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Characterization of natural water resources in Israel by inductively coupled plasma mass spectrometry

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Dedicated to the memory of Chava Lifshitz.

Abstract

Analytical procedures are applied for the determination of plutonium, uranium and strontium concentration, their isotope ratios and the analysis of rare earth elements (REE) at trace and ultratrace level in natural Israeli water resources with relatively high matrix content ($\mathrm{Na} = 20$–$150\,\mathrm{mg\,L^{-1}}$, $\mathrm{Mg} = 20$–$50\,\mathrm{mg\,L^{-1}}$ and $\mathrm{Ca} = 40$–$100\,\mathrm{mg\,L^{-1}}$) by inductively coupled plasma mass spectrometry (ICP-MS). To avoid matrix and clogging effects on the cones during mass spectrometric measurements and to analyze Pu and REE at extremely low concentration levels, separation procedures from matrices were applied. An extremely low Pu contamination of the Sea of Galilee was observed due to global nuclear fallout after the nuclear weapons test in the 1960s. The detection limit, for example, for ^{239}Pu was found to be $<10^{-19}\,\mathrm{g\,mL^{-1}}$. For uranium a natural variation of the $^{234}\mathrm{U}/^{238}\mathrm{U}$ isotope ratios by a factor of up to 2 in comparison to the IUPAC table value was detected using ICP-MS.

This paper discusses the application of double-focusing sector field ICP-MS with single and multiple ion collection as well as quadrupole-based ICP-MS (ICP-QMS) for the quantitative determination of REE, plutonium, uranium and strontium and their isotope ratios after analyte/matrix separation at trace and ultratrace levels in natural water.

Keywords: ICP-MS; Isotope ratio measurement; Long-lived radionuclide; Trace analysis; Water sample

1. Introduction

The Sea of Galilee is one of the three main sources of potable water in Israel, supplying about 20% of national water consumption. Air pollution with long-lived radionuclides, and the salinization of the lake have been increasing in the last few decades [1]. Monitoring and identifying the origin of the long-lived radionuclides and other components in the Sea of Galilee would therefore be a powerful tool for understanding the possible sources of contamination and evolution processes of salinization in the Sea of Galilee, which are crucial for future water management and remediation. In the past radioanalytical techniques such as α spectrometry or liquid scintillation radiometry were most frequently used for the determination of long-lived radionuclides. For a couple of years now, inductively coupled plasma mass spectrometry (ICP-MS), due to the high accuracy of its analytical data and excellent detection limits, has proved to be the best analytical technique for the determination of long-lived radionuclides combined with isotope ratio measurement capabilities at the ultratrace level [2–7].

Advanced analytical methods for the determination of natural and artificial radionuclides at the $\mathrm{pg\,L^{-1}}$ range and below (^{236}U, ^{234}U, ^{235}U, ^{238}U, ^{239}Pu, ^{240}Pu, ^{90}Sr or ^{226}Ra) and isotope ratio measurements of uranium, plutonium and also non-radioactive strontium in the water samples [8–10] collected from the Sea of Galilee were developed and successively applied in two labs in Juelich and Jerusalem using ICP-SFMS and MC-ICP-MS, respectively. ^{90}Sr ($T_{1/2} = 29.1$ years) that appears as a radionuclide in the decay series of nuclear fission was released into the environment during the atmospheric nuclear weapons tests of the 1950s and 1960s and during the Chernobyl nuclear accident in 1986, and therefore, it is of interest due to its impact in the

