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Isotope ratio measurements of spent reactor uranium in environmental samples by using inductively coupled plasma mass spectrometry

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Abstract

As a result of the accident at the Chernobyl nuclear power plant (NPP) the environment was contaminated with spent nuclear fuel. The ^{236}U isotope was used in this study to monitor the spent uranium from nuclear fallout in soil samples collected in the vicinity of the Chernobyl NPP. A rapid and sensitive analytical procedure for uranium isotopic ratio measurement in environmental samples based on inductively coupled plasma quadrupole mass spectrometry with a hexapole collision cell (HEX-ICP-QMS) was developed. Figures of merit for the HEX-ICP-QMS were studied with a plasma-shielded torch using different nebulizers [such as an ultrasonic nebulizer (USN) and a Meinhard nebulizer] for the solution introduction. An $^{238}U^+$ ion intensity of up to 27 000 MHz/ppm in HEX-ICP-QMS with USN was observed by introducing helium into the hexapole collision cell as the collision gas at a flow rate of 10 mL min^{-1}. The formation rate of uranium hydride ions UH^+/U^+ of 2×10^{-6} was obtained by using USN with a membrane desolvator. The detection limit for ^{236}U in 10 μg L^{-1} uranium solution was 3 pg L^{-1}corresponding to the limit of $^{236}U/^{238}U$ ratio determination of 3×10^{-7}. In the case of low isotopic abundance of ^{236}U ($<10^{-5}$), the measured isotopic ratio in the synthetic mixture was systematically lower than the calculated ratio. The precision of uranium isotopic ratio measurements in 10 μg L^{-1} laboratory uranium isotopic standard solution was 0.13% ($^{235}U/^{238}U$) and 0.33% ($^{236}U/^{238}U$) using a Meinhard nebulizer and 0.45% ($^{235}U/^{238}U$) and 0.88% ($^{236}U/^{238}U$) using an USN. The isotopic composition of all investigated Chernobyl soil samples differed from those of natural uranium; i.e. in these samples the $^{236}U/^{238}U$ ratio ranged from 10^{-5} to 10^{-3}. Results of isotopic ratio measurement by HEX-ICP-QMS in soil samples are in agreement with those obtained by using a double-focusing sector field ICP-MS within experimental errors. (Int J Mass Spectrom 203 (2000) 143–154) © 2000 Elsevier Science B.V.

Keywords: Inductively coupled plasma mass spectrometry; Hexapole collision cell; Isotopic ratio measurements; Uranium; Spent nuclear fuel

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1. Introduction

The most dangerous constituents of spent reactor fuel are the α-emitting nuclides of uranium and transuranium elements. Environmental contamination with these nuclides is probable during reprocessing of spent fuel elements of nuclear reactors or during accidents involving nuclear devices and nuclear power plants (NPPs). As a result of the Chernobyl NPP accident about 3.5% of the radioactive fuel inventory was released into the atmosphere and dispersed over a large area of Eastern Europe. The main fraction of actinide fallout took place in the vicinity of the Chernobyl NPP, contaminating adjoining territories of the Ukraine and Belarus [1]. Thus their identification and determination is required for environmental monitoring of large contaminated regions. Initially actinide elements were incorporated in nuclear fuel particles, in aggregates of fuel with reactor graphite and carbon–bitumen particles as well as in the composition of secondary radioactive particles, which were produced as a result of the capture of radionuclides from the vapour–gaseous phase by particles of atmospheric dust and soil particles [2]. Because of some differences in the chemical properties of actinides, the migration of uranium differs from the migration of other actinides (e.g. plutonium) [3]. Hence a study of the radionuclides leaching from the fuel particles in soil, which requires ultrasensitive isotope analytical methods for direct determination of spent reactor uranium, is important for the control and forecast of the radio-ecological situation in the contaminated regions. As a tracer of nuclear fallout in an environmental sample the ^{236}U isotope ($T_{1/2} = 2.3416 \times 10^7$ years) can be used, which is absent in natural uranium isotopic composition, but is produced in nuclear reactors via the ^{235}U (n,γ) ^{236}U reaction. ^{236}U has been detected in environmental samples due to nuclear fallout from nuclear accidents and contamination in the vicinity of uranium recycling plants [4–6]. Along with conventional alpha spectrometry, which is not very sensitive for long-lived radionuclides, a number of analytical techniques have been proposed for uranium isotopic measurements, such as thermal ionisation mass spectrometry (TIMS) [7–10], resonance ionisation mass spectrometry (RIMS) [11,12], accelerator mass spectrometry (AMS) [13], laser-excited atomic fluorescence spectrometry [14], etc. Inductively coupled plasma mass spectrometry (ICP-MS) is one of the most suitable methods for routine uranium isotopic ratio determination due to its sensitivity, accuracy and simple sample preparation procedure [6,15,16]. The excellent precision of isotopic ratio measurements of long-lived radionuclides by double-focusing sector field inductively coupled plasma mass spectrometry (DF-ICP-MS) (down to 0.07% for ^{235}U/^{238}U ratio in 10 μg L^{-1} uranium solution) and by ICP-QMS (down to 0.028% for ^{235}U/^{238}U ratio) has been demonstrated in various studies by our laboratory [17–21]. However, high-sensitive sector field ICP mass spectrometers are expensive and not always available for routine applications. On the other hand, the sensitivity offered by quadrupole-based ICP-MS is often not satisfactory for the determination of a low isotopic abundance of ^{236}U in environmental materials, because the isotopic ratio of ^{236}U/^{238}U ranges from 10^{-2} in nuclear fuel to 10^{-10} and lower in contaminated environmental samples [22]. Another problem is the relatively high content of natural uranium in soil samples (in the μg g^{-1} range) and the possible formation of hydride ions ^{235}UH^{+} from ^{235}U, which is contained both in reactor fuel and in natural uranium from environmental samples, strongly affecting the detection limits of ^{236}U in ICP-MS. A quadrupole-based plasma mass spectrometer with a hexapole collision cell (HEX-ICP-QMS) combined with an effective solution introduction system consisting of an ultrasonic nebulizer (USN) with a membrane desolvator is a powerful and less expensive tool (compared to sector field ICP-MS) for sensitive isotopic ratio measurement especially for greatly differing isotopic ratios. The application of a gas-filled collision cell in ICP-MS [23,24] enables an increase of instrument sensitivity based on an improvement of ion transmission ability of the interface due to a decrease of initial energy of ions to less than 1 eV [25]. In the collision cell deceleration and thermalisation of the introduced ion beam occurs by interaction of ions with reaction gas atoms. The ions are then efficiently transmitted via a multipole device due to the effect of collisional focusing as is known for quadrupoles, too [26]. Furthermore, the application of a plasma-shielded torch [27] in ICP-MS is useful for sensitivity improvement [21]. A plasma-shielded torch prevents a capacitive coupling from the load coil into the ICP, and the secondary discharge between the ICP and sampling cone is reduced. The production of a narrow ion energy distribution results in a higher transmission and therefore in an increase in sensitivity for ions. In order to find the best experimental parameters for accurate and precise uranium isotope measurements while keeping a reasonable total analysis time for different solution introduction systems the figures of merit of HEX-ICP-QMS were studied. The aim of this work was the development of a rapid and ultrasensitive isotope analytical procedure for ^{236}U determination in environmental samples based on inductively coupled plasma quadrupole mass spectrometry.

