

Mamoune El Himri · Agustín Pastor
Miguel de la Guardia

Determination of uranium in tap water by ICP-MS

Received: 14 October 1999 / Revised: 27 December 1999 / Accepted: 31 December 1999

Abstract A fast and accurate procedure has been developed for the determination of uranium at $\mu\text{g L}^{-1}$ level in tap and mineral water. The method is based on the direct introduction of samples, without any chemical pre-treatment, into an inductively coupled plasma mass spectrometer (ICP-MS). Uranium was determined at the mass number 238 using Rh as internal standard. The method provides a limit of detection of 2 ng L^{-1} and a good repeatability with relative standard deviation values (RSD) about 3% for five independent analyses of samples containing $73 \mu\text{g L}^{-1}$ of uranium. Recovery percentage values found for the determination of uranium in spiked natural samples varied between 91% and 106%. Results obtained are comparable with those found by radiochemical methods for natural samples and of the same order for the certified content of a reference material, thus indicating the accuracy of the ICP-MS procedure without the need of using isotope dilution. A series of mineral and tap waters from different parts of Spain and Morocco were analysed.

Introduction

The average content of uranium in the earth's crust corresponds to $2 \mu\text{g}$ uranium per g of soil, being concentrated mainly in the acidic magmatic rocks with lesser amounts in basic minerals and sediments [1, 2]. Soluble U(VI) carbonate complexes produced in soil uranium can be transferred into natural water.

The dangerous health effects are well documented [3]. Concentrations of uranium as low as $500 \mu\text{g L}^{-1}$ can affect the reproductive capability of aquatic organisms [4]. The concentration varies from 200 to $350 \mu\text{g L}^{-1}$ for *hydra*

viridissima [5], and the toxicity of uranium for fish was evidenced [6]. Therefore the interest on the determination of uranium in drinking and natural waters is still increasing [7].

Various methods have been used for the determination of uranium in environmental and water samples based on α -spectroscopic measurements [8], spectrophotometry [9], fluorescence spectrometry [10], laser-induced fluorescence [11–12] and neutron activation analysis [13]. However, these techniques generally offer serious limitations due to the high sample volume required [8], expensive and rare equipment [13], long counting times [8] and high limits of detection, which involves the requirement of a preconcentration of samples prior to their analysis [9, 10].

Inductively coupled plasma mass spectrometry (ICP-MS) offers an interesting alternative for the determination of uranium at ng L^{-1} trace levels, requiring a small sample volume, providing a fast analysis free from spectral interferences [14].

There are few precedents on the use of ICP-MS for the determination of uranium in waters [15–23] mainly using a preconcentration step [15–17, 19], ultrasonic nebulisation [22] or the need of a long analysis time of 6 h for a triplicate analysis. Memory effects in uranium determination were observed [20] as well as the need of using isotope dilution in order to get the most accurate results [18, 21, 23]. However, it seems that for other aqueous samples like urine, the direct ICP-MS determination is easier [24, 25]. The internal standard used for uranium determination were Ir [24, 25] and Th [22], but in all these cases the authors determined only uranium.

Here a simple strategy for the determination of uranium in tap and natural waters based on measurements at the mass number 238 and using Rh as internal standard was developed. This method was validated by comparison with radiochemical measurements and applied to the determination of uranium in Spanish and Moroccan samples.

M. El Himri¹ · A. Pastor · M. de la Guardia
Department of Analytical Chemistry,
University of Valencia 50 Dr. Moliner St,
46100 Burjassot (Valencia), Spain

Present address:

¹Coming from the University of Oujda, Dep. Anal. Chem.,
Route Sidi Mâafa BP 524, 6000 Oujda (Morocco)

Experimental

Instrumentation. All measurements were made using a Perkin-Elmer Sciex® ELAN™ 5000 ICP-MS spectrometer (Toronto, Canada) equipped with a Perkin Elmer Ryton Scott-type spray chamber and cross-flow nebuliser. Sample solutions were aspirated into the argon plasma via a peristaltic pump and data were acquired using an IBM PS/2 Model 77 computer with a Perkin-Elmer semiquantitative (TotalQuant®) and quantitative software.

For validation of the ICP-MS data, α -spectrometric measurements were carried out using a Tennelec instrument model TC 256 with a power source Tennelec mod MB-1 and equipped with a PC-XT computer.

