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International Journal of Mass Spectrometry 242 (2005) 203–209
International Journal of Mass Spectrometry
www.elsevier.com/locate/ijms

Determination of ^{90}Sr and Pu isotopes in contaminated groundwater samples by inductively coupled plasma mass spectrometry

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Received 22 October 2004; accepted 29 November 2004
Available online 12 January 2005

Abstract

A sensitive analytical method for determining the artificial radionuclides ^{90}Sr, ^{239}Pu and ^{240}Pu at the ultratrace level in groundwater samples from the Semipalatinsk Test Site area in Kazakhstan by double-focusing sector field inductively coupled plasma mass spectrometry (ICP-SFMS) was developed. In order to avoid possible isobaric interferences at *m/z* 90 for ^{90}Sr determination (e.g. $^{90}Zr^+$, $^{40}Ar^{50}Cr^+$, $^{36}Ar^{54}Fe^+$, $^{58}Ni^{16}O_2^+$, $^{180}Hf^{2+}$, etc.), the measurements were performed at medium mass resolution under cold plasma conditions. Pu was separated from uranium by means of extraction chromatography using Eichrom TEVA resin with a recovery of 83%. The limits of detection for ^{90}Sr, ^{239}Pu and ^{240}Pu in water samples were determined as 11, 0.12 and 0.1 fg ml^{-1}, respectively. Concentrations of ^{90}Sr and ^{239}Pu in contaminated groundwater samples ranged from 18 to 32 and from 28 to 856 fg ml^{-1}, respectively. The ^{240}Pu/^{239}Pu isotopic ratio in groundwater samples was measured as 0.17. This isotope ratio indicates that the most probable source of contamination of the investigated groundwater samples was the nuclear weapons tests at the Semipalatinsk Test Site conducted by the USSR in the 1960s.
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Keywords: Inductively coupled plasma mass spectrometry; ^{90}Sr; Pu isotopes; Groundwater; Trace-matrix separation

1. Introduction

Determination of artificial radionuclides is a challenging task for analytical chemistry and is required in the environmental monitoring of nuclear contamination in nuclear safeguards and nuclear forensic studies [1–4]. In particular, the determination ^{90}Sr and plutonium isotopes (e.g. ^{239}Pu, ^{240}Pu) at the ultratrace concentration level is of increasing importance [5–10]. Usually, strontium and plutonium radionuclides are produced in nuclear reactors: ^{90}Sr is formed in the process of the fission of heavy nuclei, such as ^{235}U, while ^{239}Pu and ^{240}Pu are produced due to the capture of an extra neutron by ^{238}U ($^{238}U + {}^1n \rightarrow {}^{239}U \rightarrow {}^{239}Pu$) and ^{239}Pu ($^{239}Pu + {}^1n \rightarrow {}^{240}Pu$), respectively. However, large amounts of ^{90}Sr and plutonium were produced during the main atmospheric nuclear weapons tests (e.g. at Bikini and Enewetak Atolls [11] and the Semipalatinsk Test Site in Kazakhstan [12]) in the 1950s and 1960s and dispersed worldwide. Furthermore, during the accident at the Chernobyl nuclear power plant in 1986, additional ^{90}Sr and plutonium were released into the environment and a large part of it was deposited in the post-Soviet Republics. Because of that, the Earth surface in the northern hemisphere is contaminated due to global nuclear fallout.

Determination of radioactive ^{90}Sr is of interest because of its impact in both environmental and health areas. Deposition mainly occurs with rain or other precipitation and strontium is very accessible to plants via soil uptake mechanisms [7]. When the ^{90}Sr is ingested or inhaled, it processed by the body in the same way as calcium and accumulates in bones or teeth (about 20–30% of total ingested ^{90}Sr). In the human body radioactive ^{90}Sr can ionize molecules by the emission of a medium energy β-particle of 0.5 MeV (specific activity of ^{90}Sr is about 5.1×10^{12} Bq g^{-1}) creating the risk of cancer, especially bone cancer and leukemia. It decays into

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doi:10.1016/j.ijms.2004.11.023

^{90}Y, which is also a β-emitter in equilibrium with ^{90}Sr, thus doubling the specific activity of the material.