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environmental and health areas. The determination of ^{90}Sr at ultratrace level in water samples was described by Vonderheide et al. using double-focusing sector field ICP-MS with detection limits at 3 pg L^{-1} [11] and applied to contaminated ground water samples from the Semipalatinsk test site area in Kazakhstan, where the ^{90}Sr concentrations varied between 18 and 32 pg L^{-1} [9]. An analytical procedure has been proposed for the determination of ^{226}Ra with a detection limit of 0.02 pg L^{-1} in ground water samples using double-focusing sector field ICP-MS (ICP-SFMS). For the pre-concentration and separation of radium from the matrix elements in water a tandem of a laboratory-prepared filter, based on MnO_2, and Eichrom “Sr-specific” resin was used [8]. In selected ground water samples from Germany a ^{226}Ra concentration of about 1–5 pg L^{-1} was measured. $^{236}U/^{238}U$ isotope ratios in a natural uranium mineral sample (U_2O_3) from Israel were measured by double-focusing sector field ICP-MS using heavy water (D_2O) as a solvent in order to reduce the disturbing $^{235}UH^+$ formation which results in an isobaric interference on $m/z = 236$ [10]. Recently, an $^{236}U/^{238}U$ isotope ratio of 7×10^{-7} was found in a natural sample from Israel (pitchblende from the Precambrian mineralization in the Timna mines in southern Israel) by ICP-SFMS using heavy water as the solvent. Plutonium isotope analysis at femtogram level by multicollector ICP-MS was described by Taylor et al. [12]. An analytical procedure for environmental monitoring of plutonium at the ultratrace level after effective Pu separation from a huge volume (100 L/sample) of water matrix from the Sea of Galilee was developed at the Geological Survey in Israel [4]. The detection limits of ^{239}Pu were determined as 0.1 and 0.03 fg L^{-1} using sector field ICP-MS with single ion detector and multiple ion collector ICP-MS (MC-ICP-MS), respectively.

The aim of this work is to apply and compare advanced mass spectrometric techniques using double-focusing sector field ICP-MS with single and multiple ion collectors for the characterization of natural water samples in Israel. Separation and pre-concentration of the analytes from the samples with respect to long-lived radionuclides or strontium will be performed due to the relatively high salinity (about 600 mg L^{-1} TDS) and low concentration of the trace elements of interest in the water samples.

2. Experimental

2.1. ICP-MS instrumentation

ICP-SFMS (ELEMENT, Thermo Electron Corporation, Bremen, Germany) was applied in the Central Division of Analytical Chemistry at Research Centre Juelich for Pu, U and Sr isotope ratio measurements in water samples from the Sea of Galilee. The microconcentric nebulizer PFA-100 (CETAC Technologies, Inc., Omaha, NE, USA) was used for sample introduction. Aqueous solutions were introduced in the continuous flow mode using a peristaltic pump (Perimax 12, Spetec GmbH, Erding, Germany). The ICP torch was shielded with a grounded platinum electrode (GuardElectrode^{TM}, Thermo Electron Corporation, Bremen, Germany).

Comparative measurements of isotope ratios were performed using MC-ICP-MS with a Nier–Johnson geometry (Nu Instruments, UK, installed in Geological Survey of Israel, Jerusalem). A microconcentric nebulizer combined with a desolvator (Aridus, CETAC Technologies Inc., Omaha, Nebraska, USA) was used for sample introduction. Multielement determination of major and minor elements as well as measurements of relative oxide formation rates of REEs was performed in both laboratories by quadrupole-based ICP-MS (Elan 6000 and DRC II, respectively, Perkin-Elmer SCIEX Corp., Norwalk, CT, USA).

2.2. Standards and reagents

A laboratory standard solution of U and Sr (0.5 $\mu g\,L^{-1}$) with a natural isotopic pattern was used for optimization of the experimental parameters. An aqueous laboratory standard solution with known plutonium isotopic ratio composition ($^{240}Pu/^{239}Pu = 0.2962 \pm 0.0003$) was used for the determination of the precision and accuracy of $^{240}Pu/^{239}Pu$ isotope ratio measurements. Uranium and strontium isotopic standard solutions (NBL 120B and SRM NIST 987, respectively) were applied to control recovery of the developed procedure. High-purity deionized water (18 MΩ cm), obtained from a Milli-Q-Plus water purifier (Millipore Bedford, MA, USA), was subjected to the same co-precipitation and separation procedures as the sample in order to obtain the procedural blank. All chemicals used were of supragrade (Merck, Darmstadt, Germany). Nitric acid was further purified by subboiling distillation.

