

ON ICP-MS DETERMINATION OF URANIUM
IN DRINKING, GROUND AND MINERAL WATERS

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Abstract

A method for the determination of uranium in surface and ground water samples is developed and validated. The method is based on ICP-MS measurement under optimized instrumental parameters using Re as an internal standard. Model solutions containing major cations in natural waters such as Na, K, Ca, Mg are prepared and used to study the observed matrix interferences on U signal in ICP-MS measurements. Routinely used internal standards La, Tl for U ICP-MS measurement in natural waters are compared to newly proposed internal standard Re. Results obtained showed more efficient interference correction and better reproducibility in the presence of Re applied at concentration level of $10 \mu\text{g L}^{-1}$ for internal standard calibration. Analytical procedure developed is characterized by determination limit of $0.04 \mu\text{L}^{-1}$ and relative standard deviation in the range 4–6% for the U concentration range from 0.04 to $50 \mu\text{L}^{-1}$. The method is validated through the analysis of parallel water samples by using proposed method, by using standard UV-VIS method (arsenazo III), and by analyzing a certified reference material.

Key words: uranium, ICP-MS, water samples, internal standards

Introduction. Uranium is a radiotoxic and chemotoxic element existing as three naturally occurring radioactive isotopes: ^{238}U , ^{235}U and ^{234}U . Uranium as U(IV) is sparsely soluble and immobile found mostly in reducing environments, whereas U(VI) is soluble in water, mobile, and toxic to the environment found

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under oxidizing conditions [1]. Anthropogenic activities such as mining and processing mineral ores, fertilizer manufacturing and other industrial activities result in uranium contamination of water bodies [2]. Increased uranium concentration in water threatens human health because of its chemical toxicity which is much greater than its radiotoxicity [3]. Long-term exposure to high uranium concentrations can lead to kidney failure and bone damage [4]. Abandoned uranium mines are a very important local concern for Bulgaria as they pose real or potential threats to human safety and health, as well as environmental damages as their poor treatment leads to uncontrolled spreading of U in natural water bodies. Because all natural isotopes of U are radioactive their concentrations in water samples can be determined by different radiometric methods such as alpha spectrometry [4]. Limitations of this method are prolonged sample preparation, need of radioactive tracer and the time-consuming measurement. Inductively coupled plasma mass spectrometry (ICP-MS) techniques are widely used for determination of long-lived radionuclides due to its relatively high sensitivity and short measurement time. Depending on the application and the need of precision, relatively cheap quadrupole ICP-MS may give sufficiently good results under optimal instrumental parameters and well corrected matrix interferences [5]. These matrix interferences might be corrected using various techniques one of which is the internal standard method. Several internal standards have been proposed for determination of uranium with ICP-MS for different matrices: ^{103}Rh [6] for drinking waters, ^{207}Bi for geological samples [7], ^{207}Bi and ^{205}Tl for biological samples [8], ^{193}Ir [9,10] mostly for urine samples, ^{115}In for sea water [11]. Re have been applied as an internal standard for uranium measurement primarily in ore samples [12].

In this study rhenium is proposed as an internal standard for U determination in natural waters with high mineralization. Analytical procedure developed permits determination of U in various types of waters – drinking, ground and mineral with very high mineralization, with low detection limits and good reproducibility. Accuracy of results obtained was established by parallel sample analysis using standard UV-VIS (arsenazo III) method, by participating in the frame of proficiency testing programme and by certified reference material SLRS-6 River water. Very good agreement achieved confirmed validity and versatility of the developed method for U determination in natural waters.

Experimental. Instrumentation. All measurements are carried out on “Analytik Jena AG” “PlasmaQuant MS” mass spectrometer equipped with a MicroMist™ nebulizer and a double-pass spray chamber cooled at 3 °C to lower oxide formation. The samples are introduced via peristaltic pump at 14 rpm pump rate. Table 1 shows the instrument parameters used.

Reagents. All model and calibration standards are prepared using analytical grade HNO_3 TraceSELECT™ from Honeywell diluted to 2% (v/v) with high purity water type 1 MiliPoreQ with 18.2 M Ω /cm resistivity. CPA Chem certified reference material with 10 g L $^{-1}$ initial concentration is used for the prepara-

T a b l e 1

Optimized instrument parameters for U measurement by ICP-MS

ICP-MS operating conditions		Mass spectrometer acquisition settings	
RF power	1280 W	Dwell time	50 ms
Nebulizer flow	1.10 L/min	Scans per replicate	10
Auxiliary flow	1.50 L/min	Replicates per sample	10
Plasma flow	9.0 L/min	Scan mode	Peak hopping

tion of working uranium standards. Titrilsols of Re, La and Tl are used for the preparation of internal standard solutions with concentration 10 mg L^{-1} .

Reference material provided by LGC Standards in the frame of proficiency testing programme AQ 629 is used for method validation. In addition, certified reference material SLRS-6, River water certified reference material for trace metals, and other constituents was used.