Accumulated in bone and teeth ^{90}Sr can be used as a powerful tool for age determination [13–15]. For instance, Tolstykh et al. [16] studied age dependencies of ^{90}Sr incorporation in dental tissues by measurements of ^{90}Sr in the teeth of residents living in settlements along the Techa River.

Plutonium as one of the most toxic elements [17] has to be studied with respect to isotopic ratio for evaluating the source of possible contaminations in the environment (nuclear power plants accident [8,18], nuclear weapons tests [19], etc.). Recently, the ^{240}Pu/^{239}Pu isotopic ratio distribution of plutonium in the Sea of Galilee at the ultratrace level after trace-matrix separation and Pu enrichment was studied in our laboratory. It was demonstrated that the water from the Sea of Galilee had been contaminated with artificial transuranium elements and the probable contamination source was global fallout after nuclear weapons tests in the 1960s.

The most widely used analytical techniques for the determination of ^{90}Sr and Pu are radioanalytical techniques, such as β- and α-spectrometry, respectively, or liquid scintillation radiometry [10,11]. However, with respect to β- and α-spectrometry very large sample volumes, typically 2–20 L, are processed which is time- and labor-consuming. On the other hand, the major disadvantage of these spectroscopic techniques relates to the counting period, which can take from days to several weeks depending on the sensitivity and precision required [20]. Additionally, ^{90}Sr as well as ^{239}Pu and ^{240}Pu isotopes are difficult to analyze by spectrometric techniques: the β-radiation from ^{90}Sr is usually interfered with by that from ^{90}Y and ^{89}Sr and the α-spectrometry of plutonium is complicated due to the similar energy of ^{239}Pu and ^{240}Pu (5.157 and 5.168 MeV, respectively). Therefore, a readily available method for monitoring these radionuclides in contaminated areas with faster analysis times may prove favorable [21].

Accelerator mass spectrometry (AMS) and resonance ionization mass spectrometry (RIMS) have been applied for the determination of ^{90}Sr [22–24] and Pu isotopes [25–27] at the ultratrace level in different matrices. However, because AMS is very expensive and instruments for RIMS are not available on the analytical market at present, these techniques have not found wide application. In contrast, thermal ionization mass spectrometry (TIMS) is a well-established mass spectrometric technique for the analysis of long-lived radionuclides with an ionization potential lower than 7 eV (e.g. Pu, U) [28,29] at the ultratrace level, but analytical methods for the determination of ^{90}Sr with a half-life of 29 years by TIMS are not described in the current literature.

Inductively coupled plasma mass spectrometry is one of the most suitable methods for the ultratrace determination and isotope analysis of radionuclides (such as ^{90}Sr, Pu, U, ^{129}I and others) due to its high sensitivity, good accuracy and precision, and generally simple sample preparation procedure [1,30]. However, depending on the matrix composition, isobaric interferences by molecular or atomic ions can be expected on analyte ions, thus decreasing the accuracy of ICP-MS determination of ^{90}Sr and Pu isotopes. In Table 1, possible isobaric interferences in the determination of ^{90}Sr and plutonium isotopes and the required mass resolution are summarized. The recently developed ICP-MS methods [5,8,31–35] with trace-matrix separation have been found to possess the greater efficiency of ICP-MS (e.g. avoiding matrix effects, increasing sensitivity for the ultratrace analysis of ^{90}Sr and isotope ratio measurements of Pu). In the investigation of ^{90}Sr in urine using ICP-MS with collision cell (ICP-CC-MS) and double focusing sector field ICP-MS (ICP-SFMS) detection limits of 20 and 0.4 fg ml^{-1}, respectively, have been achieved (assuming the pre-concentration factor of 200).