2.3. Samples and samples preparation

Water samples from the Sea of Galilee were collected in containers previously washed repeatedly with 2% (v/v) nitric acid in 18 MΩ cm water. In order to avoid possible isobaric interferences on analyte ions, matrix effects and clocking effects on the cones of the ICP several special element-specific sample preparation steps were developed. A schematic diagram of the separation and enrichment procedures for a precise isotope analysis of Pu, U and Sr using double-focusing sector field ICP-MS with single and multi ion collection is given in Fig. 1. In addition, the multielement trace analysis of rare earth elements (REE) at sub $\mu g\,L^{-1}$ concentration range is difficult due to the relatively high matrix content. Therefore, a lanthanide group separation and purification was proposed before mass spectrometric multielement analysis using AF-Chelate-650 M Toyopearl® resin (TOSOH Bioscience) (Fig. 2). Detailed descriptions of the separation procedures are given elsewhere [4,11,17,18].

Samples for U depth profile in the Sea of Galilee were collected using a 40 m plastic tube (Tygon R 3603 i.d. 8.0 mm) connected to persitaltic pump (MasterFlex by Cole-Parmer) with an on-line filter (cellulose nitrate filter 0.45 μm Whatman).

2.4. Optimization of experimental parameters in ICP-MS and measurement procedure

Optimization of the experimental parameters of the ICP-MS instruments was performed with respect to the maximum ion intensity of analytes using a laboratory standard solution of uranium with natural isotopic pattern, natural strontium and REE.

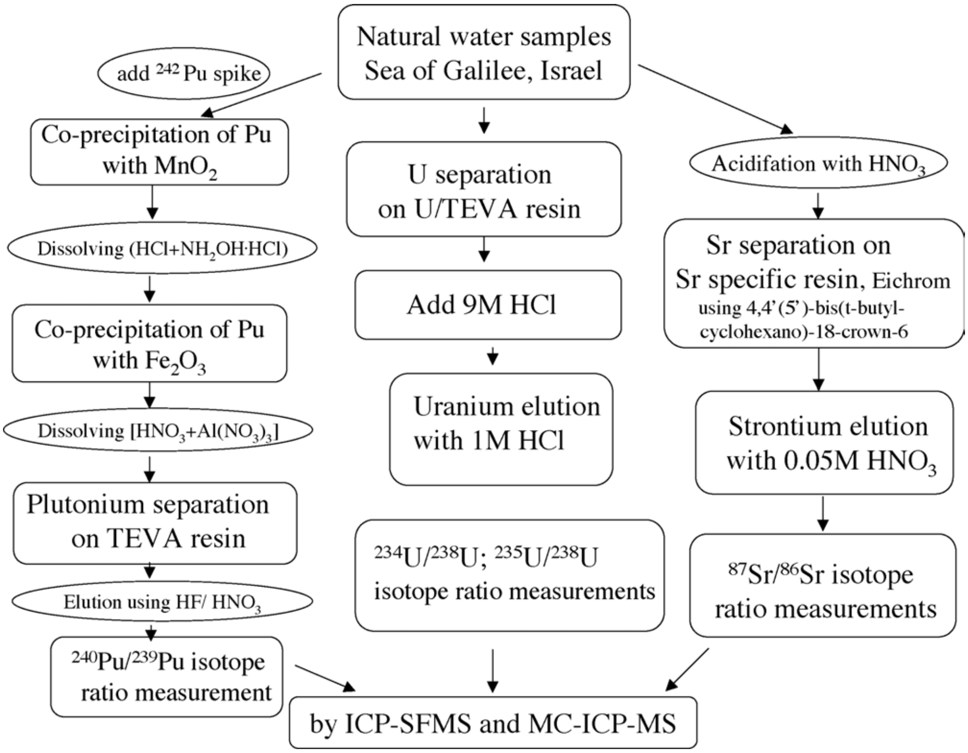

Fig. 1. Schematic diagram of the separation and enrichment procedures for precise isotope analysis of Pu, U and Sr [4,9].

