power and nebulizer gas flow rate was found in DF-ICP-MS on aqueous solution [23].

The relative oxide and hydride ion intensity of long-lived radionuclides in a concrete matrix measured by LA-ICP-QMS as summarized in Table 10 varied in the sub-% range. The molecular ions formed disturb the analysis of different actinides (e.g., the determination of ^{239}Pu at a trace level is not possible with LA-ICP-QMS in the presence of a high uranium concentration in radioactive waste because of isobaric

Table 9
Results of isotope ratio measurements of uranium and thorium on real radiowaste materials measured by LA-ICP-QMS in comparison to ICP-MS after digestion and analyte separation

Method	$^{235}U/^{238}U$	$^{230}Th/^{232}Th$
	Radioactive filter sample	
LA-ICP-QMS	0.00711 ± 0.00015	0.00150 ± 0.00006
ICP-MS[a]	0.00703 ± 0.00003[b]	0.00167 ± 0.00003[c]
	Radioactive silt sample	
LA-ICP-QMS	0.00713 ± 0.00012	0.00291 ± 0.00004
ICP-MS[a]	0.00712 ± 0.00002[b]	0.00335 ± 0.00003[c]

[a] After analyte separation as described in [22].
[b] Measured by ICP-QMS.
[c] Measured by DF-ICP-MS [20].

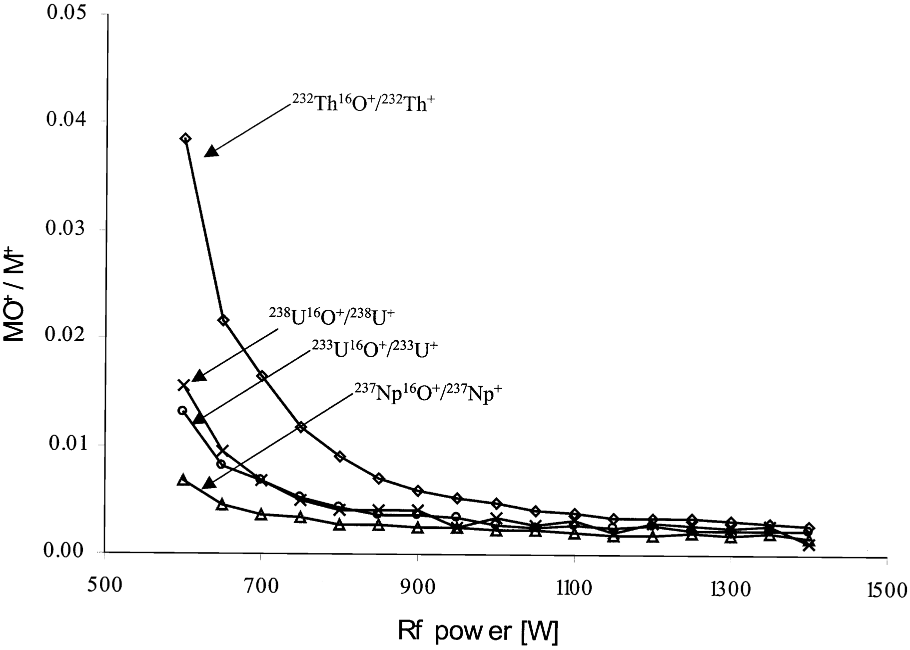

Fig. 8. Relative oxide ions of long-lived radionuclides as a function of ICP-rf power in LA-ICP-QMS (concrete matrix); carrier gas flow rate = 0.9 L min^{-1}.

interference with the $^{238}U^1H^+$ ion). Therefore, a Pu isotope analysis in a radioactive waste sample is possible only after digestion and a uranium/plutonium separation.

Considering the oxide ion formation in analogy to DF-ICP-MS on aqueous solutions [23] the following sequence with decreasing relative oxide ion intensities was observed:

$$ThO^+/Th^+ > UO^+/U^+ > NpO^+/Np^+$$

For the oxide ions measured by LA-ICP-QMS, a correlation for U and Th was found with the known dissociation energies. From this correlation curve, the bond energy for NpO with 733 ± 36 kJ mol^{-1} using the measured oxide ion formation rate can be estimated (Figure 10).

A similar correlation of the oxide ion intensity of actinides and dissociation energy was found for U, Th, Np, Pu and Am in DF-ICP-MS in aqueous solution as well [23]. From this correlation the bond dissociation energy of NpO was estimated to be 730 ± 15 kJ mol^{-1}. Recently, the experimental bond dissociation energy was published for NpO on the Internet in the WebElements page of Sheffield University [24]. The experimental bond enthalpy of 718 ± 42 kJ mol^{-1} is in excellent agreement with our value of 733 ± 36 kJ mol^{-1} determined by mass spectrometry for LA-ICP-QMS on solid concrete synthetic standard and 730 ± 15 kJ mol^{-1} for DF-ICP-MS on aqueous solution.

