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Introduction of the Inductively coupled plasma (ICP–OES) method for the characterization of ”Guber” Srebrenica mineral waters

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Abstract

The mineral waters of ”Guber” Srebrenica are highly mineralized waters with a significant content of soluble iron. They belong to iron-sulfate waters, which are rich in arsenic and therefore also called iron-arsenic waters with low pH values. Some of the ”Guber” waters of Srebrenica were used for therapeutic purposes in the past. Spectrophotometric methods were used for their characterization. Today, instrumental methods are known which are faster and more efficient. This work focusses on using the Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) for the characterization of Guber Srebrenica mineral waters. Two standards were used to determine the elemental composition of these mineral waters, which differ in concentration and number of elements present. The results obtained by this method for soluble iron from different sources were compared with the spectrophotometric method of iron determination. The obtained results show that the lower iron concentrations in the samples obtained by the ICP method coincide with the results of the spectrophotometric method. However, with higher concentrations of iron (Očna voda), the deviations of the ICP method from the standard spectrophotometric method are greater and this may be the subject of further research. There are also discrepancies in the results between the standards for lead and arsenic, with higher values occurring in the samples where standards with a smaller number of present elements were used, which necessitates the use of standard methods.

Keywords: mineral waters, spectrophotometric methods, ICP-OES methods, soluble iron.

1. INTRODUCTION

Although planet Earth is abundant in water, only a small percentage is directly available to humans for personal consumption. This is because many surface and subsurface waters are polluted as a result of anthropogenic emissions. That is why considerable attention is now paid to the quality of drinking water, which is purified before consumption using very expensive techniques. High-quality pure water is also essential for aquatic life, industrial and agricultural use, recreation, etc. Water from certain natural sources, such as mineral water and hyperthermal water which usually comes from great depths, is pure enough to be utilized directly for drinking and other human purposes. Such high-quality and often therapeutic water is frequently bottled and sold as such. Dissolved gases, dissolved organic and inorganic chemicals, and solid suspended debris are all present in natural waters. Water temperature, contact with the atmosphere, the type of sediment it is in contact with, the amount of rainfall that enters surface waters, and the amount of waste materials that humans bring into water all influence the amount of dissolved and suspended substances in water (Prodovic 2012; Quattrini 2016).

Groundwater has recently become the subject of research in many scientific fields. Within hydrogeology, new scientific fields have been formed, ranging from hydro-geothermal energy to the exploitation of useful raw minerals from highly mineralized waters. Natural mineral water is categorized into four marketing groups based on the total quantity of dissolved mineral compounds (dry residue at 180 °C). The first group includes natural, extremely low mineral or light mineral water with a mineral salt content of less than 50 mg/L. The second group of water is low mineral content water, which has a mineral salt content of less than 500 mg/L. The third group includes medium mineral content water with a mineral salt content ranging from 500 to 1500 mg/L, while the fourth group includes high mineral content water with a mineral salt content greater than 1500 mg/L (Blagojević 2007; Quattrini 2016; Tautkus, Steponeniene, & Kazlauskas 2004).”Guber” Srebrenica mineral waters are classified as high mineral content iron-arsenic waters. The Srebrenica area is divided into two sections: the lower hilly area (200-500 m above sea level) and the middle hilly area (500-1000 m). As for the climate, this area belongs to the warmer region of the temperate continental belt, and the amount of precipitation is highest in the summer months. Tests have shown that the mechanical composition of the soil is loamy sand, which turns into sandy loam and loam as depth increases. The percentage of colloidal clay increases with depth. The environment is highly acidic. The terrain of Crni Guber was formed on dacite. Dacite belongs to the igneous group of rocks. These are common acidic to intermediate rocks with free quartz, with or without alkali feldspar, and intermediate plagioclase. The occurrence of high-quality mineral springs near Srebrenica is related to the varied geological structure and large amounts of non-ferrous metal ores: silver, lead, zinc and iron (Blagojević 2007).