Procedure. After plasma ignition the instrument is allowed to reach equilibrium conditions for 30 min. The plasma alignment is optimized and further mass calibration is performed daily. Analysis is performed using ^{238}U isotope applying as internal standards: ^{139}La , ^{185}Re and ^{205}Tl . All water samples are filtered and acidified with conc. HNO_3 prior to analysis. The internal standards used are added to the calibration standards and water samples to the final concentration of $10 \text{ } \mu\text{g L}^{-1}$.

UV-VIS determination of U is performed on a Varian Cary[®] 50 UV-Vis spectrophotometer using Arsenazo III as a chromofor (see details [13]) by using U enrichment [14].

Results and discussion. Optimization of the instrumental parameters. Several parameters, such as the dwell time, the number of readings per replicate, the number of replicates and the sample flow rate were optimized using solution of uranium with concentration $10 \text{ } \mu\text{g L}^{-1}$. Results obtained showed that the optimal parameters are 50 ms dwell time, 10 scans per replicate, 10 replicates per one sample and a sample flow of 1.1 ml/min.

Analytical performance of the ICP-MS determination of ^{238}U . First calibration of uranium is performed with calibration standards of: 0, 10, 25 and $50 \text{ } \mu\text{g L}^{-1}$ and the calibration line obtained is $I_r = (4269 \pm 325) + 181400 \cdot \text{conc}$, where concentration is expressed in $\text{ } \mu\text{g L}^{-1}$, regression coefficient achieved is 0.99997. Calibration curve constructed for lower concentration range e.g. 0.05– $10 \text{ } \mu\text{g L}^{-1}$ showed almost identical calibration equation.

Matrix interferences. The effect of macro elements Na, K, Ca and Mg as nitrates on the uranium measurement was studied at concentration levels of 50 and 100 mg L^{-1} of Na, K, Ca and Mg. Results obtained are depicted in Fig. 1 for Ca and Mg as examples. As seen the slopes of calibration curves are lowered in the presence of 50 mg L^{-1} and 100 mg L^{-1} concentration of salts, more substantially

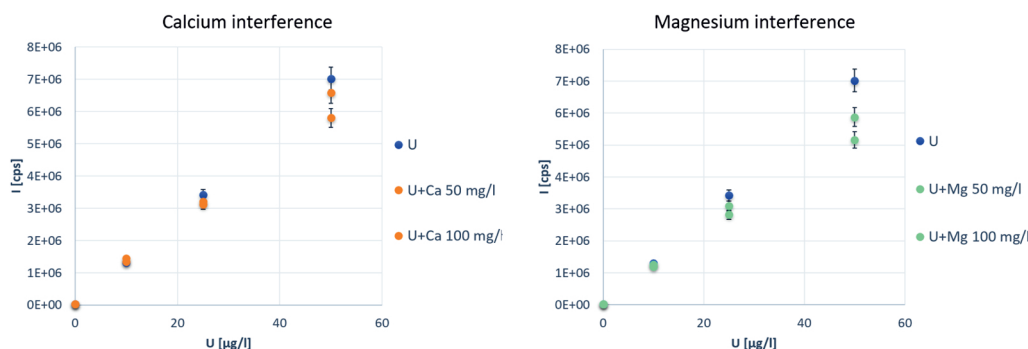


Fig. 1. Matrix interference on U measurement in the presence of Ca and Mg

in the presence of Ca and Mg salts in comparison to the slope of calibration curve prepared with aqueous standard solution of U (see Fig. 1).

Most probably high mineralization leads to decreased ionization efficiency in the plasma in combination with physical effects (sample orifice blockage) and chemical effects (matrix-induced interferences) to the ICP-MS measurement. This makes the quantification of U unreliable due to the changes of the slope of calibration curve (see Table 2) and calls for suitable calibration method.

In the present study most widely used internal standards for U determination in natural waters were tested in comparison with newly proposed Re for efficient correction of observed matrix interferences. As a first step several water samples were analyzed to confirm the absence of the internal standards in them. As a second step comparison of ionization potentials and masses of the internal standards to these of U was performed – the best internal standard would be with ionization potentials and mass as close to ^{238}U (ionization potential 6.19) as possible. Finally, two model solutions containing $50 \mu\text{g L}^{-1}$ U and additions of 100 mg L^{-1}

T a b l e 2

Matrix interferences evaluated as a ratio between the slopes obtained for aqueous standard solutions (b_0) and in the presence of interferent matrix (b_i)

Matrix	Ratio between the slopes of calibration curves
$50 \text{ mg L}^{-1} \text{ NaNO}_3$	0.95 ± 0.2
$100 \text{ mg L}^{-1} \text{ NaNO}_3$	0.91 ± 0.3
$50 \text{ mg L}^{-1} \text{ KNO}_3$	0.94 ± 0.2
$100 \text{ mg L}^{-1} \text{ KNO}_3$	0.92 ± 0.3
$50 \text{ mg L}^{-1} \text{ Ca}(\text{NO}_3)_2$	0.91 ± 0.3
$100 \text{ mg L}^{-1} \text{ Ca}(\text{NO}_3)_2$	0.82 ± 0.4
$50 \text{ mg L}^{-1} \text{ Mg}(\text{NO}_3)_2$	0.83 ± 0.5
$100 \text{ mg L}^{-1} \text{ Mg}(\text{NO}_3)_2$	0.73 ± 0.2