Reagents. Stock solution of 100 mg L⁻¹ uranium was prepared from UO₂(NO₃)₂ · 6(H₂O) 99.999% (Merck, Darmstadt, Germany). Solution of 10 mg L⁻¹ Rh was employed as internal standard. It was prepared from RhCl₃ · 3H₂O 38% (Merck, Darmstadt, Germany). In both cases, ultrapure HNO₃ 69% (w/w) (Romil, Cambridge, UK) and high purity water of 18.2 M Ω cm⁻¹ resistivity, obtained from a MilliQ system (Millipore, Saint-Quentin Yvelines, France), were employed.

High purity argon (C-45) of 99.995% purity was supplied by Carubos Metalicos (Barcelona, Spain).

A drinking water reference material (CRM-TMDW Lot # 490915) from HPS (Charleston, United States), was employed to evaluate the accuracy of the quantitative ICP-MS measurements.

General procedure

ICP-MS determination of uranium. Before starting the analytical measurements, the plasma instrument was allowed to equilibrate for 30 min and it was initialised with a 10 μ g L⁻¹ solution of Mg, Pb and Rh by varying the ion lens voltage and cones position in order to maximise the ¹⁰³Rh signal and to equalise the ²⁴Mg and ²⁰⁸Pb signals. After that, uranium was determined by using both the quantitative and the semiquantitative mode.

To 4.88 mL of sample 50 μ L of 10 mg L⁻¹ Rh solution as internal standard and 70 μ L of ultra pure nitric acid (69% w/w) was added. Samples were aspirated into the ICP-MS with 1 mL min⁻¹ carrier flow and measured at ²³⁸U mass number, using the experimental conditions indicated in Table 1. Measurement data obtained were interpolated in a calibration curve of aqueous standards covering a concentration range from 0.05 μ g L⁻¹ to 125 μ g L⁻¹, prepared with the same reagents as the samples. The system

Table 1 ICP-MS operating conditions employed for the determination of U

Rf power (W)	1000	
Plasma gas flow-rate (L min ⁻¹)	9–11	
Auxiliary flow-rate (L min ⁻¹)	1.2–1.4	
Nebuliser flow-rate (L min ⁻¹)	0.8–0.9	
Sample delivery rate (mL min ⁻¹)	1.0	
Mass spectrometer pressure (Pa)	(1.3–2.7) · 10 ⁻³	
Interface pressure (Pa)	5.3 · 10 ⁻²	
Sampler orifice diameter (Nickel) (mm)	1.14	
Skimmer orifice diameter (Nickel) (mm)	0.89	
	TotalQuant	Quantitative
Replicate time (s)	45	39
Dwell time (s)	0.05	0.250
Reading replicate number	1	1
Number of replicates	1	5
Number of sweeps per reading	5	2
Points per spectral peak	1	5

was washed during 45 s after each measurement with a washing solution of 2% (v/v) HNO₃.

In the semiquantitative mode, in addition to Rh and HNO₃, a standard mixture of Be, Ge, Re and Tb was added to the samples for internal calibration and uranium was determined without the use of external standards.

α -Spectrometric determination of uranium. α -Spectrometric measurements of ²³⁸U were carried out by using ²³²U as tracer after a preconcentration of 5 L sample by coprecipitation with FeCl₃ at pH 8 and extraction with isopropyl ether, followed by ionic exchange on an anionic Dowex column and electrodeposition. The method involves several steps and an average time of analysis of 10 days [26, 27] and a limit of detection of 2 ng L⁻¹.

Results and discussion

Conditions for ICP-MS determination of uranium

ICP-MS measurements were made by varying several parameters, such as the dwell time, the number of readings per replicate, the number of replicates and the sample flow rate. A 100 μ g L⁻¹ solution of uranium was employed in this study.

In spite of the generally accepted use of Ir or Th as internal standard for uranium determination, Rh was selected because it is a generally employed standard for the determination of different elements in waters.

Figure 1 shows the effect of dwell time on the relative signals of uranium and their RSD, established from 5 independent experiments and, as can be seen, a dwell time higher than 150 ms provides an appropriate repeatability of the signals, being thus selected a dwell time of 250 ms, which provides a fast practicability in the quantitative mode. However, for semiquantitative determinations of 73 elements 50 ms must be employed in order to reduce the time spent per analysis.

