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Determination of ^{235}U and ^{238}U in urine samples using sector field inductively coupled plasma mass spectrometry

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Abstract

The high sensitivity of SF-ICP-MS (sector field inductively coupled plasma mass spectrometry) using a torch with the ''guard-electrode'' (capacitive decoupled plasma) allows the determination of ^{238}U (isotope abundance 99.2%) and ^{235}U (0.8%) and their isotope ratio in human urine samples down to the physiological level of <10 ng/l total uranium. For sample preparation UV photolysis was used. Some quality criteria like for the detection limit, the reproducibility, recovery and the isotope ratio are given. The method can be applied in occupational as well as in environmental medicine because of its outstanding detection power.

Keywords: Isotope ratio; Uranium

1. Introduction

In a previous paper the use of quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) for the determination of uranium was described [1]. There, a detection limit of 1 ng/l was achieved which was not sufficient enough for the simultaneous determination of ^{235}U due to the natural isotope abundance of only 0.8%. Sector field (SF) ICP-MS in combination with the ''guard-electrode'' [2] improves the detection limit by more than a factor of 100 down to the 10 pg/l range.

That is the prerequisite for the determination of total uranium by using both isotopes and for measuring deviations from the natural isotope ratio.

The aim of this paper was the development of an adequate method using SF-ICP-MS.

Uranium is a naturally occurring radioactive element belonging to the actinides. All isotopes are α-emitters. The following naturally occurring isotopes are known (isotope abundance and half-lives in parentheses): ^{234}U (0.005%; $2.46 \cdot 10^5$ years), ^{235}U (0.711%; $7.04 \cdot 10^8$ years) and ^{238}U (99.283%; $4.47 \cdot 10^9$ years). Monitoring of the uptake of uranium is normally based on the measurements of daily urinary excretion [3]. Uptake of this element in non-exposed subjects is mainly due to ingestion [4]. For this reason the physiological level of excretion may change in a relatively wide range (5–100 ng/l) due to the concentrations in foodstuffs and in drinking waters, especially in mineral waters which sometimes show high concentrations of uranium [5] dependent on their geological origin. The physiological concentration in urine samples of unexposed people is given as 7.9 ± 3.1 ng/l with a variation of 2–18 ng/l [1,6,7].

In contrast, incorporation due to occupational exposure, e.g., in mining, milling and production of nuclear fuel elements, occurs most probably by inhalation. Mainly nephrological damage is described in the literature after uranium intoxication [8,9]. In these cases monitoring of the $^{238}U/^{235}U$

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ratio seems very important for judging on an exposure with a definite enriched U-isotope.

The commonly used analytical techniques such as α-spectrometry, fluorimetry or neutron activation analysis are very time consuming and do not show sufficient detection limits for monitoring the physiological levels [10,11]. In contrast, ICP-MS offers very low detection limits and very fast analysis (approx. 3 min/samples) with only little sample preparation. Additionally a good correspondence between α-spectrometry and ICP-MS was achieved for higher uranium concentrations of exposed workers [6]. Certainly this comparison was done with Q-ICP-MS, but it may be assumed that it will be valid also for SF-ICP-MS because the only difference in both the instruments is sensitivity due to the use of the same mass resolution.

2. Experimental

2.1. Sample and sample preparation

For the development of the method and establishing the quality criteria a pool-urine with uranium concentration of about 10 ng/l was used.

Because of the organic matter in urine samples a sample digestion step is recommended to reduce carbon residues on the cones of the interface. One of the most sufficient procedures for urine concerning time consumption and reagents needed for the digestion is UV-photolysis [12]. The UV 1000 system (Kürner, Germany) was used in all cases: to 4 ml urine 4 ml H_2O_2 and 0.5 ml HNO_3 are added and irradiated by UV for approx. 1 h. The solution is filled up to 20 ml with ultra-pure water (Milli-Q, Millipore, Germany), which corresponds to a final dilution of the urine of 1:5.

In order to reduce the risk of contamination, the complete handling of samples, standards and reagents was performed in a clean bench (laminar flow system, Bleymehl, Germany). Also the complete sample introduction unit including the sample changer of the ICP-MS system was under such a laminar flow system.

Table 1
Instrumental parameters

Resolution	$m/\Delta m=300$
Radio frequency (RF) power	1.2 kW
Scan type	Magnetic jump, electric scan
Torch	Fassel type with ''guard electrode''
Nebulizer	Meinhard
Pump speed	1 ml/min
Spray chamber	Scott-type water cooled (9°C)
Cones	Ni (high performance)
Auxiliary gas	Argon, 0.85 l/min
Sample gas	1.200 l/min
Sample gas	14 l/min
Wash time	90 s
Masses	7, 193, 235, 238

2.2. Instrumentation

An SF-ICP-MS Model ELEMENT 1 (Finnigan MAT, Germany) was used for all experiments.

Including the mass 7 (Li) allows full range working of the magnetic field, which avoids hysteresis effects of the magnet and improves the stability of the instrument.

No polyatomic interferences can be expected at the masses of ^{235}U and ^{238}U, respectively, so that low resolution can be applied because of the higher sensitivity.

The instrumental parameters are given in Table 1. The analytical programme used is shown in Table 2.

