DETERMINATION OF IRON CONTENT IN NATURAL MINERAL WATER: COMPARISON OF ICP-OES AND SPECTROPHOTOMETRIC METHOD

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Abstract: Crni Guber natural mineral water belongs to a group of highly mineralized iron-arsenic waters, which can be used for therapeutic purposes. In order to determine a more precise and accurate method for determining iron content, a comparison of ICP-OES and spectrophotometric method was performed. For the purposes of analysis using the ICP-OES method water samples were prepared with identical and different dilutions compared to the samples for the analysis performed using the spectrophotometric method. The G-test was used to check for the existence of outlier values in the obtained results, while the precision and accuracy of the method were verified by using the F-test and t-test. The aforementioned tests showed that the spectrophotometric method was more precise and accurate when the samples were prepared with identical dilution. When analyzing samples with different dilutions, the spectrophotometric method proved to be more precise, while in terms of accuracy there was no statistically significant difference between the methods.

Keywords: ICP-OES method, spectrophotometric method, iron, natural mineral water.

1. INTRODUCTION

There is a large number of medicinal waters present in nature and they can be classified according to different criteria, but for practical use in the area of healthcare the most useful classifications are the ones based on chemical composition.

According to the content of specific components, medicinal mineral waters are divided into eight different groups, and one of those groups concerns iron-rich, arsenic waters and waters with elevated contents of manganese, aluminum, copper, zinc and other elements. The medicinal properties of this group of waters are determined by the presence of iron, arsenic and other metals. Ferrous waters occur in nature as low-mineralized waters, with a relatively low iron content, and as highly mineralized ferrous-sulfate (ore mine) waters, with mineralization of up to 80 g/L. According to the basic chem-ical composition, they can be sulfate or hydrogen carbonate waters [1]. Sulfate-iron waters are highly concentrated and rich in arsenic. These waters have a very low pH value due to the presence of sulfuric and phosphoric acid. Hydrogen carbonate-iron waters are poor in arsenic and have a pH value of around 6 [2]. Sulfate-ferrous arsenic waters are used in the treatment of anemia, because the iron (II)-form is better absorbed in the intestines than the iron (III)-form. They also contain trace elements (copper and cobalt) that have a positive effect on health [3].

Since Crni Guber water belongs to the group of highly mineralized sulfate-iron-arsenic waters and can be used for therapeutic purposes, it is extremely important to select an adequate method that will enable determination of the iron content with acceptable levels of accuracy and precision. For this purpose, the precision and accuracy of ICP-OES, as a newer

method, was tested in relation to the standard spectrophotometric method.

The determination of iron in water is carried out by different methods: flame atomic absorption spectroscopy [4], spectrophotometrically: using 8-hydroxyquinoline [5], as a thiocyanate complex [6], colorimetrically with O-phenanthroline [7], using an LED spectrophotometer [8].

Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES) is one of the most powerful and popular analytical methods for the determination of trace elements in various types of samples. Gaseous and liquid samples can be directly injected into the instrument, while solid samples require extraction or acid digestion to convert the analyte into a solution. The solution is converted into an aerosol and introduced to the source of the plasma, where it evaporates and breaks down into atoms and ions. The source of the plasma is induced when an inert gas, most often argon, passes through an alternating electric field that creates an inductively coupled coil [9]. This is an emission spectrometric technique that takes advantage of the fact that excited electrons emit energy of a certain wavelength when they return to the ground state. The light intensity of the selected wavelength is proportional to the concentration of the element in questionin the analyzed sample. ICP-OES is a fast and highly sensitive multi-element technique that can be used for different types of samples: metals, archaeological, biological, medical samples, as well as samples from the environment [10].

There are numerous examples of ICP-OES application, including: determination of Fe, Co, Mn, Cu, Pb and Zn in ores [11], selected metals in surface waters [12], determination of steel composition [13], analysis of metallurgical samples [14], multielement analysis of apple peel [15], detection of heavy metals in biological material [17], analysis of hazardous waste [17], determination of silicon dioxide in bauxite [18], determination of mercury in freshwater fish [19], determination of trace elements in human breastmilk and baby formulas [20].

Spectrophotometry is a method that studies the absorption of precisely defined monochromatic radiation obtained by special prisms or grids. In UV-VIS spectrophotometry, the absorption of radiation takes place in the ultraviolet (UV) and visible (VIS) regions of the spectrum and causes the excitation of an electron. Based on the obtained absorption spectrum, qualitative and quantitative analysis can be performed [21]. Qualitative analysis is based on the fact that the absorption spectrum of a substance depends on its composition and structure. Quantitative analysis is based on the Lambert-Beer law, according to which the absorbance of a solution is proportional to its concentration, the thickness of the solution layer through which light passes, and the absorptivity of the dissolved substance [22].