Instrument operation conditions for isotope analysis using both sector field ICP-mass spectrometers with single and multiple ion collection (ELEMENT and Nu Plasma, respectively) are summarized in Table 1. All measured ion intensities in the case of ICP-SFMS were corrected taking into account the dead time of the ion detector, which was found to be 45 ns. The mass bias factors (assuming an exponential correction [9]) for uranium and strontium were determined using a 0.5 μg L^{-1} NIST U500 and SRM 987 standard solution, respectively. Since the uranium concentration after the second separation of the sample on TEVA resin did not exceed 5 ng L^{-1}, the influences of uranium hydride molecular ions as well as the peak tailing effect from ^{238}U on the background of m/z 239 were considered negligible. Between each run the solution introduction systems was washed with mixture of pure 0.5 M HCl and 0.05 M HF. Details of MC-ICP-MS measurements are given elsewhere [4,13,17].

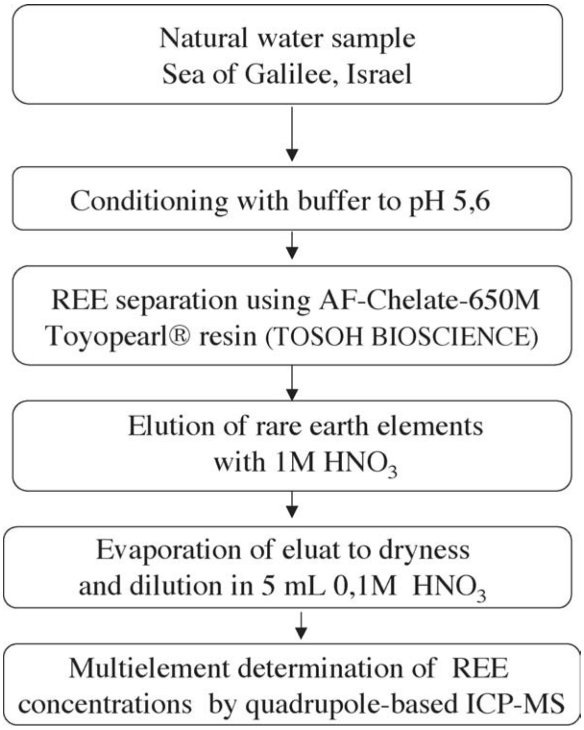

Fig. 2. Lanthanide group separation and purification.

Table 1
Optimized experimental conditions of double focusing ICP-SFMS and MC-ICP-MS for isotope analysis of Pu, Sr, U in water sample from Sea of Galilee

	ICP-SFMS ELEMENT		MC-ICP-MS Nu Plasma
Nebulizer type	PFA-100	Aridus	Aridus
RF power (W)	1199	1199	1300
Cooling gas flow rate (L min^{-1})	18	18	13
Auxiliary gas flow rate (L min^{-1})	1.04	1.2	1.3
Nebulizer gas flow rate (L min^{-1})	0.91	1.4	0.6
Sweep gas flow rate (L min^{-1})	–	3.8	3.8
Solution uptake rate (mL min^{-1})	0.58	0.1	0.08
Spray chamber temperature (°C)	–	70	70
Desolvator heating temp (°C)	–	160	160
Scanning mode	Peak hopping		–
Mass window (%)	10		–
Mass resolution ($m/\Delta m$)	300		300

Table 2
Composition of natural water from Israel collected at different locations and in Sea of Galilee measured by quadrupole-based ICP-MS

Element	ICP-MS
Ca	40–100 mg L^{-1}
Mg	30–40 mg L^{-1}
K	2–8 mg L^{-1}
Na	20–150 mg L^{-1}
B	30–200 μg L^{-1}
Ba	40–200 μg L^{-1}
Cr	0.5–2 μg L^{-1}
Cu	0.5–5 μg L^{-1}
Mn	0.3–70 μg L^{-1}
Ni	0.2–4 μg L^{-1}
Rb	0.5–3 μg L^{-1}
Se	0.3–5 μg L^{-1}
Sr	300–200 μg L^{-1}
U	0.4–5 μg L^{-1}
Zn	0.2–60 μg L^{-1}