Table 10
Relative hydride and oxide ion intensity of long-lived radionuclides (concrete matrix) in LA-ICP-QMS

	MX^+/M^+	Possible interference
$^{232}Th^1H^+$	$<1.6 \times 10^{-4}$	$^{233}U^+$
$^{234}U^1H^+$	9×10^{-4}	$^{235}U^+$
$^{238}U^1H^+$	9×10^{-4}	$^{239}Pu^+$
$^{232}Th^{16}O^+$	7×10^{-3}	$^{238}Cm^+$
$^{233}U^{16}O^+$	4×10^{-3}	$^{239}Pu^+$, $^{239}Cf^+$
$^{237}Np^{16}O^+$	3×10^{-3}	
$^{238}U^{16}O^+$	4×10^{-3}	

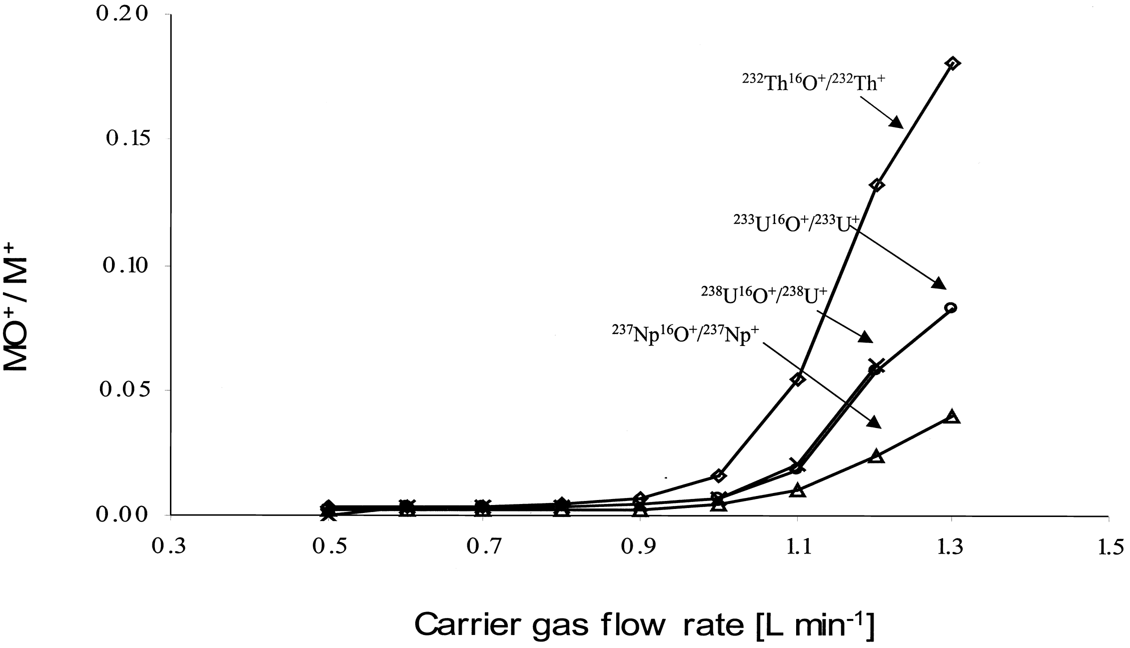

Fig. 9. Relative oxide ions of long-lived radionuclides as a function of carrier gas flow rate in LA-ICP-QMS (concrete matrix); rf power, 950 W.

4. Conclusions

LA-ICP-MS is a powerful method for sensitive trace and precise isotope ratio measurements of long-lived radionuclides in solid samples including radioactive waste materials. Analyses of long-lived radionuclides in nonconducting samples (such as concrete) are very fast with low detection limits in the pg g^{-1} range and often no sample preparation is required. The sample preparation used for the preparation of

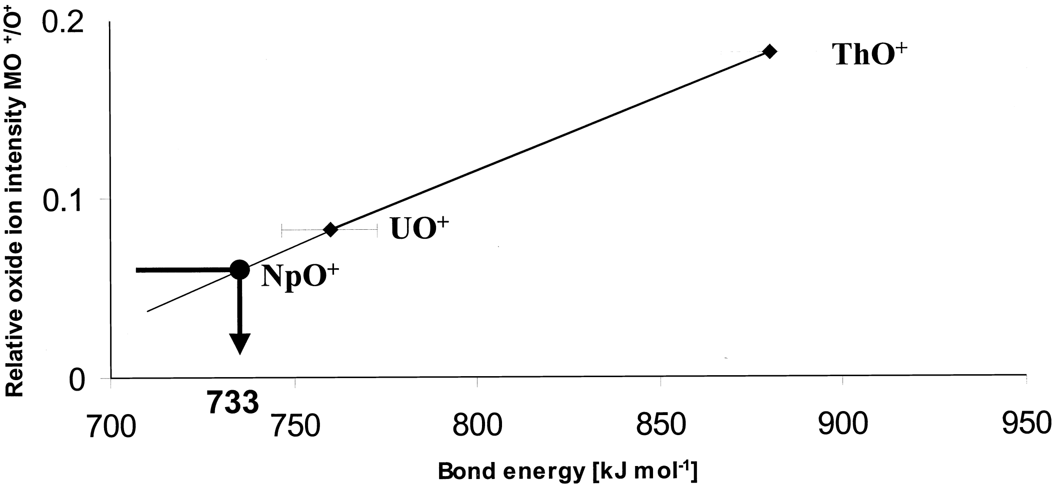

Fig. 10. Relative oxide ions of long-lived radionuclides in LA-ICP-QMS versus bond dissociation energies.

homogeneous targets for LA-ICP-MS from inhomogeneous radioactive powder waste samples by lithium-borate fusion is very simple and can be employed in every routine laboratory.