The increase of reading per replicate, from 1 to 10, reduces the RSD from 1.11 to 0.47 increasing the relative signal of 100 μ g L⁻¹ uranium from 0.746 to 0.761, but

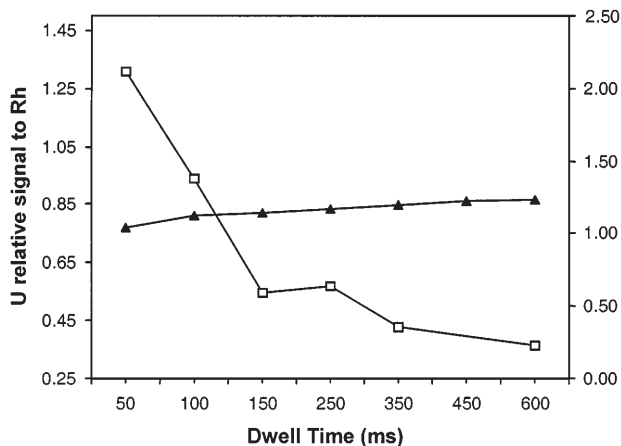


Fig. 1 Effect of dwell time (ms) on uranium relative signal to rhodium (▲) and % RSD (□). Experimental conditions: 1 reading per replicate, 5 replicates per reading, 2 sweeps per reading, 5 points spectral peak and 1 mL min⁻¹ flow rate

also increasing the required time by one order of magnitude. Thus, one reading per replicate was selected for both, semiquantitative and quantitative, mode measurements.

The RSD of the uranium signal relative to Rh is affected by the use of an increasing number of replicates, and 5 replicates were selected for the quantitative determination of uranium, using external calibration. In the semiquantitative mode, however a single measurement was employed.

The U/Rh signal was not affected by the flow rate of sample introduction between 0.87 to 1.6 mL min⁻¹. However, a reduction of the RSD, from 1.6 to 0.8%, can be found as a function of the flow rate employed. The best repeatability was obtained between 1.0 and 1.4 mL min⁻¹. A sample flow of 1 mL min⁻¹ was employed throughout.

The semiquantitative mode of analysis is highly useful in order to obtain information about the concentration level of 80 elements present in the same unknown sample. The influence of the experimental parameters was also evaluated in order to obtain, as accurate and reproducible as possible, data on this mode [28]. After the confirmation of the absence of Be, Ge, Re and Tb in a series of natural and mineral waters of different origin, these 4 elements were chosen for standardisation of measurement. Uranium was evaluated at the same time as 68 other elements in 25 samples using the operating conditions indicated in Table 1.

Analytical performance of the ICP-MS determination of ²³⁸U

In the quantitative mode, and using external solutions of uranium in the presence of 100 ng mL⁻¹ Rh, it is possible to obtain a linear relationship between U/Rh relative signals (I_r) versus uranium concentration (C).

For 17 standard solutions, with uranium concentrations ranging from 0.05 µg L⁻¹ to 125 µg L⁻¹, the following calibration line was obtained $I_r = (0.00006 \pm 0.00010) + (0.004403 \pm 0.000003)C$ being C expressed in µg L⁻¹ with a regression coefficient $R = 0.999997$. However, most of the natural samples contain concentrations of uranium lower than 10 µg L⁻¹. To obtain accurate data, a new calibration was carried out with 11 standards ranging from 0.05 to 10 µg L⁻¹. The relationship $I_r = (0.00009 \pm 0.00005) + (0.00439 \pm 0.000014)C$ was found with $R = 0.99995$, being the calibration expression for only nine standards from 0.05 to 2.5 µg L⁻¹ $I_r = (0.0001 \pm 0.00005) + (0.00438 \pm 0.00004)C$ with $R = 0.9997$.

From the aforementioned expressions it can be concluded that the analytical sensitivity for uranium using ICP-MS corresponds to 0.00438 units per µg L⁻¹ uranium, which provides a limit in detection in the order of 3 ng L⁻¹ uranium for a confidence level of 99.6% ($k = 3$).

The repeatability of the ICP-MS determination of uranium, established from 5 independent analysis of a water sample containing 73 µg L⁻¹ of uranium was 3%. Figure 2 shows data found during a period of 22 months for four

natural samples at different times in order to evaluate the between day variability of uranium determinations in the fast semiquantitative mode. Highly stable and reproducible results were obtained for trace levels of uranium from 70 to 2 µg L⁻¹.