Table 1
Possible interferences for ^{90}Sr and Pu isotopes and required mass resolution on ICP-SFMS

Nuclide	Molecular ions	Required mass resolution ($m/\Delta m$)
^{90}Sr	$^{180}W^{2+}$	1370
	$^{180}Hf^{2+}$	1372
	$^{58}Ni^{16}O_2^{+}$	2315
	$^{74}Ge^{16}O^{+}$	10765
	$^{52}Cr^{38}Ar^{+}$	19987
	$^{50}V^{40}Ar^{+}$	49894
	$^{54}Fe^{36}Ar^{+}$	155548
	$^{50}Ti^{40}Ar^{+}$	158287
	$^{90}Zr^{+}$	29877
^{239}Pu	$^{238}U^{1}H^{+}$	36885
	$^{207}Pb^{16}O^{14}N^{1}H_2^{+}$	3817
	$^{208}Pb^{16}O^{14}N^{1}H^{+}$	3430
^{240}Pu	$^{238}U^{1}H_2^{+}$	19116
	$^{208}Pb^{16}O^{14}N^{1}H_2^{+}$	3774

The aim of this work was to develop an analytical technique for the determination of ^{90}Sr and Pu in groundwater samples at the ultratrace level from contaminated areas as well as Pu isotope analysis by ICP-SFMS.

2. Experimental

2.1. ICP-MS instrumentation

A double focusing sector field ICP-MS (ELEMENT, Finnigan MAT, Bremen, Germany) was used for the determination of ^{90}Sr and ^{239}Pu concentration as well as the ^{240}Pu/^{239}Pu isotopic ratio in water samples. The ICP torch was shielded with a grounded platinum electrode (GuardElectrode^{TM}, Finnigan MAT). For sample introduction, the PFA-100 microconcentric nebulizer (CETAC Technologies, Inc., Omaha, NE, USA) was used. Aqueous solutions were introduced in the continuous flow mode using a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). For the pre-concentration of strontium, the samples were evaporated using subboiling apparatus SEP-600 IR (AHF Analysentechnic GmbH, Tuebingen, Germany). Optimized experimental conditions are summa-

Table 2
Optimized experimental conditions of double-focusing ICP-SFMS for determination of ^{90}Sr and Pu in groundwater samples from Kazakhstan, using cold and hot plasma

	^{90}Sr measurements	Pu measurements
RF power (W)	650	1200
Solution uptake rate (ml min^{-1})	0.30	0.30
Cooling gas flow rate (l min^{-1})	18	18
Auxiliary gas flow rate (l min^{-1})	1.45	1.5
Nebulizer gas flow rate (l min^{-1})	1.2	0.985
Focus lens potential (V)	−1100	−850
Sampler cone	Nickel, 1.1 mm orifice diameter	
Skimmer cone	Nickel, 0.9 mm orifice diameter	
Mass window (%)	60	20
Runs	700	7
Passes	3	50
Scanning mode	Peak hopping	
Mass resolution ($m/\Delta m$)	4400	300

rized in Table 2. Further details about the instrumentation and measurement procedure are described elsewhere [5,36]. All the measured intensities were corrected taking into account the dead time of the ion detector that was found to be 45 ns using 1, 2 and 10 ng ml^{-1} solution of NIST SRM987 standard reference material. The mass bias for ^{240}Pu/^{239}Pu isotopic ratio measurements was determined by uranium isotope SRM NIST U020 standard reference material.