An important problem for the analysis of real radioactive waste samples is the possible isobaric interference of long-lived radionuclides with stable isotopes and molecular ions that cannot be solved by LA-ICP-QMS. Therefore, a careful study of interference problems is necessary for each sample measured. In cases of disturbing interference, ICP-MS after the digestion of solid samples and analyte separation is the method of choice.

Using LA-ICP-QMS with a single ion collector, isotope ratio measurements of long-lived radionuclides in a concrete and graphite matrix are possible with a precision of 0.6%. As an accurate quantification method in solid-state mass spectrometry is the isotope dilution technique, which will be discussed in a forthcoming paper on the characterization of solid samples of radioactive waste by LA-ICP-MS in combination with solution calibration.

References

[1] S. F. Durrant, J. Anal. Atom. Spectr. 14 (1999) 1385.
[2] J.S. Becker, H.-J. Dietze, Int. J. Mass Spectrom. 197 (2000) 1.
[3] A.J. Campbell, M. Humayun, Anal. Chem. 71 (1999) 939.
[4] D. Günther, S.E. Jackson, H.P. Longerich, Spectrochim. Acta 54B (1999) 381.
[5] J.Th. Westheide, J.S. Becker, R. Jäger, H.-J. Dietze, J.A.C. Broekaert, J. Anal. Atom. Spectr. 11 (1996) 661.
[6] T.E. McCandless, T.E. Lajack, D.J. Ruiz, A.M. Ghazi, J. Geostand, Geoanalysis 21 (1997) 279.
[7] M. Gastel, J.S. Becker, G. Küppers, H.-J. Dietze, Spectrochim Acta 52B (1997) 2051.
[8] M. Ødegard, Geostandandards Newslett. 13 (1999) 173.
[9] L.P. Berdard, D.R. Baker, N. Machado, Chem. Geol. 138 (1997) 1.
[10] D. Günther , H. Cousin, B. Magyar, I. Leopold, J. Anal. Atom. Spectrom. 12 (1997) 165.
[11] J.J. Leach, L.A. Allen, D.B. Aeschliman, R.S. Houk, Anal. Chem. 71 (1999) 440.
[12] C. Pickhardt, J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 368(2/3) (2000).
[13] I. Horn, R.L. Rudnick, W.F. McDonough, Chem. Geol. 164 (2000) 281.
[14] I.T. Platzner, J.S. Becker, H.-J. Dietze, Atom. Spectrosc. 20 (1999) 6.
[15] J.S. Becker and H.-J. Dietze, Fresenius J. Anal. Chem. 365 (1999) 429.
[16] P.K. Appelblad, I. Rodushkin, D.C: Baxter, J. Anal. Atom. Spectrom. 15 (2000) 359.
[17] C.Pickhardt, I. Brenner, J.S. Becker, H.-J. Dietze, Fresenius Anal. Chem. 368(1) (2000) 79.
[18] K.P. Jochum, D.B. Dingwell, A.W. Hoffmann, B. Stoll, I. Raczek, A. Rocholl, J.S. Becker, A. Besmehn, D. Bessette, H.-J. Dietze, P. Dulski, J. Erzinger, E. Hellenbrand, P. Hoppe, I. Horn, K. Janssens, G. Jenner, M. Klein, W.M. McDonough, M. Maetz, I.K. Nikogosian, C. Pickhardt, H.M. Seufert, S.G. Simakin, A.V. Sobolev, B. Spettel, S. Straub, L. Vincze, A. Wallianos, G. Weckwerth, D. Wolf, M. Zimmer, Geostand. Newslett. (in press).
[19] J.S. Becker, R.S. Soman, K. L. Sutton, J. Caruso, H.-J. Dietze, J. Anal. Atom. Spectrom., 14 (1999) 933.
[20] J.S. Becker, H.-J. Dietze, J. Anal. Atom. Spectrom. 14 (1999) 1493.
[21] International Union of Pure and Applied Chemistry, Isotopic composition of the elements, Pure Appl. Chem. 63 (1991) 991.
[22] J.S. Becker, H.-J. Dietze, Fresenius J. Anal. Chem. 364 (1999) 482.
[23] J.S. Becker, H.-J. Dietze, Intern. J. Mass Spectrom. (in press).
[24] M. Winter, http://www.webelements.com, neptunium: bond enthalpy data.