2. Experiment

2.1. Instrumentation of ICP-MS

A quadrupole-based HEX-ICP-QMS mass spectrometer (Platform ICP, Micromass Ltd., Manchester, UK) consisting of an ICP source with a shielded torch and quadrupole mass analyser with an ion transfer system based on a hexapole collision cell was used for uranium isotopic ratio measurements. Helium was introduced into the hexapole cell as a buffer gas. Gas input into the hexapole was controlled by built-in mass flow controllers. A Meinhard nebulizer (J.E. Meinhard Associates, Inc., Santa Ana, CA USA) with a Scott double-pass quartz spray chamber cooled to 4 °C was initially applied for solution introduction in HEX-ICP-QMS for the optimisation and study of collision cell characteristics. Furthermore, an ultrasonic nebulizer with a membrane desolvation system (USN U-6000AT$^+$, CETAC Technologies Inc., Omaha, Nebraska USA) was used for effective solution introduction in ICP-MS. Comparative measurements of the uranium isotopic ratio in environmental soil samples were performed with a DF-ICP-MS (ELEMENT, Finnigan MAT, Bremen, Germany). For solution introduction a MicroMist microconcentric nebulizer with a minicyclonic spray chamber (both from Glass Expansion, Camberwell, Australia) was used and the ICP torch was shielded with grounded platinum electrode (GuardElectrode, Finnigan MAT). Further details of the instrument used can be found in [21,28].

2.2. Standards and reagents

Isotopic standard solution of uranium (CCLU-500 laboratory standard, Nuclear Research Center, Prague, Czech Republic) [20,29] was used for the optimisation and calibration procedures. Uranium isotope ratio values for the CCLU-500 laboratory standard have been established by calibration against the NIST-500 SRM by TIMS [29]. Later on, the recommended values were well defined using quadrupole ICP-MS in [20], ^{234}U/^{238}U = 0.011 122 (RSD = 0.16%), ^{235}U/^{238}U = 0.999 91 (RSD = 0.050%), ^{236}U/^{238}U = 0.002 789) (RSD = 0.39%). For the preparation of a uranium sample solution with natural isotopic composition, the uranium available in the form of a metal slug (nuclear-free uranium, Merck, Germany) was first cleaned by etching with a concentrated sub-boiled nitric acid. 100 mg of cleaned sample was subsequently heated on a hot plate for 2–3 min in 10 mL of sub-boiled nitric acid. The solution was then diluted up to 20 mL with high purity water. Later on it was further diluted to the necessary concentrations for the determination of the isotopic ratio of uranium by ICP-MS with deionised Milli-Q water (18 MΩ) obtained from a Millipore Milli-Q-Plus water purifier. The solutions were acidified to 1% sub-boiled HNO_3.