2.2. Standards and reagents

Diluted laboratory standard stock solution of strontium and zirconium of natural isotopic composition were used for optimizing the experimental parameters of the ^{90}Sr measurements. Calibration standards of concentrations of 50, 100, 200 fg ml^{-1} of ^{90}Sr were prepared for determining the concentration of ^{90}Sr. ^{242}Pu isotopic standard (NIST SRM 4334F) was applied to optimize the Pu measurements and to control the recovery of the developed procedure. The precision and accuracy of ^{240}Pu/^{239}Pu isotope ratio measurements was evaluated using a synthetically prepared aqueous laboratory standard solution with known plutonium isotopic ratio composition (^{240}Pu/^{239}Pu = 0.2960 ± 0.0026, uncertainty 2 s). Calibration standard solutions for Pu determination were prepared by diluting 1 ng ml^{-1} aqueous ^{242}Pu to the following concentrations of ^{242}Pu: 1, 10, 50, 100, 200, 500 and 1000 fg ml^{-1}. The water for dilution was high-purity deionized (18 MΩ cm^{-1}) obtained from a Milli-Q-Plus water purifier (Millipore Bedford, MA, USA). All chemicals used were supragrade (Merck, Darmstadt, Germany), nitric acid was further purified by subboiling distillation. Strontium standard reference material SRM897 and uranium NIST U020 were applied for the determination of ion detector dead time and mass bias of the ICP-SFMS, respectively.

2.3. Samples and samples preparation

Four groundwater samples were collected from different contaminated areas of the Semipalatinsk Test Site (STS) (Kazakhstan).

2.3.1. Pre-concentration of ^{90}Sr

Ten milliliters of the water sample was acidified to 2% (v/v) with concentrated nitric acid and placed in the Teflon beaker. The sample was pre-concentrated by evaporation of water (using SEP-600 IR) to a volume of 2 ml and introduced by the microconcentric nebulizer into the ICP-SFMS for ^{90}Sr analysis.

2.3.2. Chemical separation of plutonium

Plutonium was separated from sample matrix and other trace elements (mainly from uranium) by extraction chromatography using Eichrom's TEVA resin (particle size 50–100 μm, active component: aliphatic quaternary amine). Ten microliters of the investigated water sample, spiked with 4 pg of ^{242}Pu tracer, was dissolved in 13.2 ml of 6 M HNO_3. To be retained on TEVA resin Pu must be present in a Pu(IV) form so 1 ml 3 M $NaNO_2$ was added, mixed well and left to stand for 5 min to ensure that Pu (III) and Pu

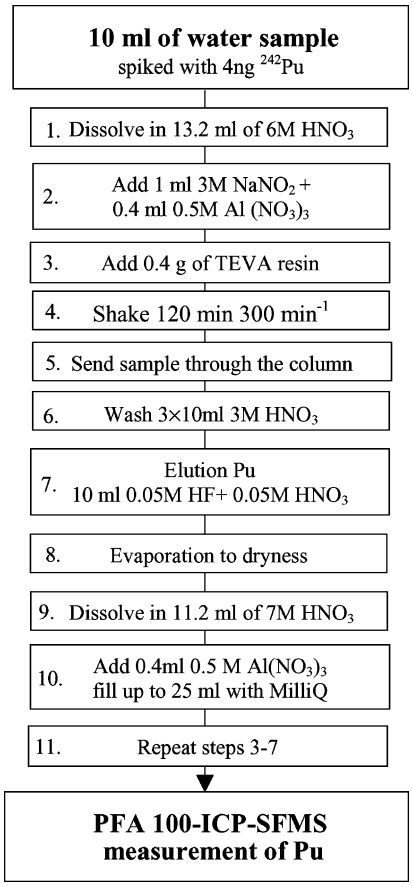


Fig. 1. Sample preparation procedure for Pu analysis in water samples from Kazakhstan.

(VI) were converted to Pu (IV). After that 0.4 ml of 0.5 M $Al(NO_3)_3$ and 0.4 g of TEVA resin were added to the sample. The sample was shaken for 120 min at a rotation speed of 300 min^{-1} and loaded into the appropriate cartridge tube. The resin was then rinsed with 3×10 ml 3 M HNO_3 and the plutonium was eluted with 2×5 ml 0.05 M HF + 0.05 M HNO_3. Because the concentration of U in the separated sample was still relatively high (about 1 ng ml^{-1}), Pu was separated for a second time on the TEVA resin. The fraction of Pu from the first separation was evaporated to dryness and dissolved with 11.2 ml of 7 M HNO_3. After that, 0.4 ml of 0.5 M $Al(NO_3)_3$ was added and the solution was diluted to 25 ml with MilliQ H_2O. Then the sample was subjected to the same TEVA separation protocol as described above and used for the determination of Pu concentration and Pu isotope ratios by ICP-SFMS. A schematic diagram of the sample preparation procedure is shown in Fig. 1. Further details about the sample preparation procedure can be found elsewhere [32].