This technique is well known and widely used in chemical and industrial laboratories. Some of the applications are: determination of Fe (II) in aqueous solutions [23], determination of Fe (III) in water and pharmaceutical samples [24], determination of traces of iron in boiler water [25], determination of free Fe (III) in samples from environmental and biological samples [26], determination of total Fe in green tea [27].

As comparative methods, ICP-OES and the spectrophotometric method with ortho-phenanthroline were used for the determination of iron in water obtained from oil fields [28], as well as for the determination of iron content in suspensions of iron oxide nanoparticles [29].

2. EXPERIMENTAL PART

For the experimental part, water from the Crni Guber source was used. Sampling was carried out with overflow, whereby an approximately fourfold volume change was made possible before taking the final sample of 1 L. After sampling, for the purpose of preservation, 5 mL conc. HNO_3 (p.a.)was added to the water sample.

Water samples for laboratory analysis are prepared in different ways, i.e. with different dilution. For spectrophotometric determination, 50 mL of the tested water sample was transferred to a 2000 mL measuring flask with a measuring pipette, and the flask was topped up with distilled water up to the mark. From this, 100 mL was taken for spectrophotometric determination (dilution 1), the necessary reagents for the ortho-phenanthroline method were added, and measurements were made on 15 such samples.

For ICP-OES analysis, 50 mL of the tested water sample was also measured, transferred to a 2000 mL volumetric flask and topped up with distilled water up to the mark. 100 mL of the prepared sample was taken for analysis. Measurements were made on 15 such samples.

After that, the samples for ICP-OES analysis were prepared in a different manner. 50 mL of the tested water sample was measured in a 1000 mL

measuring flask and topped up with distilled water up to the mark. 50 mL of the thus diluted sample was measured, transferred to a 100 mL measuring flask and topped up with distilled water up to the mark (dilution 2). 15 such samples were prepared and ICP-OES analysis was performed.

A method based on the determination of iron with ortho-phenanthroline was used for spectrophotometric determination. This method belongs to the group of standard methods for testing the hygienic correctness of drinking water [30]. The color of the resulting complex was developed for 30 min. The samples were recorded on a Shimadzu UV-VIS 1800 spectrophotometer at a wavelength of 510 nm. A 1 cm thick quartz cuvette was used for the measurement. For the purpose of making a linear calibration chart, solutions of the following concentrations were prepared from the basic Fe_2O_3 standard solution: 0, 1, 2, 3, 4, 5 and 6 mg Fe_2O_3/L. A calibration curve with a correlation coefficient of 0.9999 was obtained. The results obtained by recording water samples were re-calculated based on Fe content.

For ICP-OES analysis, MY152300001 Agilient Technologies 5100 ICP-OES was used, with software version 7.100.6821.61355 and firmware version 2994. Recording was performed at a wavelength of 259.94 nm. Other conditions under which the samples were recorded were: 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 ICP multielement solution, concentration 1000 mg/L, manufactured by Merck, Germany, was used to create the linear calibration graph, which contains: Al, B, Ba, Bi, Cd, Co, Cr, Cu, Fe, Li, Mn , Ni, Pb and Zn. Solutions of the following concentrations were prepared from this solution: 0, 0.5, 1, 1.5, 2, 3, and 4 mg/L. A calibration curve with a correlation coefficient of 0.99992 was obtained.

The verification of the obtained measurement results was performed using statistical tests [31]. The examination of the existence of an outlier was performed using the Grubbs G-test, according to formulae (1) and (2):

$$G_1 = \frac{x_{max} - \overline{x}}{s} \tag{1}$$

$$G_2 = \frac{\overline{x} - x_{min}}{s} \tag{2}$$

where:
x_{min} − minimum value in a series of measurements,
x_{max} − maximum value in a series of measurements,
$\overline{x}$ − mean value of the results of measurements,
s − standard deviation.

To check the precision of the obtained results, the F-test was used, which is calculated according to formula (3):

$$F = \frac{S_1^{\,2}}{S_2^{\,2}} \qquad v_1 = n_1 - 1 \qquad v_2 = n_2 - 1 \tag{3}$$

where:
s_1^2, s_2^2 − method variances,
v_1, v_2 − degrees of freedom,
n_1, n_2 − number of measurements in the series.