2.3. Samples

Soil samples were taken in the relocation zone of Belarus (4–10 km to the north and northwest of the Chernobyl NPP) in the areas that have been undisturbed by technogenic and anthropogenic activities since the Chernobyl accident. The relief of these control areas and types of soil included that most typical of the south of Belarus. Soil was sampled with

Table 1
Optimised operating conditions used HEX-ICP-MS and DF-ICP-MS for different sample introduction systems

ICP-MS type	HEX-ICP-MS			DF-ICP-MS
Nebulizer type	Meinhard (with and without shielded torch)			Micromist
Spray chamber	Cooled Scott type	USN	USN/Desolvator	Minicyclonic
rf power (W)	1350	1350	1350	860
Cooling gas flow rate (L $\min^{-1}$)	13.5	13.5	13.5	14
Auxiliary gas flow rate (L $\min^{-1}$)	1.0	0.9	0.9	1.0
Nebulizer gas flow rate (L $\min^{-1}$)	0.83	0.9	1.2	0.9
He flow rate (mL $\min^{-1}$)	10	10	10	
Solution uptake rate (mL $\min^{-1}$)	0.9	2.0	2.0	0.24
Con lens (V)	400–600	400–600	400–600	
Hexapole exit lens (V)	400–600	400–600	400–600	
Hexapole bias potential (V)	0	0	0	
Ion energy lens (V)	2.0	2.0	2.0	
Multiplier voltage (V)	470	470	470	
USN heating temperature (°C)	. . .	140	140	
USN cooling temperature (°C)	. . .	+3	+3	
Desolvator heating temperature (°C)	. . .	. . .	160	
Sweep gas flow (L $\min^{-1}$)	. . .	. . .	2.75	
Mass resolution ($m/\Delta m$)	300	300	300	300
Dwell time (s)	0.2	0.2	0.2	
Number of scans	200	200	200	

a coring device that was specially designed to cut 50 mm thick soil layers down to a depth of 20 cm.

2.4. Sample preparation

Collected soil samples were dried at 105 ± 5 °C. After homogenisation, 250 g of the sample was ashed at 600 ± 50 °C for 1 h. Plant roots and vegetation were incinerated separately at 550 ± 50 °C for 2 h and then the ash was mixed with the sample. The ashed samples were eached by 8 M of HCl, and the solution was then passed through anion exchange resin AV-17. Plutonium was eluted by NH_4I solution in HCl. Uranium was extracted by 8 M of HNO_3 and was purified by extraction with diethylether [30].

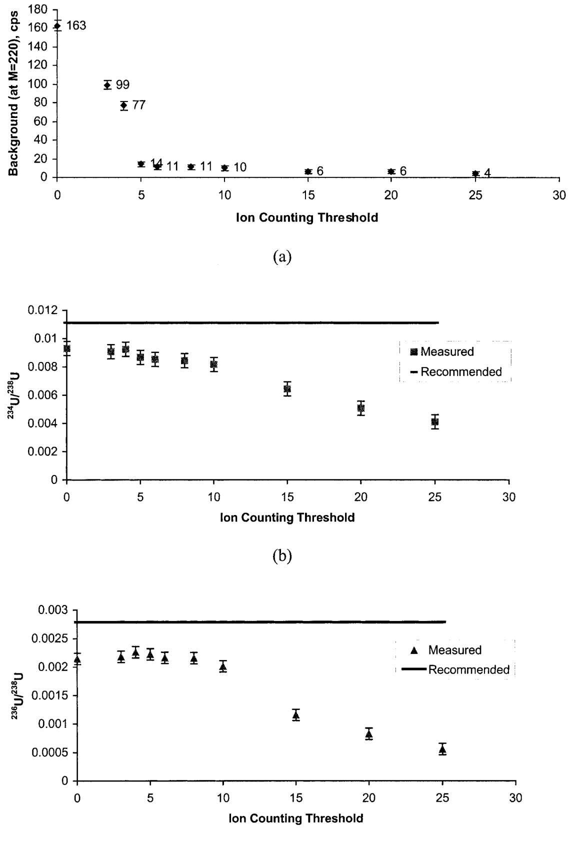
2.5. Optimisation of isotopic ratio measurements of uranium

Optimisation of experimental parameters of HEX-ICP-QMS was first done with respect to a maximal ion intensity of $^{238}U^+$ and minimal background at mass 236 u using a 10 $\mu g\, L^{-1}$ natural uranium solution introduced by a Meinhard nebulizer. In order to avoid additional hydride formation, which would occur by using hydrogen as the collision gas, only helium was introduced into the hexapole cell for the measurement of uranium isotopic composition. The measurement procedure using DF-ICP-MS was applied for the isotopic analysis of uranium as described in [21]. Optimised experimental parameters of the HEX-ICP-QMS with different sample introduction systems in comparison to those of DF-ICP-MS are summarised in Table 1. The measured uranium isotopic ratios in soil samples were corrected by using the experimentally determined mass discrimination factors by the application of laboratory isotopic standard solution CCLU-500 according to [31]. It was observed by measurement of the digested soil samples that mass discrimination changed slightly during operation, mainly as a result of clogging effects on the cones and matrix effects. Such factors impact the space charge distribution in the plasma–extraction lens region. Mass discrimination for uranium was therefore determined using 10 $\mu g\, L^{-1}$ CCLU-500 solution every time at the end of the measuring series of soil samples during the routine measurement of environmental samples.