3. Results and discussion

3.1. Determination of ^{90}Sr by ICP-SFMS

3.1.1. Isobaric interferences and peak tailing of $^{88}Sr^+$ on $m/z = 90$

The detection limit, accuracy and precision of ^{90}Sr determination in ICP-MS are mainly affected by the occurrence of isobaric atomic and molecular ions at $m/z = 90$ (see Table 1). Moreover, the peak tailing of the highly abundant ^{88}Sr isotope – strontium of natural isotope composition is usually present in the sample in the low ppm range – will also disturb the ultrasensitive ^{90}Sr determination. In order to minimize isobaric interferences and peak tailing on $m/z = 90$ the ICP-SFMS measurements were performed in the medium mass resolution mode ($m/\Delta m = 4400$). Under these experimental conditions, the abundance sensitivity of two mass units ($(m+2)/m$) in medium resolution mode was found to be 7×10^{-7} (versus 2×10^{-5} in low mass resolution mode) measuring 1 mg ml^{-1} of natural strontium as described elsewhere [37]. However, whereas several isobaric interferences (e.g. $^{180}Hf^{2+}$, $^{58}Ni^{16}O_2^+$) can be resolved from ^{90}Sr at a mass resolution of 4400, the required mass resolution of most of the interferences at $m/z = 90$ are higher than that of ICP-SFMS (see Table 1). Among others, the isobaric interference of $^{90}Zr^+$ and "Ar-based interferences" (e.g. $^{52}Cr^{38}Ar^+$, $^{50}Ti^{40}Ar^+$, etc.) are of special interest due to their relatively high abundance. In order to reduce the formation of these interfering ions the ICP-SFMS was operated in cold plasma condition (at lower forward powers in an effort to suppress ionization of elements of higher ionization potential). The effect of r.f. power on the intensity of $^{88}Sr^+$ ions and the background signal on $m/z = 90$ (see Fig. 2) was studied using 10 ppb of Sr, Zr and 100 ppb Ge, Cr, V, Fe, Ti solutions. Optimized forward power was found to be 650 W,

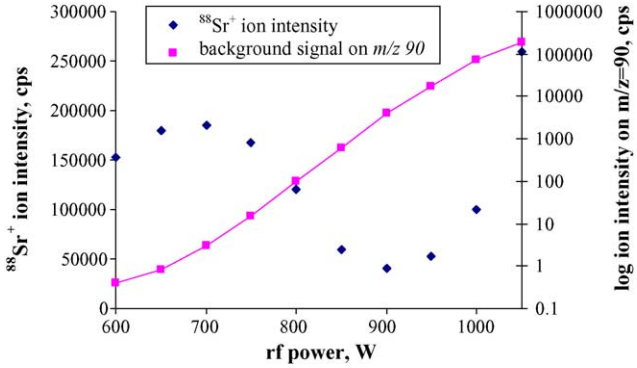


Fig. 2. . Effect of r.f. power on the response of $^{88}Sr^+$ and background intensity signal on $m/z = 90$. (Note that ion intensity signal on $m/z = 90$ is presented on a logarithmic scale).

where the sensitivity for Sr^+ of 18 MHz ppm^{-1} and the background signal on $m/z = 90$ below 0.8 cps were achieved.

However, if the application of medium mass resolution of ICP-SFMS and cold plasma conditions sufficiently reduce the influence of isobaric interferences on $m/z = 90$, the peak tailing of $^{88}Sr^+$ seems to be the critical factor in the determination of ^{90}Sr using the developed method. If the concentration of natural strontium in the sample is higher than 25 ng ml^{-1}, which is very often case, then a different approach would be necessary (e.g. use of MC-ICP-MS with better abundance sensitivity).