3. Results and discussion

3.1. Composition of major and trace elements in natural water from Israel

Quadrupole-based ICP-MS was used for the multielemental analysis of major, minor and trace elements in a multitude of water samples from Israel. Table 2 summarizes the elemental composition (concentration range of selected elements) in natural water samples from Israel measured by ICP-MS. The accuracy of the analytical methods developed was tested using a riverine water reference material for trace metals SLRS-3 (National Research Council, Canada). A comparison of mass spectrometric measurements by quadrupole-based ICP-MS using a DRC-II and Elan 6000 (both from Perkin-Elmer, Sciex) in Israeli and German laboratories, respectively, is drawn in Fig. 3. The analytical data for major and trace elements in many natural water samples from Israel determined in the two laboratories agree very well within the analytical precision.

3.2. Determination of REE at ultratrace concentration level

Due to the relatively high salt content in natural water samples from Israel a careful trace/matrix separation was carried out before measurement of rare earth elements (REE), as described in Fig. 2. To accurately determine contents at the ultratrace concentration level of rare earth elements, possible isobaric interferences with molecular ions should be investigated and considered. After a careful trace/matrix separation isobaric interferences with elements other than lanthanides (e.g., Ba) can be excluded. Nevertheless, a high oxide formation rate of light REEs could result in higher measuring ion intensities at $m/z \geq 155$. In Fig. 4, the typical oxide formation rate (MO^+/M^+) for several REEs (as a function of atomic number Z) is shown. The relative oxide formation rate varied between about 2% for La, Ce and Pr and 10^{-4} for Yb and correlates with the filling of 4f orbitals. Maximum oxide formation rates for La, Gd and Lu correspond to an empty, half-filled and filled 4f orbital for La, Gd and Lu, respectively, as described elsewhere [14]. In the trace analysis of REEs with a high content of light lanthanides possible oxide ion formation should be considered, whereas, the very low hydride formation rate of REEs could be neglected under the optimized experimental conditions (hydride formation rate: $<10^{-4}$). The results of the trace analysis of REEs from five natural water samples from Israel are summarized in Table 3.

3.3. Determination of uranium and plutonium concentrations and isotope ratios in natural water from Israel

The determination of natural and artificial long-lived radionuclides in potable water resources is of special interest to demonstrate possible past and future water pollution. In order to avoid possible interferences on analyte ions (e.g., $^{238}UH^+$ for

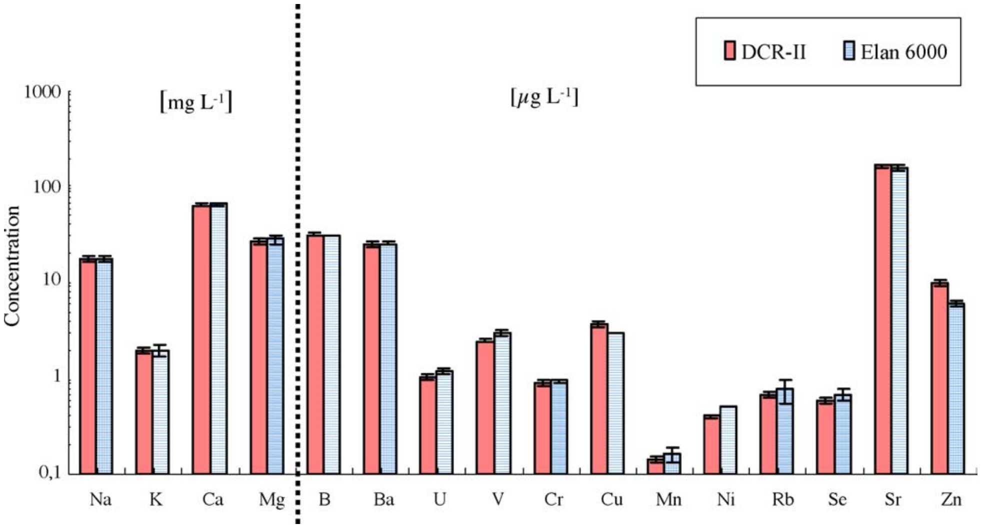

Fig. 3. Comparison of major and trace element concentrations determined by quadrupole-based ICP-MS DRC-II and Elan 6000 in natural water sample from Sea of Galilee.