3. Results and discussion

3.1. Optimisation of experimental parameters using ICP-MS with hexapole collision cell

The "Daly"-type detector system used in HEX-ICP-QMS "platform" has some advantageous features for isotopic ratio measurement. The photomultiplier, operating in the analogue mode, allows a linear output over 8–9 orders of magnitude [32], offering advantages for the measurement of isotopes with greatly differing abundance. However, the main disadvantage of the photomultiplier consists in rather high noise current. In HEX-ICP-QMS platform the electronic noise level of the acquisition system and its standard deviation are measured before the acquisition as the ion beam is switched off. The measured noise standard deviation is multiplied by an operator defined threshold value and this product sets the zero intensity level to be used. For the measurement of isotopic ratio of uranium having isotopes with strongly differing abundance, the threshold value must be carefully selected. A low threshold value leads to a higher background due to the electronic noise of the detector. As the threshold is increased, the visible noise level is reduced but the weak peaks become narrower and less intense, leading to a lower isotopic ratio than expected (Fig. 1). In this work the threshold was set to 6, which was a compromise between accurate measurement of the isotopes with low abundance and appropriate background correction. The multiplier gain of the Daly-type ion detector operated in analogue mode was set in such a way that the recorded signal intensity would be equal to the ion counting rate of a pulse counting detector [32]. Further, transmission of the ion beam through the hexapole collision cell as a function of experimental parameters of the HEX-ICP-MS was investigated. Thermalisation of the ions involved from ICP into the hexapole cell depends among other things on the mass of the ion and on collision gas pressure. The instrument used does not allow direct control of the operating gas pressure in the hexapole, therefore the gas flow was controlled during the measurement. Uranium ion intensity measured by the HEX-ICP-MS as a function of helium flow rate in 10 μg L^{-1} aqueous solution acidified to 1% HNO_3 under optimised plasma parameters is presented in Fig. 2. The investigation yielded an increase of ion transmission through the hexapole at higher collision gas flow rate (corresponding to higher gas pressure) thus improving sensitivity for uranium isotopes by approximately one order of magnitude.



(a)

(b)

(c)

Fig. 1. Dependence of (a) the background signal and (b), (c) uranium isotopic ratios on the threshold value. Isotopic ratios are given without mass discrimination correction (10 μg L^{-1} CCLU-500 laboratory isotopic standard solution were introduced into an ICP by a Meinhard nebulizer, the shielded torch is off, the extraction lens voltage set to 600 V, see Table 1 for other experimental parameters).

Table 2
Sensitivities of ^{238}U and relative hydride formation rates 9UH$^+$/$^+$) obtained with HEX-ICP-QMS attached to different solution introduction systems in comparison to sensitivities of double-focusing ICP-MS under optimised experimental conditions (see Table 1, extraction lens voltage 600 V)

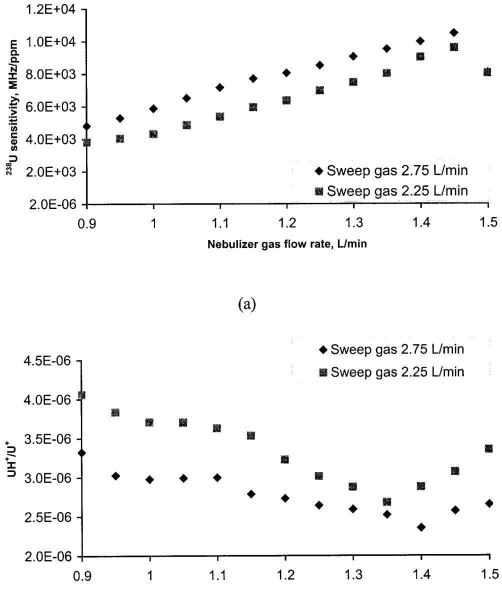
		HEX-ICP-QMS		DF-ICP-MS[a]
Sample introduction system	Shielded torch	Sensitivity for $^{238}U^+$ (MHz/ppm)	Relative hydride formation rate	Sensitivity for $^{238}U^+$ (MHz/ppm)
Meinhard nebulizer	−	500	4.5×10^{-5}	310
Meinhard nebulizer	+	1 600	1.9×10^{-5}	1 620
USN	−	15 000	1.2×10^{-4}	5 120
USN	+	27 000	8.7×10^{-5}	21 050
USA/membrane desolvator	−	12 400	2.5×10^{-6}	
USN/membrane desolvator	+	9 600	1.8×10^{-6}	

[a] See [21].

Further, by collision-induced reactions in a gas-filled multipole device the hydride formation rate is altered. Dependence of the hydride formation on helium flow was measured in Fig. 3. The investigation revealed that helium has only a weak influence on this effect.