The starting point of chemical classification methods is the chemical composition, primarily the SiO_2 content in the rocks. The mineral waters of ”Guber” Srebrenica are acidic waters with more than 66% SiO_2, and previous studies showed that this water contains over 75% SiO_2. The mineral waters of ”Guber” Srebrenica can be utilized in the treatment of anemia given the fact that they are classified as sulfate-iron arsenic waters and that the iron (II)-form is better absorbed in the intestines than the iron (III)-form (Quattrini 2016). Doctor Hans Duler was the first to mention the medicinal benefits of Srebrenica’s “Guber” waters in the early nineteenth century, and the first professional analysis of the water was performed by a Viennese chemist, dr. Ernest Ludwig. From 1886 to 1888, he examined the majority of Bosnia and Herzegovina’s mineral springs, which is around one hundred. He also analyzed five of 48 ”Guber” mineral springs and called them ”the pearl of all springs on Earth” and proposed their exploitation, which began in 1889. Until 1901, the Viennese company ”H. Matoni” filled and exported to the world 2 818 199 bottles (Quattrini 2016; Rosborg & Kozisek 2019). There are numerous therapeutic water springs in Srebrenica, including Kožna voda, Sinusna voda, Veliki (Crni) Guber, Očna voda, Ljepotica voda, Mali Guber, Novi izvor, and others. People suffering from inflammatory eye conditions can benefit from Očna voda. There are published records of people who have treated their sinuses and other skin ailments. ”Guber” waters have long been known as healing waters for many diseases, including hypochromic anemia (anemia caused by a large loss of iron), acute and chronic bleeding, insufficient iron resorption, gastric resection, gastric mucosal swelling, essential hypochromic anemia, chlorosis, increased iron consumption in pregnancy, infection, toxicosis, lack of appetite, general weakness, loss of body weight, exhaustion, and fatigue (Bezdrob 1999; Dorđievski, Krstić, Stanković, & Petrović 2014; Quattrini 2016; Rosborg & Kozisek 2019). For the characterization of these waters, it is very important to choose an adequate method for determining the content of iron and other components present in them, especially lead, arsenic, zinc, aluminum, manganese, and other elements that are present in insignificant amounts (Dalmacija, Bečelić, Ivančev-Tumbas, & Teodorović 2004; Hou & Jones 2000; Tripathi, Gupta, & Malik 2019).

In this work, Inductively Coupled Plasma—Optical Emission Spectrometry (ICP-OES) was used for the analysis of these elements. It is one of the most important analytical methods for the determination of trace elements in various samples. Gaseous and liquid samples are injected directly into the instrument. The liquid sample is pumped into the nebulizer using a peristaltic pump, where the solution is converted into an aerosol, which is injected through the inner tube. The spray chamber removes large drops, while small drops, which make up only 1-5% of the total solution, are carried by the nebulizer gas stream into the plasma torch, which supplies the plasma with a sample for analysis. However, solid samples require extraction or acid digestion, which converts the analyte into solution. The solution is transformed into an aerosol and introduced into the plasma source, where it evaporates and breaks down into atoms and ions. The plasma source is induced when an inert gas, usually argon, passes through an alternating electric field, which creates an inductively coupled coil (Chochorek, Bobrowski, Kiralyova, & Mocak 2010; Hou & Jones 2000). It is an emission spectrometric technique, which uses the fact that excited electrons emit energy of a certain wavelength when they return to the basic state. The light intensity of the selected wavelength is proportional to the concentration of the element in the analyzed sample (Grytskiv, Grytskiv, & Trofymchuk 2009; Stojanovic et al. 2014). The operational parameters of the ICP-OES analytical equipment must be optimized in order to achieve optimal performance. The following parameters influence the right wavelength selection of the elements to be determined: RF generator power, spray gas flow rate, plasma observation height, and sample introduction speed. ICP-OES has a good ability to identify a wide range of elements that cannot be identified or are extremely difficult to identify in low concentrations by Atomic Absorption Spectroscopy - AAS (B, P, S, W, U, Zr, La, V, Ti) (Stalović & Dorđević 2013; Durović et al. 2017). ICP-OES is a comparative analytical technique in which calibration curves with known amounts of components are generated (Ostojic, Lazic, & Zeljkovic 2022; Puspitasari, Herdini, & Fauziah 2018; Stalović & Dorđević 2013; Durović et al. 2017). There are two primary ways of calibration:

Calibration using internationally accepted and acknowledged standard reference materials (SRMs).