To test the accuracy of the ICP-MS measurements, a series of recovery studies were carried out on natural samples spiked with known amounts of uranium and, for added concentrations ranging from 1 to 100 µg L⁻¹, recovery percentages from 91 to 106% were obtained, thus indicating the reliability of the procedure developed.

Real sample analysis

Two drinking water samples, a mineral bottled water and a spring sample, were analysed by both the ICP-MS procedure and a reference procedure based on α-spectrometric measurements, and, as can be seen from Table 2, comparable results were obtained, which correspond also to a high and a low concentration level of uranium. This fact evidences that the ICP-MS procedure provides an accuracy comparable to that found by radiochemical measurements. The reference procedure employed, required the use of 5 L sample and 10 days.

The accuracy was also evaluated by measuring a drinking water reference material containing 10 µg L⁻¹ uranium (Table 2). Results obtained by ICP-MS are in a good agreement with the certified value.

Additional studies, carried out in order to verify the applicability of the ICP-MS measurements for natural sample analysis, were focused on the comparison between data found by external calibration and those obtained by the standard addition. Figure 3 shows the regression between data obtained by both procedures for a series of 11 tap water samples. It can be seen that the method is free from matrix interferences. The slope and the intercept of the regression line were statistically comparable with 1 and 0, respectively, which shows that the use of external calibration does not cause constant relative errors or blank errors.

Test evaluation of uranium by semiquantitative analysis

As it has been indicated in the experimental part, the ICP-MS instrument can be operated in a semiquantitative mode (called TotalQuant[®]) by using a few elements for internal standardisation of the signals over the whole mass range. This experimental mode allows to obtain a fast determination of uranium along with information about other elements present in the sample [28].

Uranium was measured in the same run of analysis together with other elements. Table 3 shows the analytical report for 5 independent analyses of a sample of Chulilla water. The methodology used provides a good picture on the nature of water samples and can be useful for an appropriate external calibration to be employed in quantitative determination. Concerning data found for uranium,