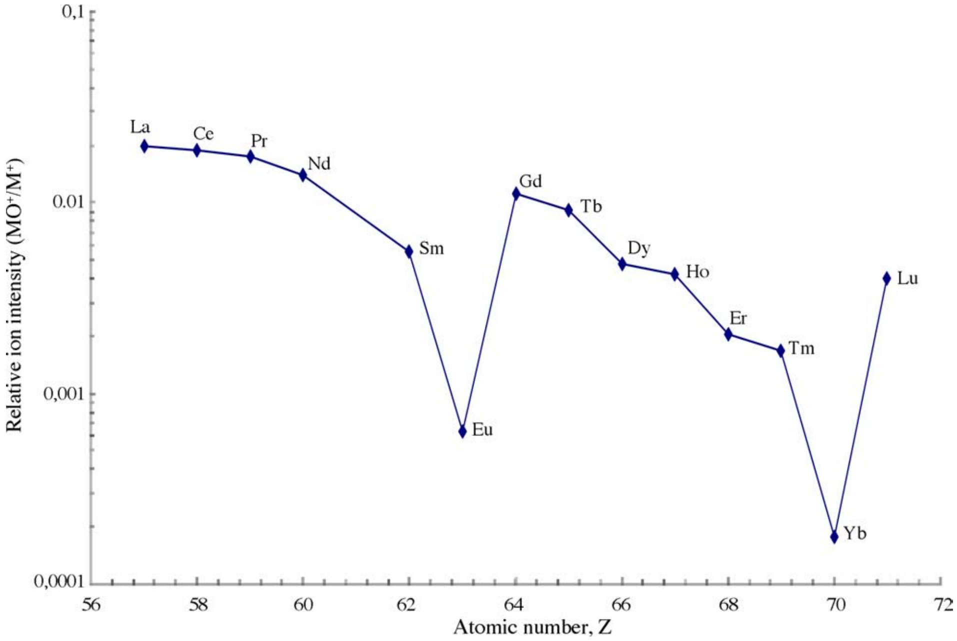

Fig. 4. Relative oxide formation rate of selected REEs as determined by ICP-QMS.

determination of $^{239}Pu^+$) isotope ratio measurements by advanced mass spectrometric methods were performed after a careful separation of uranium and plutonium as analytes using UTEVA and TEVA resins, respectively, as described before (Fig. 1). The U concentration measured by quadrupole-based ICP-MS in natural waters from Israel varied between 0.4 and 5 $\mu g\,L^{-1}$.

While investigating the uranium concentration in the Sea of Galilee no homogeneous distribution as a function of depth of the lake was found. In Fig. 5, the depth profile of uranium concentration from the surface down to 35 m is illustrated. Whereas, the uranium concentration from the lake surface down to 10 m is nearly constant at about 0.6 $\mu g\,L^{-1}$, with increasing depth after a slight enrichment of uranium concentration from 10 to 20 m a significant depletion at depths lower than 20 m down to nearly 0.4 $\mu g\,L^{-1}$ uranium was found. This experimental result of mass spectrometric measurements can be explained by the changing environmental conditions at different depths. Whereas, under oxidation conditions (down to a depth of 20 m in the Sea of Galilee) natural uranium exists as $UO_4{}^{2-}$ in water, with increasing depth the environmental behaviour of sea water changes to reducing conditions and consequently the oxidation state of uranium changes from 6+ to 4+. A depletion of uranium in the Sea of Galilee at depths >20 m could be the result of the formation of heavy dissolved US_2 and consequently partly a precipitation of uranium.