3.1.2. Additional optimization of ICP-SFMS for ^{90}Sr measurements

Further ICP-SFMS tuning was carried out with respect to the nebulizer gas flow rate, ion focus lens voltage and XYZ torch position (see Fig. 3). First, nebulizer gas flow was slightly increased (up to 1.2 l min^{-1}) to ensure additional cooling of the plasma and, therefore, a further reduction of "Ar-based interferences" [38]. A small increase in Sr^+ ion intensity was found. After that, the focus lens voltage was optimized, as it corrects for differences in the ion kinetic energy and, therefore, differs between hot and cold plasma. A two-fold increase in sensitivity for Sr was observed by

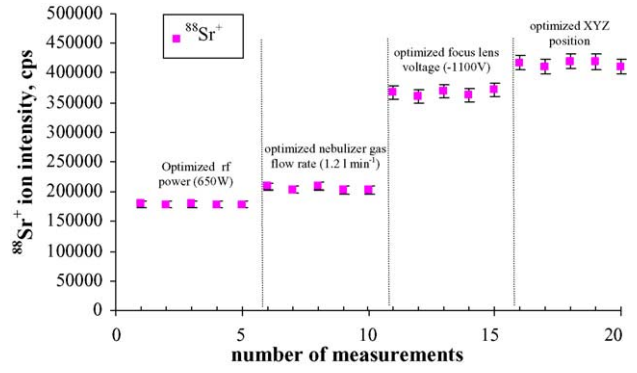


Fig. 3. Effect of optimized nebulizer gas flow rate, focus lens voltage and *XYZ*-position on the $^{88}Sr^+$ ion intensity under cold plasma conditions.

Table 3
Concentration of selected elements in analyzed groundwater samples measured by ICP-SFMS ($m/\Delta m = 4400$, r.f. power = 1200 W) in medium mass resolution mode under hot plasma conditions

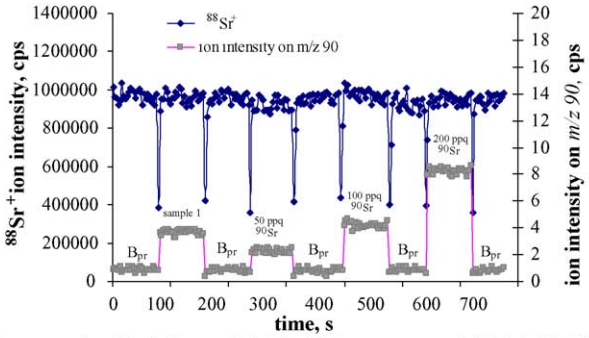
Element	Concentration (ng ml^{-1})				LOD (ppb)
	Sample 1	Sample 2	Sample 3	Sample 4	
Ti	<LOD	<LOD	<LOD	<LOD	0.2
V	0.2	0.7	0.3	<LOD	0.01
Cr	0.1	0.1	0.5	0.2	0.07
Fe	6.1	9.7	17	7.1	0.5
Ge	<LOD	<LOD	<LOD	<LOD	0.08
Sr	5.8	6.0	2.2	5.9	0.09
Zr	0.1	0.2	2.5	<LOD	0.01
U	7414	5796	1638	4935	8.9×10^{-5}

changing the focus lens potential from −850 V (which was optimal for hot plasma) to a more negative −1100 V. Finally, after tuning the *XYZ* position, a sensitivity for Sr in ICP-SFMS of 42 MHz ppm^{-1} under cold plasma conditions was achieved, while the background on *m*/*z* remained below 0.8 cps. The limit of detection (3σ-criterion) and limit of quantification (10σ-criterion) for ^{90}Sr under these optimized parameters was determined to be 11 and 35 fg ml^{-1}, respectively.