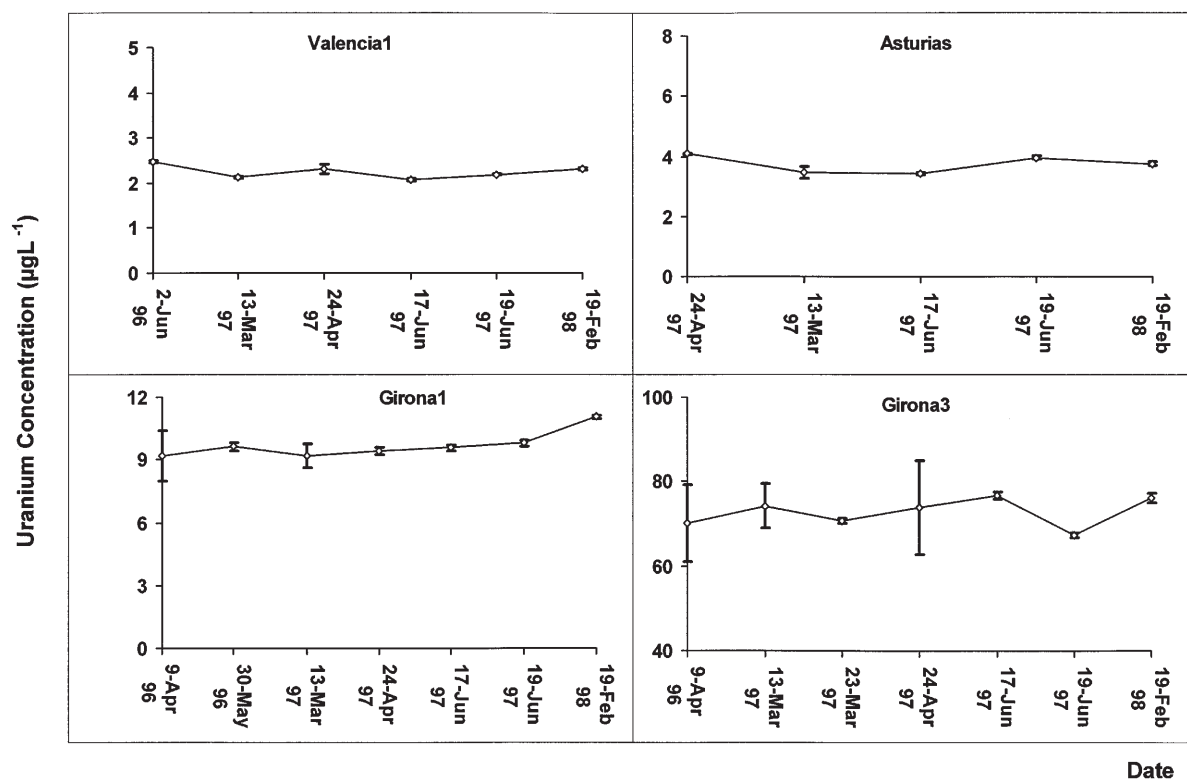


Fig.2 Between day evaluation of the uranium concentration in drinking water samples of different origin. Data obtained in the fast semiquantitative mode

Table 2 Comparison of results obtained by ICP-MS and α -radiochemical measurements for the determination uranium in drinking waters

Sample	ICP-MS ($\mu\text{g L}^{-1}$)	Radioactivity ($\mu\text{g L}^{-1}$)	Certified value ($\mu\text{g L}^{-1}$)
Mineral (Girona 3)	73 ± 2	72 ± 10	–
Spring (Pedralva)	2.3 ± 0.2	2.0 ± 0.3	–
HPS Reference water	10.3 ± 0.1	–	10.000 ± 0.005

the agreement between results found by this fast methodology and those found by using an external calibration was checked. Table 4 summarises results obtained for 23 samples. The regression between both procedures provided $y = (1.031 \pm 0.003)X + (0.03 \pm 0.04)$ with a regression coefficient $R = 0.99990$. It demonstrates that both methodologies are comparable in terms of analytical results, also providing a comparable precision (see Table 4).

Determination of uranium in natural samples

23 waters samples from different parts of Spain and Morocco were analysed (see Table 4). The content of uranium in Moroccan samples varies between $0.24 \mu\text{g L}^{-1}$ and $0.42 \mu\text{g L}^{-1}$, thus providing a low concentration level. Samples, taken from the south of Spain (Sierra Nevada

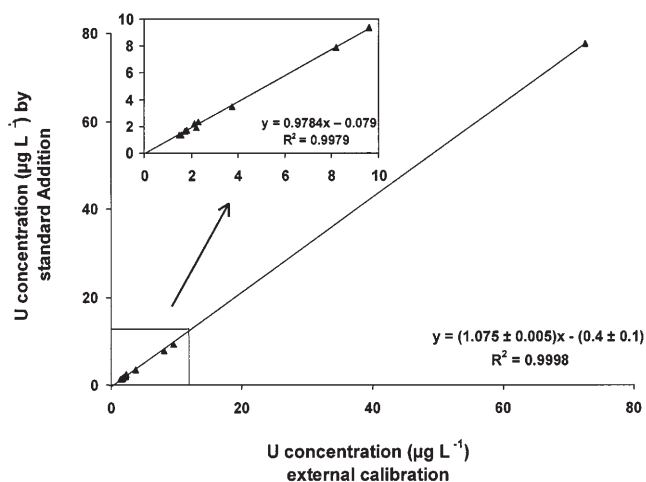


Fig.3 Comparison of standard addition and direct quantitative ICP-MS methods for the determination of uranium in tap water

and Granada) provided values of 0.42 and $0.7 \mu\text{g L}^{-1}$, respectively. In the east of Spain (Canet, Chulilla, Castellón, Pedralba and Valencia) the concentration of uranium varies between 0.1 and $2.3 \mu\text{g L}^{-1}$, but in Cuenca an uranium concentration level of $2.1 \mu\text{g L}^{-1}$ was found and in the north of Spain (Girona and Asturias) the concentration varied from 0.05 to $73 \mu\text{g L}^{-1}$. These differences in analytical data clearly indicate the influence of the geological nature of the sampling zone and could reveal some particular phenomena related to specific sources.