To study the small isotope variation of uranium in natural water and samples from the Sea of Galilee were analysed by sector field ICP-MS with single and multiple ion collectors. For all water samples an agreement of the measured $^{235}U/^{238}U$ isotope ratio with the IUPAC table value of the isotopic composition of elements ($^{235}U/^{238}U = 7.25 \times 10^{-3}$) was observed [15]. The results of isotope ratio measurements of $^{234}U/^{238}U$ are summarized in Table 4. For the $^{234}U/^{238}U$ isotope ratio an enrichment by up to a factor of 2 was found by using ICP-SFMS with a single ion collector in good agreement within the analytical precision with results obtained by MC-ICP-MS. The reason for the small

Table 3
Results of REE determination in water samples from Israel (concentration in $ng\,L^{-1}$)

REE	I	II	III	IV	V
La	21.5	12.1	8.4	3.4	0.85
Ce	20.4	6.3	5.3	2.7	1.3
Pr	5.3	3.0	1.9	0.43	0.17
Nd	19.3	13.2	8.6	1.7	0.62
Sm	3.7	2.3	1.6	0.49	0.16
Eu	1.1	0.68	0.39	0.06	0.04
Gd	4.1	2.6	1.9	0.36	0.15
Tb	0.55	0.37	0.29	0.05	0.03
Dy	3.7	2.5	1.9	0.48	0.16
Ho	0.85	0.58	0.42	0.10	0.03
Er	2.4	1.6	1.3	0.33	0.12
Tm	0.37	0.23	0.18	0.07	0.02
Yb	2.1	1.3	1.0	0.53	0.08
Lu	0.34	0.24	0.15	0.15	0.03

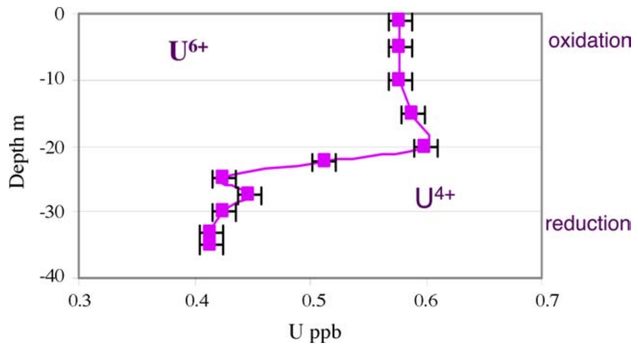

Fig. 5. Depth profile of uranium concentration in Sea of Galilee.

Table 4
Uranium isotopic ratios in water samples from Israel

Sample	Uranium concentration (μg/L)	ICP-SFMS $^{234}U/^{238}U$	MC-ICP-MS $^{234}U/^{238}U$
Ahi-Semeh-1	1.82	$(7.28 \pm 0.5) \times 10^{-5}$	$(6.87 \pm 0.1) \times 10^{-5}$
Eshtaol-3	1.42	$(8.76 \pm 0.5) \times 10^{-5}$	$(9.09 \pm 0.1) \times 10^{-5}$
Kakun-6	1.06	$(8.98 \pm 0.5) \times 10^{-5}$	$(8.73 \pm 0.1) \times 10^{-5}$
Modiin-2	0.92	$(9.94 \pm 0.5) \times 10^{-5}$	$(9.93 \pm 0.1) \times 10^{-5}$
Modiin-3	0.61	$(10.9 \pm 0.5) \times 10^{-5}$	$(11.33 \pm 0.1) \times 10^{-5}$
Table value		5.54×10^{-5}	

variation of $^{234}U/^{238}U$ in natural water, that means an enrichment of ^{234}U abundance, can be explained as a result of the α decay of ^{238}U ($t_{1/2}$, 4450 Ma) via short-lived ^{234}Th and ^{234}Pa nuclides (due to β^- decay with $t_{1/2}$ of 2.4 days and 6.7 h, respectively) in ^{234}U ($t_{1/2}$, 0.245 Ma) via chemical activity (recoil effect). The isobaric daughter radionuclides (^{234}Th, ^{234}Pa and ^{234}U) leave the crystal lattice as ions (e.g., in the mineral) and become free. Therefore, decay products are more chemically active than the parent ^{238}U radionuclides and the leaching of decay products by water leads to ^{234}U enrichment in the samples investigated.