3.2. Optimisation of sample introduction system

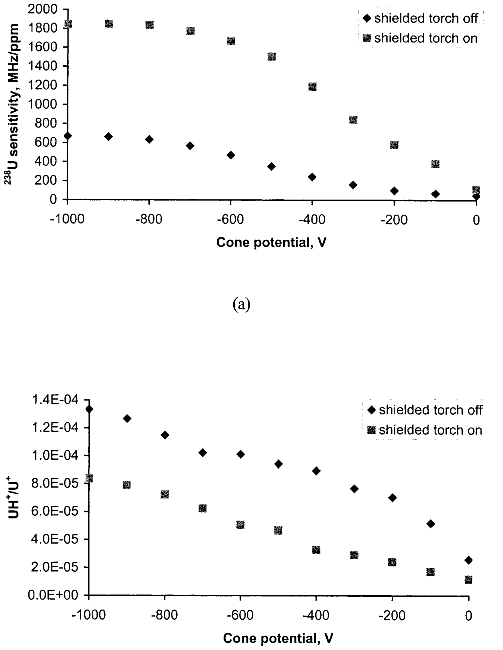
The efficiency of the solution introduction system in HEX-ICP-QMS was studied under optimum experimental conditions using different nebulizers (a Meinhard nebulizer and an ultrasonic nebulizer with and without a membrane desolvator) with respect to maximum U sensitivity and minimum UH$^+$ formation rate. Table 2 summarises the sensitivities of uranium for different solution introduction devices in HEX-ICP-QMS with and without a shielded torch. Maximum sensitivity of 27 000 MHz/ppm for ^{238}U was observed by using an USN. This is comparable with results achieved by a DF-ICP-MS ELEMENT with a shielded torch and an USN [21]. Application of an USN with a HEX-ICP-QMS without a shielded torch improved sensitivity by a factor of 30 compared to the Meinhard nebulizer. However, the hydride formation rate (UH$^+$/U$^+$) was observed to be the highest using USN. The UH$^+$/U$^+$ rate in a HEX-ICP-QMS coupled to an USN without a desolvator increased because more water vapour was transported to the plasma in comparison to the Meinhard nebulizer with a cooled Scott spray chamber. This hydride formation results in an increase of detection limits of the radionuclide of ^{236}U due to interference by $^{235}U^1H^+$. By using a microporous Teflon membrane desolvator the solvent is removed from the aerosol stream by an argon sweep gas, which reduces the hydride formation rate by up to 2 orders of magnitude (see Table 2). An additional optimisation was performed with respect to the nebulizer and the sweep gas flows in order to achieve a lower hydride formation and better sensitivity. However at the experimental conditions optimised for minimal hydride formation rate, a slight decrease in sensitivity was observed compared to an ultrasonic nebulizer without a membrane desolvator. Fig. 4 shows the dependence of $^{238}U^+$ ion intensity and hydride formation rate UH$^+$/U$^+$ on a nebulizer gas flow rate at two sweep gas flow rates. Changing the nebulizer gas flow rate alters the residence times of aerosol in the desolvator of an USN, in the membrane desolvator and in the ICP, which influences the hydride formation rate and the ionisation rate of uranium. For minimal hydride formation and nearly maximum ^{238}U sensitivity, the optimal nebulizer gas flow rates and sweep gas flow rates were in the range of the of 1.3 to 1.4 L min^{-1} and 2.7 to 2.8 L min^{-1}, respectively. When changing the cooling temperature of an USN from –3 to +5 °C and the heater temperature of an USN and a membrane desolvator from 120 to 160 °C, no significant change in the sensitivity for uranium was observed. However, the hydride formation rate of uranium varied within the range of 50%



(a)

(b)

Fig. 4. Dependence of (a) $^{238}U^+$ ion intensity and (b) relative hydride formation rate UH^+/U^+ on a nebulizer gas flow rate at different sweep gas flows. (10 μg L^{-1} natural uranium solution were introduced into an ICP by an USN with a membrane desolvator, the shielded torch is off, the extraction lens voltage set to 600 V, see Table 1 for other experimental parameters).



(a)

(b)

Fig. 5. Dependence of (a) $^{238}U^+$ ion intensity and (b) relative hydride ion intensity UH^+/U^+ on a cone (extraction lens) potential with (shielded torch on) and without (shielded torch off) a shielded torch. (10 μg L^{-1} natural uranium solution were introduced into an ICP by a Meinhard nebulizer, see Table 1 for other experimental parameters).

with changing the parameters mentioned previously. The optimal parameters are given in Table 1. The hydride formation rate UH^+/U^+ of 2×10^{-6} obtained using an USN and a membrane desolvator was better by approximately 1 order of magnitude (or more) than that obtained by using other solution introduction methods in this study and as reported by Kim et al. [33]. Further, the influence of a grounded electrode placed between the rf load coil and the quartz torch on the performance of the HEX-ICP-QMS was studied. The shielded torch altered the plasma conditions and hence the figures of merit were changed, e.g. application of the shielded torch in HEX-ICP-QMS reduced uranium hydride formation for all sample introduction configurations (Table 2). The effect of a shielded torch on the sensitivity for uranium was not the same for different nebulizers under the chosen experimental conditions (Table 1). By the application of a plasma-shielded torch the uranium sensitivity was improved by a factor of 3 for the Meinhard nebulizer, however, the uranium sensitivity decreased in the case of an USN attached to a membrane desolvator (see Table 2). Investigation of this phenomenon will be the subject of further studying the HEX-ICP-QMS performance. In Fig. 5 the dependence of $^{238}U^+$ intensity and hydride formation rate UH^+/U^+ on cone (extraction lens) potential with and without a plasma-shielded torch are presented. The optimal value of cone potential for achieving better sensitivity is about -600 V, however, a lower potential can be used in order to achieve a lower hydride formation rate. All the curves in Figs. 1–5 were measured taking into account the blank values measured under the same experimental conditions, because background ion intensity varied with changing experimental parameters.

