Experimental procedure for the analysis of the drinking water „Diapetra", well No 1. village Slavkovica, Ljig, Serbia

Sample preparation

Water samples in sterile glass vials of different color (light-brown and transparent) in duplicates without preparation step directly analysed. Analyses has been conducted in the Laboratory for Water and Elemental Analyses No 538, 548 and 548A http://www.chem.bg.ac.rs/analiticka/oprema-l.html, responsible Professor Dragan Manojlovic http://helix.chem.bg.ac.rs/osoblje/38-en.html that is a memebr of Center of Excellence for Molecular Food Sceinces http://helix.chem.bg.ac.rs/cmnh/index-en.html. Analysis was conducted in february 2014 by Professor Jelena Mutić http://helix.chem.bg.ac.rs/osoblje/66-en.html . None of the personell at the Lab 538 and 548 did not have prior data about the quality of the water or difference between lighter and darker glass containers. Only dr Katarina Smiljanić http://helix.chem.bg.ac.rs/osoblje/429-en.html, from the Department of Biochemistry and the menber of the Center of Excellence for Molecular Food Sceinces knew that the water samples were exactly the same and aliquoted as per the GLP. The analysis results are attached at the end of this description of methods and intrumemts used for its conducting.

Instrumentation

The measurements of all major and trace elements were carried out in a Inductively Coupled Atomic Emission Spectrometer, ICP-OES (Thermo Scientific, United Kingdom), model 6500 Duo, equipped with a CID86 chip detector. This instrument operates sequentially with both radial and axial torch view. The entire system controlled with Iteva software. Instrument conditions and selected wavelengths of some elements are given in Table 1.

The measurement of all ultra trace elements were carried out in a ICP-MS (iCAP Q, Thermo Scientific X series 2). The entire system controlled with Qtegra Instrument Control Software. Measured isotopes of some elements are given in Table 2.

REEs studied are Sc La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y. Analyses were performed with ICP-MS (iCAP Q, Thermo Scientific X series 2; Thermo Fisher, USA). Operating conditions for the ICP-MS were as follows: nebulizer gas flow, 0.75 L/min; ICP RF power, 1050 W; lens voltage, 7 V; pulse stage voltage, 950 V; and sample uptake rate, 24 rpm.

To determine the limit of detection (LOD) and limit of quantitation (LOQ), ten blank solutions were prepared, fololowing our standard procedure. The blank solutions were measured and the standard deviation was determined. Each sample was analyzed in duplicate, and each analysis consisted of three replicates.

LOD and LOQ were determined as three and ten times the standard deviation of the blank solutions.

Reagents and chemicals

All chemicals were of analytical grade and were supplied by Merck (Darmstadt, Germany). All glassware was soaked in 4mol/L HNO_3 for minimum 12 hours and rinsed well with distilled water. Ultra-pure water was prepared by passing doubly de-ionized water from Milli-Q system (Millipore Simplicity 185 System incorporating dual UV filters (185 and 254 nm) to remove carbon contamination).

Multi-element stock solution containing 1.000 g/L of major elements was used to prepare intermediate multi-element standard solutions for ICP-OES measurements and multi-element stock solution containing 10 mg/L of each elements was used to prepare intermediate multi-element standard solutions for ICP-MS measurements.

ICP-MS rare earth multi-element standard (VHS, Manchester, UK) containing 10.0 mg/L of elements were used for determination of rare earth elements. REE calibration standards were prepared from multi-element standard solutions in 1.0% nitric acid. Internal standards were 6 Li, 45Sc, 115In, and 159Tb (VHG standards, Manchester, UK). Standard stock solutions were used to prepare calibration standard solutions after appropriate dilution with 1.0% v/v nitric acid.

Standard reference material SRM 1633C (NIST) was employed in order to check the accuracy and precision of instrumentation.

Table 1. Instrument operating conditions for deternination

Spectrometar	iCAP 6500 Thermo scientific
Nebulizer	Concentric
Spray chamber	Cyclonic
Radio frequency power (W)	1150
Principal argon flow rate (L/min)	12
Auxiliary argon flow rate (L/min)	0.5
Nebulizer flow rate (L/min)	0.5
Sample flow rate (ml/min)	1.0
Detector	CID86

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Selected wavelenghts (nm)	Fe (259.9); Ca (373.6); Mg (279.5); Pb (220.3) Zn (202.5); Cu (324.7); Cr (283.5); Mg (280.2) Ni (231.6); Sr (407.7); Mn (259.3); Li (670.7); In (230.6)

Table 2. and instrument operating conditions for determination

Rf power (W)	1548
Gas flows (L/min)	13.9: 1.09; 0.8
Acquisition time	3 x 50 s
Points per peak	3
Dwell time (ns)	10
Detector mode	Pulse
Replicates	3
Measured isotopes	^{59}Co, ^{75}As, ^{202}Hg

List of Rare earth elements
Sc La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu Y

Appendix – ICP/OES and ICP/MS analysis of Diapetra drinking spring water from feb 2014

ICP-MS	Uzorak voda (water sample)	
	Svetlija bocica (lighter vial)	Tamnija Bocica (darker vial)
Element	**µg/L**	**µg/L**
P	2.543	3.405
Sc	0.1498	0.1567
Ga	0.0098	0.0151
Se	0.0682	0.3100
Y	0.0110	0.0111
In	<DL	<DL
Ba	9.4784	9.6341
Pr	<DL	<DL
Ce	<DL	<DL
Eu	0.0023	0.0021
Sm	0.0061	0.0047
La	<DL	<DL
Th	<DL	<DL
Nd	<DL	<DL

Gd	<DL	<DL
Dy	<DL	<DL
Tb	<DL	<DL
Er	<DL	<DL
Ho	<DL	<DL
Tm	<DL	<DL
Yb	<DL	<DL
Lu	<DL	<DL
Tl	0.0050	0.0010
Rb	1.7843	1.7486
Pb	0.0157	0.0179
U	0.3840	0.3720
Ti	<DL	<DL
Mo	2.6486	1.783
Au	0.7370	0.2810
Hg	0.4540	0.3710
Be	0.0052	0.0046
Al	2.2427	2.1808
V	0.0624	0.0437
Cr	0.0391	0.0247
Mn	8.2327	7.9720
Fe	4.1692	3.7580
Co	<DL	<DL
Ni	<DL	<DL
Cu	<DL	<DL
Zn	<DL	<DL
As	0.4309	0.4573
Ag	<DL	<DL
Cd	<DL	<DL
Sb	0.0183	0.0131
Li	3.1990	3.2190
Bi	<DL	<DL
Sn	<DL	<DL
Ru	<DL	<DL
Pd	<DL	<DL
Pt	<DL	<DL
Zr	<DL	<DL
Ge	0.0580	<DL

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ICP-OES	Uzorak voda	
	Svetlija bocica (ligheter color vial)	Tamnija bocica (darker color vial)
Element	**µg/L**	**µg/L**
Ca	5611.00	5848.00
K	634.4	652.3
Mg	2536.00	2565.00
Na	69040.00	69490.00
Si	6885.00	6898.00
Sr	386.10	380.30
B	195.00	194.10

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