Calibration using synthetic standard solutions prepared in a matrix similar to the matrix of the unknown samples.

Each method has its advantages and disadvantages. The selection of appropriate SRMs for calibration depends on the expected concentration range of the unknown samples. A successful calibration can be performed with 5 SRM samples and a blank solution. Currently, the ICP-OES technique is used to determine almost all elements of the periodic table, with an adequate selection of burners, mixing chambers and optimization of working conditions (Mandal, Banjanin, Kujović, & Malenica 2015; Medenica & Malešev 2002; Durović et al. 2017). The absorption of precisely defined monochromatic radiation obtained by specific prisms or gratings is the basis of the spectrophotometric method (Jelić 2002; Štrkalj & Glavaš 2016). UV-VIS spectrophotometry involves the absorption of photons in the ultraviolet (UV) and visible (VIS) regions of the spectrum, which induces electron excitation. A qualitative and quantitative study can be performed using the obtained absorption spectra (Ahmed & Roy 2009; Sarenqiqige, Maeda, & Yoshimura 2014; Shahat, Elamin, & Abd El-Fattah 2021). The qualitative analysis is based on the fact that the absorption spectrum of a substance depends on its composition and structure. The Lambert-Beer law states that the absorbance of a solution is proportional to its concentration, the thickness of the solution layer through which the light flows, and the absorbance of the dissolved component (Alberti et al. 2019; Costo et al. 2018; Mandal et al. 2015; Miller & Miller 2018; Wang et al. 2022).

2. EXPERIMENTAL

For the experimental part, water from different springs of ”Guber” Srebrenica was used, namely: Kožna voda, Crni (Veliki) Guber, Ljepotica voda, Mali Guber, Novi izvor, Sinusna voda and Očna voda. Sampling was carried out with overflow, whereby an approximately four-fold volume change was made possible before taking the final sample. After sampling, 5 ml of conc. HNO_3 (p.a.). was added to the water samples in order to preserve them. In addition to HNO_3, Vitamin C (500 mg) was added to the water sample from the Crni Guber spring for the purpose of stabilization, and a non-preserved sample was also taken.

Water samples for laboratory analysis were prepared in different ways, i.e. with different dilution. For the spectrophotometric determination of iron, 25 mL of the tested water sample was transferred with a measuring pipette into a 1000 mL volumetric flask, the flask was topped up with distilled water up to the mark (dilution 1). 100 mL of such a solution was taken, the necessary reagents for the ortho-phenanthroline method were added, and a spectrophotometric measurement was performed. Due to the high concentrations of iron in the water from the springs Mali Guber, Novi izvor, Sinusna voda and Očna voda, another dilution was made, where 20 mL of the 1000 mL already diluted sample was taken (dilution 1), transferred to a 200 mL flask and made up with distilled with water to the mark (dilution 2).

Water samples from the springs Mali Guber, Novi izvor, Sinusna voda and Očna voda were prepared in the same way as for the spectrophotometric determination of iron. A volume of 25 mL of the sample was transferred to a 1000 mL volumetric flask and topped up with distilled water up to the mark. From the thus diluted sample, 20 mL was transferred to a 200 mL volumetric flask and topped up with distilled water up to the mark (dilution 2). The complete analysis of all parameters of Crni Guber mineral water was made from an undiluted sample and a diluted sample, which was prepared by transferring 5 mL of the water sample into a 200 mL volumetric flask and filling it up to the mark with distilled water.

For the ICP analysis, Standard 1 and Standard 2 were utilized to create calibration curves, with Standard 1 producing two calibration curves for the range of lower and higher values. For the spectrophotometric determination, a method based on the determination of iron with ortho-phenanthroline was used. This approach is one of the standard ways for determining the sanitary quality of drinking water (Čoha 1990). The color of the resulting complex was developed for 30 min. The samples were measured using a Shimadzu 1800 UV-VIS spectrophotometer at a wavelength of 510 nm. For the measurement, a 1 cm thick quartz cuvette was employed. The calibration curve was created by preparing solutions of different concentrations from the basic standard Fe_2O_3 solution, namely 0, 1, 2, 3, 4, 5, and 6 mg Fe_2O_3/L. A calibration curve was obtained with a correlation value of 0.9999. The results of sample measuring were converted to Fe content.