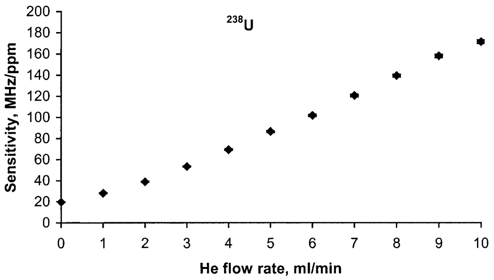


Fig. 2. Dependence of $^{238}U^+$ ion sensitivity on helium flow rate. (10 μg L^{-1} natural uranium solution were introduced into an ICP by a Meinhard nebulizer, the shielded torch is off, the extraction lens voltage set to 400 V, see Table 1 for other experimental parameters).

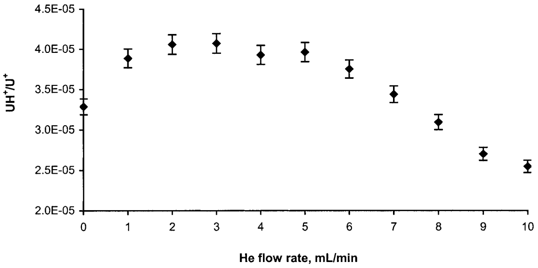


Fig. 3. Dependence of the hydride formation rate UH$^+$/U$^+$ on the He flow rate. (10 μg L^{-1} natural uranium solution were introduced into an ICP by a Meinhard nebulizer, the shielded torch is off, the extraction lens voltage set to 400 V, see Table 1 for other experimental parameters).

3.3. Precision and accuracy of isotopic ratio measurements of uranium

In order to determine the precision and accuracy of the determination of isotopic ratios of uranium in HEX-ICP-QMS six measurements of ^{235}U/^{238}U ratio were performed in 100 and 10 μg L^{-1} CCLU-500 laboratory isotopic standard solution (recommended value ^{235}U/^{238}U = 0.999 91) introduced into the ICP by a Meinhard nebulizer and an ultrasonic nebulizer, respectively. Mass discrimination per mass unit (MD) was determined by using different solution introduction systems under experimental conditions optimised for each system. The relative standard deviations of ^{235}U/^{238}U isotopic ratio achieved using different sample introduction configurations and the mass discrimination per mass unit are summarised in Table 3. By using a Meinhard nebulizer the precision of 0.13% and 0.2% was obtained without and with shielded torch, respectively, whereas by using an ultrasonic nebulizer it was about 0.6%–0.8%, which is comparable to the data presented for this isotopic ratio from other quadrupole and sector field instruments with a single detector [6,17–20]. The MD per mass unit for uranium was found to be lower by using a Meinhard nebulizer (without a shielded torch) for solution introduction into the ICP (about 0.2% in comparison to 0.8% by using an ultrasonic nebulizer for all possible configurations). The precise measurement of the ^{236}U/^{238}U ratio is important for evidence of contamination of environmental samples with uranium from nuclear reactors. Also, the ^{234}U/^{238}U ratio is of interest because it provides additional information about the characteristics of nuclear fuel contaminating the sample (e.g. it can be higher than the natural ratio because of the alpha decay of ^{238}Pu). The results of five measurements of isotopic ratios of ^{234}U/^{238}U and ^{236}U/^{238}U in CCLU-500 isotopic standard solution are presented in Table 4. The values in Table 4 were corrected taking into account the background at the masses of interest, formation of hydride ions $^{235}UH^+$ (from the measured $^{238}UH^+/^{238}U^+$ ratio) as well as mass discrimination (determined from ^{235}U/^{238}U ratio) using the power equation [15]. The obtained results for ^{234}U/^{238}U isotopic ratio differ by less than 1% from the recommended value. However, experimental values of the ^{236}U/^{238}U isotopic ratio differ by up to 3% from the recommended value

Table 3
Precision of ^{235}U/^{238}U isotopic ratio measurements (n = 5) and mass discrimination per mass unit obtained using different sample introduction configurations with HEX-ICP-QMS

Sample introduction system	Shielded torch	Precison of ^{235}U/^{238}U ratio (RSD), %	Mass discrimination per mass unit
Meinhard nebulizer	−	0.13	0.0020
Meinhard nebulizer	+	0.20	0.0065
USN	−	0.67	0.0076
USN	+	0.63	0.0080
USN/membrane desolvator	−	0.45	0.0085
USN/membrane desolvator	+	0.57	0.0076

Table 4
Measured isotopic ratios of uranium and their relative standard deviation ($n = 5$) for six measurements of CCLU-500 laboratory isotopic standard solution