3.1.3. ^{90}Sr determination in groundwater samples

Before measurements were made of ^{90}Sr under cold plasma conditions, the concentrations of Ti, V, Cr, Fe, Ge, Sr and Zr were determined in the groundwater samples analyzed using common hot plasma conditions (see Table 3). The concentration of natural strontium in the samples ranged from 2.2 to 6.0 ng ml^{-1}, while concentrations of other measured elements were below 17 ng ml^{-1}. Based on these results, for each of the analyzed samples, matrix-matched aqueous standard solutions with a similar composition and concentration of Sr, Ti, V, Cr, Fe, Ge and Zr were prepared, and were further used as procedural blanks for ^{90}Sr and Pu measurements. Moreover, because the concentration of ^{88}Sr in the samples was lower than 25 ng ml^{-1}, the groundwater samples and also synthetic standards were subjected to a pre-concentration procedure using SEP 60 IR (assuming a pre-concentration factor of 5). Recovery using the experimental procedure was determined as 82% using Sr of natural composition.

After pre-concentration, the ^{90}Sr in the samples was determined by ICP-SFMS with cold plasma conditions as follows. Mass-to-charge ratios of 88 and 90 were monitored. The analyzed groundwater sample and three pre-concentrated procedural blanks, spiked with 50, 100 and 200 fg ml^{-1} of ^{90}Sr standard, respectively, were measured one after the other in one ICP-MS run and with washing by appropriate pre-concentrated procedural blank steps in between. Typical results of these measurements (e.g. for sample 1) are presented in Fig. 4. Because the concentration of the elements that may cause the formation of isobaric interferences on $m/z = 90$, as well as the concentration of natural Sr, was equivalent in all measured solutions, the influence of these effects on the accuracy of the measurements was considered to be minimized. All results of the measurements are summarized in Table 4. The concentration of ^{90}Sr in the groundwater samples analyzed ranged from 18.0 to 32.3 fg ml^{-1} and that in sample 3 was below the procedural LOD.



*B_{pr} – procedural blank for sample 1 (five fold pre-concentrated 0.2, 0.1, 6.1, 5.8, 0.1 ng ml-1 of V, Cr, Fe, Sr, Zr, respectively)

Fig. 4. Ion intensities on $m/z = 88$ and $m/z = 90$ measured in pre-concentrated procedural blank, sample 1 solution and procedural blank spiked with 50, 100 and 200 fg ml^{-1} of ^{90}Sr.

Table 4
^{90}Sr concentration in analyzed groundwater samples measured by ICP-SFMS and β-spectrometry

	^{90}Sr concentration (fg ml^{-1})	
	ICP-SFMS	β-spectrometry
Sample 1	18.8 ± 1.9	19.2 ± 0.61
Sample 2	32.3 ± 2.2	30.1 ± 1.8
Sample 3	<2.2	1.31 ± 0.01
Sample 4	18.0 ± 3.1	16.5 ± 1.2

To further evaluate the developed method, comparative determination of radioactive ^{90}Sr in the samples analyzed was performed by β-spectrometry (see Table 4). The results obtained show a good agreement between the two spectrometric techniques. The precision of the analytical data is slightly better using β-spectrometry. Whereas 1 h is necessary for ICP-MS measurements for ^{90}Sr determination, the β-spectrometric measurement needs 3 days.

3.2. ICP-SFMS measurements of plutonium

3.2.1. Precision and accuracy of Pu measurements

Precision and accuracy of the ^{240}Pu/^{239}Pu isotope ratio of the developed method was studied using a synthetically prepared Pu standard solution. A value of 0.3001 ± 0.0034 for the ^{240}Pu/^{239}Pu isotopic ratio in the standard (0.2960 ± 0.0026 was expected) was determined, which results in a precision (R.S.D., $n = 10$) and an accuracy of 0.9 and 1.3%, respectively. A precision of 5% was determined for ten independent measurements of 100 fg ml^{-1} of ^{242}Pu solution.