For ICP-OES analysis, MY152300001 Agilent Technologies 5100 ICP-OES was used, with the software version of 7.100.6821.61355 and firmware version 2994.

Imaging was done at various wavelengths depending on the element being identified. Other conditions under which the samples were measured included the following: Number of Replicates: 3, Pump Speed: 12 rpm, Read time: 5s, RF power: 1.2 kW, Stabilization time: 15 s, Viewing mode: radial, Viewing height: 8 mm, Nebulizer flow: 0.7 l/min and Plasma flow: 12 l/min. The basic standard solution of ICP multielement, with a concentration of 1000 mg/L (Standard 2), from Merck, Germany, was used to create the calibration curve; the solution contained Al, B, Ba, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb and Zn.

Solutions of the following concentrations were prepared from this standard solution: 0, 0.5, 1, 1.5, 2, 3, and 4 mg/L. A calibration curve with a correlation coefficient of 0.9999 was obtained for cadmium, cobalt, nickel and zinc, while for silver, the correlation coefficient was 0.9995, aluminum 0.9997, boron 0.9991, barium 0.9998, bismuth 0.9985, chromium 0.9998, copper 0.9997, lithium 0.9996, manganese 0.9997 and lead 0.9998.

A standard (Standard 1) was also used which contained the following concentrations of the elements: Mn (2500 mg/L); Zn (2500 mg/L); As (1000 mg/L): Co (1000 mg/L); Cr (1000 mg/L); Cu (1000 mg/L); Ni (1000 mg/L); Pb (1000 mg/L); Be (100 mg/L); Cd (100 mg/L). Two calibration curves were made from this solution. The first calibration curve (lower concentrations range) was made in the range of 0.1-2.0 mg/L for the elements present in the standard in concentrations of 2500 mg/L and 1000 mg/L, and for the elements present in the standard in a concentration of 100 mg/L, the calibration curve was in the concentration range of 0.1-0.8 mg/L. The second calibration curve (higher concentrations range) was made in the concentration range of 0.5-7.5 mg/L for the elements present in the standard at a concentration of 2500 mg/L, and for the elements present in the standard at a concentration of 100 mg/L, the calibration curve was in the range of 0.5-3.0 mg/L. In the first case, 1 mL of the stock solution was measured and transferred to a 100 mL flask. In the second case, 10 mL of the stock solution was measured, transferred to a 100 mL flask, and diluted to the mark with distilled water. For the first calibration curve, 1, 2, 4, 6 and 8 mL were taken from the first diluted basic standard solution, and for the second calibration curve, 0.5, 1, 1.5, 2, 2.5, 3, and 4 mL. The calibration curves (for higher concentrations range) had a correlation coefficient of 0.9999, except for lead, which was 0.9996 and zinc 0.9998. The calibration curves (for lower concentrations range) had a correlation coefficient of 0.9999, except for lead, which was 0.9973 and for cadmium 0.9995.

3. RESULTS AND DISCUSSION

In order to determine the composition of mineral waters ”Guber” Srebrenica by introducing a modern instrumental technique (ICP-OES), the standard spectrophotometric method was used as a comparative method. As stated earlier, standards (Standard 1 and Standard 2) were used for the analysis of water samples from the Crni Guber source, on the basis of which calibration curves were created for the range of lower and higher concentrations. Table 1 shows the results of the analysis, which were obtained based on the calibration curves of Standard 1.

From previous table, SCR is Calibration curve 1 for smaller concentration range (0.1–2 mg/L), HCR represents Calibration curve 2 for higher concentration range (0.5–7.5 mg/L), while 1, 2 and 3 represent unpreserved sample, sample preserved with HNO_3 and sample preserved with Vitamin C, respectively.