Sample introduction system	Shielded torch	Uranium concentration (μg L^{-1})	^{234}U/^{238}U	RSD (%)	^{236}U/^{238}U	RSD (%)
Meinhard nebulizer	−	100	0.011 201	0.19	0.002 785	0.29
Meinhard nebulizer	+	100	0.011 235	0.30	0.002 870	0.54
USN	−	10	0.011 204	0.66	0.002 876	0.55
USN	+	10	0.011 185	0.53	0.002 831	0.72
USN/membrane desolvator	−	10	0.011 241	0.37	0.002 88	0.88
USB/membrane desolvator	+	10	0.011 244	0.63	0.002 869	0.67
Recommended isotopic ratio[a]			0.011 122	0.16	0.002 789	0.39

[a] See [20].

because of a lower isotopic abundance and therefore a lower counting rate for ^{236}U as well as the interference of hydride ions ^{235}UH^{+} (^{235}U abundance is 49.99% in the standard solution used). The best precision of 0.2% for ^{234}U/^{238}U and 0.3% for ^{236}U/^{238}U was obtained using HEX-ICP-QMS without a shielded torch with a Meinhard nebulizer and a water-cooled Scott spray chamber. The precision varied from 0.37% to 0.66% for ^{234}U/^{238}U and from 0.55% to 0.88% for ^{236}U/^{238}U by using an ultrasonic nebulizer. Thus the use of an USN improved sensitivity, but reduced the precision of isotopic ratio measurement due to the lower stability of the ion beam.

3.4. Detection limits for ^{236}U determination

The main factors affecting the ^{236}U detection limit were the instrumental background of HEX-ICP-QMS at mass 236 u including electronic noise of the Daly-type detector and hydride formation from ^{235}U. The detection limits of ^{236}U defined using the 3σ criterion are given in Table 5 (the detection limit of ^{236}U is given as $(m_5+3\sigma_5)/S$, where m_5 and σ_5 are the mean intensity at mass 236 u and standard deviation of five independent measurements of natural uranium solution containing no ^{236}U, cps, respectively; $S$is the sensitivity for uranium, cps/[mg L^{-1})]. By using a 50 μg L^{-1} natural uranium solution introduced by a Meinhard nebulizer with a water-cooled spray chamber into HEX-ICP-QMS with a shielded torch the background at mass 236 u was (45 ± 12) cps corresponding to a minimum detectable concentration of ^{236}U of 35 pg L^{-1}. Thus the minimum detectable ^{236}U/^{238}U isotopic ratio was 7×10^{-7}. As the hydride formation rate was reduced to 2×10^{-6} by using a membrane desolvator and the ^{235}U/^{238}U ratio was less than 1% in ordinary soil samples the background caused by ^{235}UH^{+} at mass 236 u did not practically affect the detection limit for ^{236}U. However, blank ion intensity at mass 236 u caused by the instrument background mentioned previously could not be reduced to less than 30 cps without significant losses in the analyte intensity and it remained the main factor restricting detection limits. The detection limit of ^{236}U was about 3 pg L^{-1}by introducing 10 μg L^{-1} natural uranium solution using an USN with a membrane desolvator corresponding to a minimum detectable ^{236}U/^{238}U ratio of 3×10^{-7}. In order to test the accuracy of the measurement of very different isotopic ratios the mixture consisting of CCLU-500 laboratory standard solution and natural uranium solution with a ^{236}U/^{238}U ratio of up to 7×10^{-7} was measured by using HEX-ICP-QMS by using an USN with

Table 5
Limits of ^{236}U/^{238}U ratio determination and detection limits for ^{236}U obtained using HEX-ICP-QMS

Sample introduction system	Detection limit for ^{236}U (pg/L^{-1})	Limit of ^{236}U/^{238}U ratio determination
Meinhard nebulizer and shielded torch	35	7×10^{-7}
USN/membrane desolvator	3	3×10^{-7}

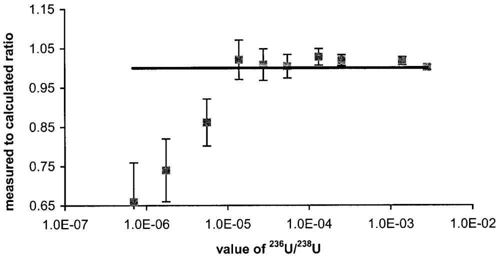


Fig 6. Deviation of the measured ^{236}U/^{238}U isotope ratio from the calculated ratios. (Mixture of natural uranium solution and CCLU-500 laboratory isotopic standard solution was introduced into an ICP by an USN with a membrane desolvator, the shielded torch is off, the extraction lens voltage set to 600 V, see Table 1 for other experimental parameters).

a desolvator for solution introduction. In the case of low isotopic abundance of ^{236}U ($<10^{-5}$) in the synthetic mixture, the measured intensity of ^{236}U was $<10^3$cps and the measured isotopic ratio was found to be systematically lower than the calculated ratio (Fig. 6). For a calculated isotopic ratio of 8×10^{-6} and 1×10^{-6}, the measured ratio reached the value of 0.86 and 0.66 of that calculated, respectively. This effect was reproducible from measurement to measurement. A possible explanation may be the influence of the real electronic noise of the Daly detector and the threshold based method applied for removing this noise from the mass spectrum, discussed in Sec. 3.1.