Whereas, the uranium concentration was determined in the low $\mu g\,L^{-1}$ and below a possible plutonium concentration as contamination of water with artificial radionuclides is several orders of magnitude lower. Therefore, Pu was separated, enriched and purified from 100 L of natural water spiked with a few pg of ^{242}Pu. Using a co-precipitation procedure for plutonium based on MnO_2 and $Fe(OH)_3$, concentration factors of more than 6600 were achieved [4]. The ^{239}Pu concentration in the Sea of Galilee was measured after separation, enrichment and purification as about 0.36 $fg\,L^{-1}$. The detection limits of ^{239}Pu in 100 L of lake water were determined by MC-ICP-MS at 10^{-19} $g\,mL^{-1}$, whereas, using ICP-SFMS the detection limits were three times poorer. A $^{240}Pu/^{239}Pu$ isotope ratio of 0.17 measured by MC-ICP-MS demonstrates a plutonium contamination of the Sea of Galilee at the extreme ultratrace level due to global nuclear fallout after the nuclear weapons tests in the 1960s.

3.4. *Strontium isotope ratio measurements*

Isotope variations in strontium are well known and have often been described in the literature [16]. The radioactive β-decay of ^{87}Rb to ^{87}Sr takes place with a half-life of 48.8 billion years and lead to the natural variation of $^{87}Sr/^{86}Sr$ isotope ratio, widely used in the Rb/Sr geochronological dating method.

In this work on studying strontium isotope variation comparative measurements in Jerusalem and Juelich were performed whereby in both labs samples were prepared as described in Fig. 1. To avoid matrix effects and clocking effects on the cones strontium was carefully separated as described in Fig. 1, using Sr specific resin from Eichrom with a recovery yield of about 70%. A comparison of strontium isotope ratio measurements ($^{87}Sr/^{86}Sr$) in natural water samples from Israel using a sector field ICP-MS with single and multiple ion collection is illustrated in Fig. 6. The accuracy of strontium isotope ratio measurements was checked with certified isotope standard reference material SRM 987. Whereas, the $^{87}Sr/^{86}Sr$ isotope ratios measured with both sector field instruments agree well, a significantly better precision was found using MC-ICP-MS (Nu Plasma), as expected, compared to that observed by ICP-SFMS (ELEMENT).

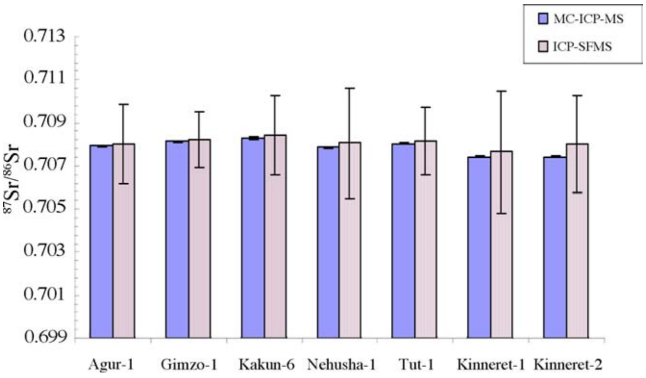

Fig. 6. Comparison of $^{87}Sr/^{86}Sr$ isotope ratios in natural water samples from Israel measured by sector field ICP-MS with single and multiple ion collection.

4. Conclusions

This study demonstrates that double-focusing sector field ICP-MS with single and multiple ion collection, combined with preconcentration and matrix separation, represents a useful analytical technique suitable for the analysis of uranium, plutonium and strontium in water at different concentration levels. Disturbing interferences affecting the accurate determination of analytes and matrix effects were avoided by careful removal and separation of the analytes from water samples using several special separation techniques. The limits of detection of ICP-MS were measured in the $ng\,L^{-1}$ to sub $pg\,L^{-1}$ range, e.g., for plutonium in 100 L lake water using MC-ICP-MS the LOD was about 0.1 $fg\,L^{-1}$. A fine isotope variation of uranium in natural water samples from Israel was detected.

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