Complete analysis of Crni Guber mineral water samples was done from undiluted samples. Components present in very low concentrations were registered in both calibration curves within the limits of tolerance. Due to the high concentrations of dissolved iron, zinc, aluminum and other components present, which were outside the calibration curves, the mineral water was diluted (5 mL/200 mL). Components present in low concentrations were not registered in the same curves, because the samples were too diluted. Soluble iron, zinc and manganese were confirmed, as well as in the undiluted samples. Crni Guber water samples were also analyzed using the calibration curve of Standard 2, because some of the essential elements present in the water were not found in Standard 1 (Fe, Al, B, Ag, Bi, Be and Li). Unpreserved samples, preserved samples with HNO_3 and samples to which Vitamin C had been added were used for the analysis. Water samples were recorded on an ICP-OES instrument at appropriate wavelengths, depending on the element. The analysis of Crni Guber samples prepared with HNO_3 and Vitamin C was repeated after a few months from new samples. The contents of trace elements in Crni Guber water samples, which were obtained from undiluted samples, were within the limits of the analyses obtained using the calibration curves of Standard 1.

Table 2. shows the results of the analysis of water samples from the Crni Guber spring in relation to the calibration curve of Standard 2.

The results of the analyses of aluminum (Al) obtained were quite uniform. It can be concluded that they are in accordance with the values obtained in other test laboratories for the water of the Crni Guber spring (Table 2). The contents of manganese (Mn) and zinc (Zn) were within the expected limits by both standards, and they were also of the same order of magnitude as in other test

Table 1. Analysis of Crni Guber mineral water compared to the calibration curves of Standard 1.

Component (mg/L)	**Standard 1 (Sample dilution 5 mL/200 mL)**									
	HCR			**SMR**			**HCR**		**SCR**	
	1	2	3	1	2	3	2	3	2	3
As	3.36	3.55	3.56	3.43	3.61	3.63	3.99	4.03	-	-
Be	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	-
Cd	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	-	-
Co	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	-
Cr	n.d.	n.d.	n.d.	0,01	0,01	0,01	0,01	0,01	-	-
Cu	0.08	0.08	0.08	0.09	0.09	0.09	0.05	0.04	-	-
Mn	0.57	0.56	0.57	0.59	0.59	0.59	0.54	0.56	0.55	0.53
Ni	0.01	n.d.	n.d.	n.d.	0.01	0.01	0.02	n.d.	-	-
Pb	0.82	0.83	0.81	0.87	0.83	0.89	0.78	0.75	-	-
V	0.03	0.03	0.03	0.03	0.03	0.03	0.04	0.04	-	-
Zn	9.06	8.78	8.94	9.59	9.33	9.64	9.57	9.83	9.85	9.38

Table 2. Analysis of Crni Guber mineral water compared to the calibration curve of Standard 2.

Element(mg/L)	**Standard 2 (16.12.2021.)**						**Standard 2 (30.03.2022.)**			
	Undiluted sample			**Diluted sample (5 mL/200 mL)**			**Undiluted sample**		**Diluted sample (5 mL/200 mL)**	
	1	2	3	1	2	3	2	3	2	3
Ag	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Al	36.79	35.75	36.63	33.85	36.48	35.60	36.96	37.62	38.42	35.92
B	0.107	0.12	0.12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ba	0.0105	0.0105	0.0105	n.d.	n.d.	n.d.	0.01	0.01	n.d.	n.d.
Bi	0.0383	0.0128	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cd	0.0679	0.0679	0.0679	n.d.	n.d.	n.d.	0.067	0.066	n.d.	n.d.
Co	0.001	0.001	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	0.01	0.01	0.01	n.d.	n.d.	n.d.	0.0093	0.0093	n.d.	n.d.
Cu	0.0113	0.0113	0.0113	n.d.	n.d.	n.d.	0.046	0.055	n.d.	n.d.
Fe	117.72	115.91	118.35	121.4	122.7	121.4	121.21	122.64	121.58	123.17
Li	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mn	0.598	0.586	0.586	n.d.	n.d.	n.d.	0.56	0.58	n.d.	n.d.
Ni	0.023	0.011	0.023	n.d.	n.d.	n.d.	0.0189	0.0095	n.d.	n.d.
Pb	0.32	0.331	0.342	n.d.	n.d.	n.d.	0.385	0.395	n.d.	n.d.
Zn	9.34	9.01	9.24	9.05	9.05	9.05	9.47	9.81	10.4	10.8

Table 3. Comparative analysis of iron content in ”Guber” Srebrenica mineral waters obtained by spectrophotometric and ICP-OES methods.