T a b l e 3

Uranium measurement ($50 \mu\text{g L}^{-1}$) in model solution containing 100 mg L^{-1} Ca or 100 mg L^{-1} Mg in the presence of internal standards La, Re and Tl (three parallel determinations)

Analyzed solution	Ca 100 mg L^{-1}	Mg 100 mg L^{-1}
U $50 \mu\text{g L}^{-1}$	47.8 ± 1.8	44.5 ± 1.6
U $50 \mu\text{g L}^{-1}$ + La	44.4 ± 1.6	46.3 ± 1.7
U $50 \mu\text{g L}^{-1}$ + Re	50.4 ± 1.8	49.9 ± 1.8
U $50 \mu\text{g L}^{-1}$ + Tl	53.3 ± 2.0	54.2 ± 2.0

Ca and Mg were prepared. Uranium concentration was measured by using defined optimal instrumental parameters in the presence of $10 \mu\text{g L}^{-1}$ of the studied internal standards ^{139}La (ionization potential 5.58), ^{185}Re (ionization potential 7.83), and ^{205}Tl (ionization potential 6.11). Table 3 shows the correction of the results with the proposed internal standards.

Results presented in Table 3 show that Re is the most suitable and effective internal standard for the correction of matrix interference due to the high mineralization in mineral and ground waters. As expected, La correction is inefficient because La is much lighter than U. The overcorrection of U signal using Tl may be due to different chemical behaviour of the two elements in the plasma and in the instrument. In order to prove the possibilities of Re as internal standard, proposed for U determination in waters, several ground waters with low and high mineralization were spiked with U in the concentration range $5\text{--}50 \mu\text{g L}^{-1}$ and measured. Recoveries achieved varied between 98–101% thus confirming the efficiency of Re as internal standard for matrix interferences correction. Internal standard corrects not only matrix effects but is an excellent tool for decreasing the drift of the instrument over a period of time due to the changing instrument and plasma conditions (minimizing the influence of the clogging of sampler and skimmer cones). Experimental results showed that for a period of 50 min a signal for uranium at a concentration level of $10 \mu\text{g L}^{-1}$ decreased to $8.41 \pm 0.11 \mu\text{g L}^{-1}$, however when Re is applied as an internal standard the measured signal decreased only to $9.95 \pm 0.09 \mu\text{g L}^{-1}$.

Analytical figures of merit. The developed analytical method for U determination is characterized by determination limit $0.04 \mu\text{g L}^{-1}$ and relative standard deviation 4–6% for the concentration range $0.04\text{--}50 \mu\text{g L}^{-1}$. The accuracy of the proposed analytical procedure was confirmed by parallel analysis of samples with relatively high U content and high mineralization by using standard spectrophotometric UV-VIS method (Arsenazo III) after U preconcentration [13,14]. Very good agreement achieved for all analyzed samples verified analytical approach for U determination in water samples applying Re as internal standard. In addition, validity of developed method for U determination is confirmed by the analysis

of certified reference material SLRS-6 River water certified reference material for trace metals for low U concentration, and water sample from proficiency testing scheme AQ 629-LGC (AQUACHECK 2022) for high U concentration. The result (three parallel determinations) obtained in proficiency testing for AQ 629 - LGC (34.70 ± 2.67) coincides well with referent value of provider; result achieved for certified reference material SLRS-6 (0.0712 ± 0.0042) agrees well with certified value (0.0698 ± 0.0034) which confirms versatility of proposed analytical method for U determination in natural waters.

The developed analytical method was applied for the determination of U content in mineral, drinking and ground water samples from various regions in Bulgaria. Results obtained in $\mu\text{g L}^{-1}$ as min-max range are as follows: Gorna Banya – 0.14–0.71; Drinking water from Haskovo Region – 7.53–22.4; Drinking water from Pazardzhik Region – 1.47–4.55; Drinking water from Ruse Region – 0.91–6.50; Drinking water from Petrich Region – 0.35–7.33; Drinking water from Devnya Region – 1–4.39; Drinking water from Blagoevgrad Region – 0.39–1.31; Ground water from Asenovgrad Region – 3.44–47.1; Ground water from Dobrich Region – 1.7–5.93; Ground water from Sofia Region – 1.21–8.24; Ground water from Burgas Region – 22.3–32.0; Ground water from Yambol Region – 39.9–41.3; Ground water from Pernik Region – 3.19–10.8; Ground water from Plovdiv Region – 2.57–41.3; Ground water from Stara Zagora Region – 0.90–2.18.

Conclusions. Analytical method is developed and validated for U determination by ICP-MS in drinking, mineral and ground waters. Matrix interferences observed in waters with high mineralization is corrected by using Re as internal standard. Data for U content in drinking and ground waters from different regions in Bulgaria are presented.

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