Additional studies on the presence of major anions and cations in samples analysed did not provide any correla-

Table 3 Data found by semiquantitative analysis of a Chulilla water sample

Element	X ± s (µg L ⁻¹)	Element	X ± s (µg L ⁻¹)
Li	66 ± 9	Cu	1.2 ± 0.1
B	92 ± 10	Zn	1.6 ± 0.1
Na ^a	122 ± 19	Ga	0.34 ± 0.08
Mg ^a	41 ± 6	As	0.9 ± 0.1
Al	1.4 ± 0.3	Se	2.0 ± 0.4
Si ^a	2.8 ± 0.3	Br ^a	0.92 ± 0.06
K ^a	3.0 ± 0.6	Rb	8 ± 1
Ca ^a	145 ± 24	Sr ^a	3.5 ± 0.7
Sc	1.5 ± 0.3	Y	0.033 ± 0.008
Ti	0.9 ± 0.2	Zr	0.014 ± 0.005
V	1.3 ± 0.3	Mo	0.85 ± 0.11
Cr	1.1 ± 0.5	I	1.51 ± 0.14
Mn	0.16 ± 0.05	Cs	2.6 ± 0.5
Fe	21 ± 4	Ba	23 ± 3
Co	0.14 ± 0.04	La	0.075 ± 0.007
Ni	1.7 ± 0.5	U	1.6 ± 0.2

^aResults expressed in mg L⁻¹. Results are the average of 5 independent analysis

Table 4 Semiquantitative and quantitative results for ICP-MS determination of uranium in natural water samples

Water sample	Quantitative	Semiquantitative	Deviation (%)
	X ± s (µg L ⁻¹)	X ± s (µg L ⁻¹)	
Asturias	3.7 ± 0.3	3.5 ± 0.4	-5.4
Canet 1	1.06 ± 0.03	1.33	25.5
Canet 2	0.098 ± 0.005	0.16	63.3
Cantabria	1.0 ± 0.1	1.0 ± 0.1	-1.02
Castellón 1	0.31 ± 0.04	0.30 ± 0.06	-3.2
Castellón 2	0.6 ± 0.1	0.6 ± 0.1	-9.7
Chulilla	1.6 ± 0.2	1.6 ± 0.2	0.6
Cuenca	2.1 ± 0.1	1.9 ± 0.2	-10.8
Girona 1	9.6 ± 0.4	9.1 ± 1.0	-5.2
Girona 2	0.05 ± 0.01	0.04 ± 0.01	-20
Girona 3	73 ± 2	70 ± 2	-4.1
Girona 4	8.2 ± 0.6	7.3 ± 1.0	-11.0
Girona 5	0.6 ± 0.1	0.6 ± 0.2	-9.1
Godella	1.7 ± 0.2	1.6 ± 0.2	-7.5
Granada	0.7 ± 0.1	0.59 ± 0.07	-10.6
Oujda ^a	0.31 ± 0.02	0.80 ± 0.05	158
Pedralba	2.3 ± 0.2	2.0 ± 0.2	-13.04
Sierra nevada	0.42 ± 0.04	0.40 ± 0.05	-4.8
Sidi Ali ^a	0.24 ± 0.03	0.24 ± 0.03	0
Sidi Hrazem ^a	0.4 ± 0.1	0.42 ± 0.06	-14.3
Valencia 1	2.2 ± 0.2	2.0 ± 0.3	-9.5
Valencia 2	1.5 ± 0.2	1.6 ± 0.6	6.7
Valencia 3	1.8 ± 0.2	1.7 ± 0.1	-8.8

^aSamples from Morocco. Data reported correspond to the average of 5 independent determinations carried out by both modes

tion between the uranium concentration and that of major components. Only for samples with an uranium concentration higher than 3 µg L⁻¹ the content of Sr was lower than 0.1 mg L⁻¹ also accompanied by low levels of other alkaline earth elements, caused by geology.

Additional remarks

Some problems have been reported in the literature related to uranium determination by ICP-MS concerning memory effects [20] and oxide formation [20, 29]. To avoid these effects, throughout the present study, the system was washed between different samples for 45 s with a nitric acid solution of 2% (v/v), and plasma parameters, like forward power, nebuliser flow rate and auxiliary flow, were fixed at 1000 W, 0.87 L min⁻¹ and 1.2 L min⁻¹ in the quantitative determination of ²³⁸U. A series of experiments evidenced no memory effects were introduced for uranium concentrations in the order of 150 µg L⁻¹. On the other hand, analytical measurements made at masses 238 and 254, corresponding to ²³⁸U and ²³⁸U¹⁶O, provided a signal relationship between 9 and 13, as a function of the working conditions, which was the same for both, samples and pure standards of uranium, thus evidencing that a probable formation of uranium oxide in an extension of 10% (three times lower than that reported before [20]), does not affect the accuracy of the determination of uranium through ICP-MS.