SAMPLE	Spectrophotometric method Iron content (mg/L)						ICP-OES method Iron content (mg/L)		
	Number of measurement						Number of measurement		
	1	2	3	4	5	6	1	2	3
Kožna voda	50.73	50. 56	50.64	51.42	50.7	50.82	51.2	50.8	50.8
Ljepotica voda	87.37	87.10	87.24	86.9	87.01	87.15	85.6	76.8	86.0
Crni Guber	121.82	121 74	121.93	121.52	121.61	121.64	123.6	122.4	124.8
Mali Guber	32132	320.34	320.69	322.55	322.52	324.86	320.0	320.0	320.0
Novi izvor	586.1	587.60	587.81	584.39	584.66	584.63	580.0	576.0	568.0
Sinusna voda	587.06	587.06	587.81	584.4	584.66	584.63	588.0	584.0	572.0
Očna voda	1248.5	1247.1	1249.3	1228.2	1229.1	1230.1	1052.0	1044.0	1044.0

laboratories (Table 2). However, the content of arsenic (As) obtained on the basis of the calibration curve of Standard 1 was in the range of 3.3-4.0 mg/L, which is a higher value compared to the tests in some other testing laboratories. Toxic elements such as As, Hg, Pb, Sb and Sn are usually measured by atomic absorption spectrophotometry using the hydride technique. The ICP-OES instrument normally enables the hydride technique, but it was not used in these analyses, because the device on which the analysis was performed does not have that technique. In order to obtain more reliable results, it is necessary to check the analysis with a standard method and the hydride technique.

The content of lead (Pb) was determined on the basis of the calibration curve of Standard 1 and on the basis of the calibration curve of Standard 2. The results differed. The values obtained on the basis of the calibration curve of Standard 1 were twice higher than the values obtained on the basis of the calibration curve of Standard 2, which were closer to the analyses of other test laboratories. It is also necessary to verify the analysis using some standard method or the hydride technique (Table 1, Table 2). The content of iron (Fe) in the samples from Crni Guber source was determined by the ICP-OES method based on the calibration curve of Standard 2 from undiluted and diluted samples (5 mL/200 mL).

The results obtained from diluted samples are much more reliable, because they are within the calibration curve. The obtained results are within the limits of the analyses of other test laboratories. It is important to emphasize that iron was also determined by the standard spectrophotometric method from a diluted sample (25 mL/1000 mL). The results obtained by the spectrophotometric method coincide with the analyses obtained by the ICP-OES method and are within the limits of tolerance (Table 3).

The ICP-OES method was used to analyze samples from other springs as well: Kožna voda, Ljepotica, Mali Guber, Novi Izvor, Sinusna voda and Očna voda. Water samples with a significant amount of dissolved iron were diluted to match the sample concentration to the calibration curve. These samples were also analyzed by the standard spectrophotometric method from the same dilutions as the samples that were made by the ICP-OES method (25 mL/1000 mL), Kožna voda, Ljepotica and Veliki (Crni) Guber (50-130 mg/L Fe^{2+}). Due to the significant percentage of iron in the samples of Mali Guber, Novi izvor, Sinusna voda and Očna voda (300-1250 mg/L Fe^{2+}), the samples were additionally diluted (25 mL/1000 mL, then 20 mL/200 mL), because it was necessary adjust the sample to the calibration curves by both methods (Table 3).

Based on the results obtained for the samples from the springs Kožna voda, Ljepotica voda and Crni Guber, it can be concluded that the values of soluble iron obtained by both methods were within the limits of tolerance. However, with the increase in the concentration of soluble iron in the samples from Mali Guber, Novi izvor and Sinusna voda, slight differences between the spectrophotometric and ICP-OES methods appeared, which can be interpreted as excessive dilution of the samples. This was especially noted in the Očna voda sample, where a significant difference between the spectrophotometric and ICP-OES methods (Table 3) occurred. Too much dilution affected the differences in the analyses, and therefore it is necessary to adjust the calibration curve to the given concentration, so that the dilution is smaller and the concentration difference is reduced according to the mentioned methods.