3.5. Uranium isotopic ratio measurements in soil samples

This method was applied for the determination of uranium isotopic ratios in soil samples from the vicinity of the Chernobyl NPP after uranium extraction. In spite of the lower stability, an ultrasonic nebulizer with a membrane desolvator was attached to a HEX-ICP-MS for the uranium isotopic measurements because this configuration provides the highest sensitivity for uranium and a low hydride formation rate (UH$^+$/U$^+$ is about 2×10^{-6}). The digested and diluted soil samples (~10 μg L^{-1} for uranium) were measured after matrix separation by a HEX-ICP-QMS. For quality assurance, comparisons beween the measurements of five samples were performed by using a DF-ICP-MS, which is well established for such kinds of measurements [17,18,21]. Experimental results obtained by both a HEX-ICP-QMS and a DF-ICP-MS, summarized in Table 6, are within the experimental errors. The isotopic composition of all Chernobyl soil samples differed from the isotopic composition of natural uranium. In all soil samples non-natural ^{236}U from the radioactive fallout was detected. The first three samples were taken at the same place but from different depths of soil layers (an upper vegetative layer, a 5 cm deep layer, and a 5–10 cm layer). The fourth and the fifth samples represent a soil cutoff taken at another place (a 5 cm deep layer and a 5–10 cm layer, respectively). The fraction of spent uranium in the “spent uranium/natural uranium” mixture decreases with increasing soil depth thus decreasing the contamination. Further, the ^{235}U/^{238}U ratio correlates with ^{236}U/^{238}U, i.e. it decreases with increasing soil depth. This means that the spent uranium from the Chernobyl NPP migrates slowly under the effect of environmental factors. At a depth of more than 20 cm the natural isotopic composition was observed. The obtained results are in a good agreement with those for americium and plutonium [34].

4. Conclusion

High sensitivity, low background, and good stability are important for ratio measurements of uranium isotopes with greatly differing abundances. A HEX-ICP-QMS with a gas-filled hexapole collision cell applied in this study offered an outstanding improvement in the sensitivities for uranium determination especially by using an ultrasonic nebulizer for solution introduction. The sensitivity of a HEX-ICP-QMS with a shielded torch obtained using an USN for solution introduction (27 000 MHz/ppm) is comparable to that obtained by a DF-ICP-MS with a shielded torch and the same solution introduction system (21 050 MHz/ppm). Use of a membrane desolvator reduced the formation rate of uranium hydride ions UH$^+$/U$^+$ down to a value of 2×10^{-6}. However, background problems caused, first of all, by the electronic noise of the Daly detector did not enable

Table 6
Results of the measurement of uranium isotopic composition in soil samples from the vicinity of the Chernobyl NPP using HEX-ICP-QMS ‘‘platform’’ and DF-ICP-MS element

	$^{236}U/^{238}U$		$^{235}U/^{238}U$		$^{234}U/^{238}U$	
Sample	HEX-ICP-QMS*	DF-ICP-MS	HEX-ICP-QMS	DF-ICP-MS	HEX-ICP-QMS	DF-ICP-MS
1	0.000972 ± 0.000015	0.000977 ± 0.000014	0.00993 ± 0.00006	0.01006 ± 0.00007	0.000117 ± 0.000004	0.000125 ± 0.000003
2	0.000545 ± 0.000014	0.000569 ± 0.000012	0.00861 ± 0.00005	0.00872 ± 0.00006	0.000097 ± 0.000002	0.000098 ± 0.000002
3	0.000102 ± 0.000002	0.000101 ± 0.000002	0.00739 ± 0.00004	0.00753 ± 0.00005	0.000079 ± 0.000003	0.000072 ± 0.000002
4	0.000325 ± 0.000009	0.000333 ± 0.000008	0.00832 ± 0.00005	0.00846 ± 0.00006	0.000090 ± 0.000002	0.000090 ± 0.000002
5	0.000058 ± 0.000001	0.000056 ± 0.000001	0.00733 ± 0.00004	0.00745 ± 0.00005	0.000068 ± 0.000002	0.000064 ± 0.000002

full use to be made of high sensitivities. It also affected the measurement precision in the case of low abundance isotopes. Regardless, the detection limits for ^{236}U by a HEX-ICP-QMS with a shielded torch obtained by using a Meinhard nebulizer and an ultrasonic nebulizer/ membrane desolvator were 35 and 3 pg L^{-1}, respectively. The minimum detectable ^{236}U/^{238}U isotopic ratio (at 10 μg L^{-1} uranium introduced by an ultrasonic nebulizer in a HEX-ICP-QMS) was about 3×10^{-7}. In the case of low isotopic abundance of ^{236}U ($<10^{-5}$), the measured isotopic ratio in the synthetic isotopic mixture was systematically lower than the calculated ratio. The obtained detection limits were low enough for the determination of spent uranium in all soil samples collected in the region 4–10 km from the Chernobyl NPP. Comparison of the results of isotopic ratio measurements by aHEX-ICP-QMS with those obtained by using a DF-ICP-MS showed good agreement.

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