Table 5
Concentration of ^{239}Pu and ^{240}Pu/^{239}Pu isotopic ratio in analyzed groundwater samples from Kazakhstan measured by ICP-SFMS

	^{239}Pu (fg ml^{-1})	^{240}Pu/^{239}Pu
Sample 1	397 ± 30	0.16 ± 0.02
Sample 2	856 ± 62	0.17 ± 0.01
Sample 3	28 ± 2	0.15 ± 0.02
Sample 4	355 ± 25	0.16 ± 0.02

3.2.2. Separation of plutonium on TEVA resin

Because of the presence of uranium in the analyzed sample (see Table 3), the accurate determination of ^{239}Pu by ICP-MS was difficult due to interferences from $^{238}U^1H^+$ ion formation and the peak tailing effect from $^{238}U^+$. These interferences led to an increase in the background signal of $m/z = {}^{239}$U [32], necessitating the separation of plutonium from uranium. In the present work, separation of Pu was performed by means of extraction chromatography using Eichrom's TEVA resin as stated in Section 2. The U concentrations after the second separation step for all analyzed samples were below 4 pg ml^{-1}, and no increase in the background at $m/z = 239$ was observed. The procedural recovery of ^{242}Pu spike was found to be 83%.

3.2.3. Pu concentration and ^{240}Pu/^{239}Pu isotope ratio measurements in the groundwater sample from Kazakhstan

After separation, the water samples from Kazakhstan were measured by ICP-SFMS with respect to their plutonium content (see Table 5). The concentration of ^{239}Pu in the groundwater samples analyzed was determined by short-term repeatability and were in the range of 28–856 fg ml^{-1}. The LODs (3σ-criteria) for ^{239}Pu and ^{240}Pu were calculated to be 0.12 and 0.1 fg ml^{-1}, respectively. For the evaluation of LODs the procedural blank of the applied separation protocol was prepared and its intensity value was always subtracted from the sample results.

^{240}Pu/^{239}Pu isotopic ratios were measured in order to assess the source of contamination in the analyzed groundwaters from Kazakhstan (see Table 5). ^{240}Pu/^{239}Pu isotopic ratios determined were in the range of 0.15–0.17, which indicates that the water in the Semipalatinsk Test Site area was contaminated with plutonium due to the nuclear weapons tests conducted by USSR in the 1960s.

4. Conclusions

An analytical procedure that proves the capability of ICP-MS for the determination of artificially produced radionuclides such as ^{90}Sr and Pu in groundwater samples was developed. The study demonstrates that isobaric interferences on the mass $m/z = 90$, originating, for instance, from stable zirconium ions or argon-based polyatomic ions, can be successfully removed by a cold plasma operated at 650 W, because their formation is prohibited in such low r.f. power energy. A medium mass resolution setting proved to be adequate for the separation of nickel-based interferents, such as $^{58}Ni^{16}O_2^+$, as well as for improving the abundance sensitivity of the ICP-SFMS instrument, which enables the influence of the peak tailing effect from highly abundant ^{88}Sr to be reduced. In the present study, the concentrations of natural strontium in the samples analyzed were below 10 ng ml^{-1}, so their contribution to the intensity signal at $m/z = 90$ was considered to be negligible even after the pre-concentration of Sr in the sample by a factor of 5. Using such an approach, the ^{90}Sr in the groundwater sample from Kazakhstan was measured in the range of 18–32.3 fg ml^{-1}, without any chemical separation steps. However, in the case of a higher concentration of natural strontium in the sample (e.g. >100 ppb) or if the preconcentration steps are applied with a relatively large enrichment factor prior to the ICP-MS measurements [5], a dramatic increase in the LOD for ^{90}Sr is expected. In such cases, the use of multicollector ICP-MS with abundance sensitivity for two mass units up to better than 10^{-8} [39] would be the method of choice.

Additional measurements of Pu in the groundwater samples analyzed reveals that the water was contaminated with artificial plutonium with a ^{240}Pu/^{239}Pu isotopic ratio of 0.16. The ratio indicates that the cause of this contamination was the nuclear weapons tests conducted by the USSR at STS in the 1960s.

Acknowledgements

The authors would like to thank the Bundesministerium für Bildung und Forschung (BMBF) for financial support of the bilateral BMBF cooperation in Water Technology (project number: 02WT0334) and K. Volka (Prague) for helpful discussions.

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