Conclusions

Through this study the following has been validated by spike recovery study, α-spectrometric measurements and the use of a certified reference material: the determination of uranium in waters by ICP-MS using both, a classical quantitative strategy based on the use of external calibration and the use of Rh as internal standard and a fast semiquantitative methodology based on the use of Be, Ge, Tb and Re for signal calibration in the whole mass range, confirmed the applicability of ICP-MS developed procedures to obtain a fast and accurate information on uranium concentrations in tap and natural waters.

Acknowledgements The authors acknowledge the financial support of the Conselleria de Cultura, Educació i Ciencia de la Generalitat Valenciana, Project n° GV-2232/94, and that of Secretaria de Estado de Universidades, Investigación y Desarrollo PB 96-0779.

References

1. National Council on Radiation Protection and Measurements (NCRP) DC (1971) NCRP Report N°. 39, Washington
2. Stokinger HE (1981) Industrial Hygiene and Toxicology. Clayton CD, Clayton FE (eds), John Wiley, vol. 2A, 3rd edn. New York, pp 1995–2013
3. Najem GR, Voyce LK (1990) Am J Public Health 80:478
4. Posten Hanf S (1984) Water, Air, Soil Pollut 22:289
5. Hyne RV, Rippon GD, White J, Ellender G (1992) Aquat Toxicol (Amsterdam) 23:231
6. Labrot F, Narbonne JF, Ville P, Saint-Denis M, Ribera D (1999) Archiv Cont Toxicol 36:167
7. Roberts K, Hunsinger R, Dart J Revised (1983) Ontario Ministry of the Environment
8. Dep of the Environment (1986) Methods Exam Waters Assoc Mater London p 76
9. Burba P (1989) Fresenius Z Anal Chem 334:357

10. Jarrell-Ash MA (1981) Fluometer Model 27-000 Manual and Methods Handbooks. Thermo Jarrel-Ash, Waltham pt 004131
11. Romanovskaya GI, Pogonin VI, Chibisov AK (1987) *Talanta* 34(1):207
12. Moulin C, Beaucaire C, Decambox P, Mauchien P (1990) *Anal Chim Acta* 238(2):291
13. Bem H, Ryan DE (1984) *Anal Chim Acta* 166:189
14. Winefordner JD (1971) *Spectrochemical Methods of Analysis*. Wiley, vol 9, Interscience New York
15. D'Silva AP, Bajic SJ, Zamzow D (1993) *Anal Chem* 65:3174
16. Bettinelli M, Spezia S (1995) *At Spectrosc* 16:133
17. Dadfarnia S, McLeod CW (1994) *Appl Spectrosc* 48:1331
18. Toole J, McKay K, Baxter M (1991) *Anal Chim Acta* 245:83
19. Beauchemin D, Berman SS (1989) *Anal Chem* 61:1857
20. Boomer DW, Powell MJ (1987) *Anal Chem* 59:2810
21. Beauchemin D, McLaren JW, Mykytiuk AP, Berman SS (1987) *Anal Chem* 59:778
22. Crain JS, Mikesell BL (1992) *Appl Spectrosc* 46 (10):1498
23. Swarzenski PW, McKee BA (1998) *Estuaries* 21 (3):379
24. Werner E, Roth P, Wendler I, Schramel P, Hellmann H, Kratzel U (1997) *J Radioanal Nucl Chem* 226 (1-2):201
25. Schramel P, Wendler I, Roth P, Werner E (1997) *Mikrochim Acta* 126 (3-4):263
26. Crespo MT, Gascon JL, Acena ML (1992) *Appl Radiat Isot* 43 (1-2):19
27. Sanchez AM, Tome FV (1990) *J Radioanal Nucl Chem* 141 (1):69-74
28. Soldevila J, El Himri M, Pastor A, de la Guardia M (1998) *J Anal At Spectrom* 13:803
29. Houk RS, Olivares JA (1985) *Anal Chem* 57:2674