The ''guard electrode'' improves the sensitivity by approx. a factor of 10 because of an improved geometry, that means a higher energy density, of the plasma. Because of the tendency to higher oxide formation rates in case of the guard electrode, it is necessary to tune the instrument not only to highest sensitivity but also to lowest oxide formation of the element under investigation. The relation between ^{238}U and $^{238}U^{16}O$ should be at least 10:1. Lower ratios will lead to instabilities of the ^{238}U signal because of the very unstable oxide formation rate. Very little changes of the sample gas, in the range of 2–5% of the total flow, cause severe changes of more than 50% of both signals (^{238}U–$^{238}U^{16}O$).

The tune parameters optimising the sensitivity for ^{238}U and reducing the oxide formation will change from instrument to instrument and from day to day.

Table 2
Analytical programme for the determination of uranium by ICP-MS

Isotope	Accurate mass	Mass window (%)	Mass range	Sample time (s)	Samples per peak
^{7}Li	7.016	100	7.004–7.028	0.010	10
^{193}Ir	192.9629	150	192.481–193.445	0.050	30
^{235}U	235.0434	150	234.456–235.631	0.100	30
^{238}U	238.0502	150	237.455–238.645	0.100	30

Segment duration [s]	Integration window [%]	Scan type	Detection mode	Integration type	I.S.
0.100	100	Escan	Counting	Average	–
2.250	100	Escan	Counting	Average	–
4.500	100	Escan	Counting	Average	^{193}Ir
4.500	100	Escan	Counting	Average	^{193}Ir

2.3. Detection limit

The typical sensitivity for ^{235}U is about $2–3\cdot10^{4}$ counts/s and for ^{238}U about $3–5\cdot10^{6}$ counts/s for 1 μg/l U, measured as the peak height.

The evaluation was done on the average of 30 channels over the peak, as indicated in Table 2. Regarding these evaluation parameters and the analytical programme used here, the following values have been obtained (Table 3).

2.4. Calibration

A U stock standard solution of 1 g/l purchased and certified by SPEX (USA) was used for the calibration. Standard solutions of 0, 1, 2, 5, 10, 20, 50 and 100 ng/l were prepared by successive dilution using HNO_3–water (1:10, v/v).

In the same way the internal standard (I.S.) solution, in this case Ir, was prepared by successive dilution of the stock solution of again 1 g/l Ir to the appropriate final concentration of the working solution of 100 μg/l acidified with the same amount of HNO_3 as in the case of U. The concentration of the I.S. in all samples and standard solutions is 1 μg/l.

The calibration curves are linear (up to about 1 μg/l total U) and have regression coefficients of $r=>0.99$.

Outgoing from the calibration data the isotope ratio was calculated for each concentration. The values obtained are shown in Table 4.

Table 3
Measured parameters for U-determination

Parameter	^{235}U	^{238}U
Background ($n=10$) (counts/s)	1.05±0.65	50.1±3.7
3σ	2	11
DL (3σ criteria) (pg/l) (related to total U)	250	10
LOQ (in urine)	3 ng/l	150 pg/l

DL, Detection limit (instrumental parameter in aqueous solution); LOQ, limit of quantification (in real urine samples).

Table 4
Measured isotope ratios for ^{238}U/^{235}U

Sample (ng/l)	^{238}U (counts/s)	^{235}U (counts/s)	Isotope ratio ($n=5$)
1	1100	8	137.5±4.8
2	2220	16	138.7±4.1
5	5510	40	137.8±3.3
10	11 530	84	137.3±5.2
20	20 960	152	137.9±1.4
50	51 850	376	137.9±2.8
100	102 830	734	140.1±3.1
Urine (10 ng/l)	11 324	82	138.1±3.4

Table 5
Quality criteria

Parameter	^{238}U	^{235}U	Concentration (ng/l)
Precision ($n=10$) (%)	±2.3	±8.3	10.5
	±1.8	±6.1	20.5 (addition of 10 ng/l)
Recovery (%)	101	103	Addition of 10 ng/l
Day to day	±3.3	±11.4	10.5
($n=10$ days)	±2.9	±9.4	Addition of 10 ng/l

A mean value for the isotope ratio of 138.2±1.0 was obtained. That is in very good agreement to the theoretical ratio of 139.6.

2.5. Reliability criteria

In a previous paper [1] a comparison between α-spectrometry and ICP-MS was performed to test the accuracy of the ICP-MS results. A good agreement between the two methods was achieved, so it may be assumed that ICP-MS gives reliable results. This comparison was performed using Q-ICP-MS, but the results can be transferred also to SF-ICP-MS because of the application of the same resolution (300).

Standard addition method was applied because of the lack of an adequate reference sample. For these purposes 10 ng/l U was added to the original pool urine.

The Table 5 gives the quality criteria, including precision ($n=10$), recovery of the addition and the day to day precision, for the real pool urine sample (total uranium concentration=10.5 ng/l).

3. Results and discussion

SF-ICP-MS in low-resolution mode, allows highly sensitive uranium determination in human urine samples as well as the measurement of the isotope ratio $^{238}U/^{235}U$ with sufficient quality criteria. The time consumption for the analysis is very short (only some minutes), not regarding the time for the calibration of the instrument (approx. 30 min), which may be neglected in case of higher sample numbers (>10), compared with α-spectrometry (at least 2 days/sample). This method is the only possible way to measure low U concentrations and the isotope ratio simultaneously. The method is well suitable for the application in environmental and occupational medicine, respectively, because of the possibility to monitor the physiological range as well as the exposure.

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