For the ”Guber” Srebrenica mineral water springs, in addition to the iron content, the ICP-OES method determined the content of some other elements (Table 4). However, due to excessive dilution, the following elements were not registered: Ag, B, Ba, Bi, Cd, Co, Cr, Cu,

Table 4. Content of individual elements in samples from different sources determined by the ICP-OES method.

Sample	**ICP-OES method Content (mg/L)**				
	Al	Fe	Mn	Pb	Zn
Kožna voda	0.8	51.2	4.4	0.8	1.2
Ljepotica voda	8.4	86.4	3.2	0.8	2.4
Veliki (Crni) Guber	38.4	124.0	0.4	0.8	9.6
Mali Guber	200.0	320.0	8.0	4.0	16.0
Novi izvor	48.0	580.0	24.0	8.0	8.0
Sinusna voda	48.0	588.0	24.0	8.0	8.0
Očna voda	196.0	1060.0	n.d.	12.0	4.0

Table 5. Statistical analysis of the results obtained by the spectrophotometric method for samples from various sources.

Sample	**Spectrophotometric method Iron content (mg/L)**						**Mean value**	**Dispersion**	**Standard deviation**
	Number of measurements								
	1	2	3	4	5	6			
Kožna voda	50.73	50.56	50.64	51.42	50.7	50.82	50.81	0.0803	0.2835
Ljepotica voda	87.37	87.10	87.24	86.9	87.01	87.15	87.13	0.0230	0.1518
Crni Guber	121.82	121.74	121.93	121.52	121.61	121.64	121.71	0.0187	0.1369
Mali Guber	321.32	320.34	320.69	322.55	322.52	324.86	322.05	2.2789	1.5096
Novi izvor	586.10	587.60	587.81	584.39	584.66	584.63	585.86	2.0002	1.4143
Sinusna voda	587.06	587.06	587.81	584.40	584.66	584.63	585.94	1.9553	1.3983
Očna voda	1248.5	1247.1	1249.3	1228.2	1229.1	1230.1	1238.7	92.6110	9.6235

Li, and Ni. These parameters should be done from undiluted solutions, as was done for Crni Guber water.

The statistical analysis of the spectrophotometric method results (Table 5) indicated that at high dilutions, inadequately reliable results are obtained for water samples with a high iron content. For such samples, it is required to raise the concentration while producing the calibration curve of the standard, so that there is less dilution during the determination, and therefore a smaller determination error.

4. CONCLUSION

Because of the low percentage of micro components in the water from the Crni Guber spring, better results were achieved using the calibration curve of Standard 1 for a range of lower concentrations than using Standard 2. As a result, components present in trace levels, such as Be, Co, Cr, Cu, B, Bi, Cd, Ni, and V, must be examined by the ICP-OES method from undiluted samples.

Pb and As analyses cannot be considered authoritative because different results were obtained according to Standards 1 and 2, and it is required to cross-check them with a standard method and the hydride technique of the ICP-OES method or the hydride technique of the atomic-absorption spectrophotometric method.

The Zn and Mn analyses obtained using the ICP-OES method for water samples from the Crni Guber spring compared to both standards are regarded accurate, whereas the Al analysis obtained based on Standard 2 is within other test laboratories tolerance limits.

The soluble iron concentration of various Srebrenica water sources ”Guber” was evaluated using the spectrophotometric method and the ICP-OES method. Except for the results obtained for the sample from the Očna voda springs, where the iron concentration was above 1000 mg/L, the analysis results obtained by both methods are within the limits of tolerance. Over-dilution can be argued to have raised the concentration difference in both procedures. The calibration curve must be adjusted to the sample concentration so that there is less dilution and variation in the results.

Statistical analysis of the spectrophotometric method results revealed that in the samples with a higher content of iron, due to excessive dilution, a bigger standard deviation occurs, implying that the analysis results produced by both methods cannot be taken into consideration.

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