The t-test was used to test the accuracy of the obtained results. When the standard deviations of the two methods do not differ significantly, formulae (4) and (5) are used for calculation:

$$s = \frac{(n_1 - 1)s_1^{\,2} + (n_2 - 1)s_2^{\,2}}{(n_1 + n_2 - 2)} \tag{4}$$

$$t = \frac{\overline{x}_1 - \overline{x}_2}{s\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}} \tag{5}$$

s – estimated standard deviation.
n_1+n_2-2 – number of degrees of freedom

In case of existence of a significant difference between the standard deviations of the methods, the t-test is calculated based on formulae (6) and (7):

$$t = \frac{\overline{x}_1 - \overline{x}_2}{\sqrt{\left(\frac{s_1^{\,2}}{n_1} + \frac{s_2^{\,2}}{n_2}\right)}} \tag{6}$$

$$v = \frac{\left(\frac{s_1^{\,2}}{n_1} + \frac{s_2^{\,2}}{n_2}\right)^2}{\left(\frac{s_1^{\,4}}{n_1^{\,2}(n_1 - 1)} + \frac{s_2^{\,4}}{n_2^{\,2}(n_2 - 1)}\right)} \tag{7}$$

3. RESULTS AND DISCUSSION

Table 1 presents the results of determining the iron content by using the spectrophotometric method, and Table 2 shows the results obtained by using the ICP-OES method, for samples that were prepared in different ways (dilution 1 and dilution 2).

Table 1.Iron content determined by the spectrophotometric method in samples with dilution 1

Sample	Dilution 1
	Fe content (mg/L)
1	121.4855
2	121.3568
3	121.3747
4	121.6412
5	122.6171
6	120.7252
7	121.3718
8	121.5214
9	121.2760
10	120.7162
11	120.5964
12	120.6024
13	119.3212
14	119.2583
15	119.1925
Min	119.1925
Max	122.6171
$\bar{x}$	120.8704
s	0.976867

Table 2. Iron content determined by the ICP-OES method in samples with dilution 1 and dilution 2

Sample	Dilution 1	Dilution 2
	Fe content (mg/L)	Fe content (mg/L)
1	121.2145	122.4348
2	122.0254	121.2146
3	120.4039	119.5958
4	120.3896	123.5474
5	122.8000	124.4000
6	123.6066	125.6132
7	121.9803	118.8120
8	120.7974	118.0159
9	122.0000	119.2000
10	126.0389	123.4490
11	124.7440	123.0174
12	127.3338	123.4490
13	125.8895	120.4554
14	128.6066	120.4554
15	127.2480	121.8140
Min	120.3896	118.0159
Max	128.6066	125.6132
$\bar{x}$	123.6719	121.6983
s	2.765943	2.241602

The obtained results of the G-test are shown in Table 3.

Table 3. G-test values

Method	Dilution	G-test (calculated values)	
SPECTROPHOTOMETRY	Dilution 1	$G_1=1.79$	$G_2=1.72$
ICP-OES	Dilution 1	$G_1=1.78$	$G_2=1.19$
	Dilution 2	$G_1=1.75$	$G_2=1.33$

The critical value for n=15, at $\alpha=0.05$ is $G_{0.05;15}=2.41$. As the calculated values of the G-test for both methods and different dilutions are below the critical value, $G_{calc.}<G_{crit.}$, it can be concluded, with the risk of 5%, that there are no outliers in the performed measurements, and therefore suspicious values were not rejected.

To check the precision, for the samples that were prepared in the same manner (dilution 1), an F-test according to formula (3) was performed, whereby the null hypothesis that the variances of the spectrophotometric and ICP-OES methods are equal was tested. The value F=8.02 was obtained.

The critical value of the one-way F-test at $\alpha=0.05$, $\nu_1=14$, $\nu_2=14$ is $F_{0.05;14,14}=2.49$. The calculated value is greater than the critical value, which means that the difference between the variances of these two methods is significant and, with the risk of 5%, the null hypothesis of equality of variances can be rejected. The variance of the ICP-OES method is greater than the variance of the spectrophotometric method, based on which it can be concluded that the spectrophotometric method is more precise.

The critical value of the two-way F-test at $\alpha=0.05$, $\nu_1=14$, $\nu_2=14$ is $F_{0.05;14,14}=3.12$. The calculated value of the F-test is greater than this critical value, which means that the standard deviations of the two methods differ significantly. In this case, to test the accuracy of the ICP-OES method, the hypothesis about the equality of the arithmetic means of the two methods was tested, using the t-test according to formulae (6) and (7). The values $t=3.699$ and $\nu=30.40$ were obtained.

The critical value at $\alpha=0.05$, $\nu=30$ is $|t| = 2.262$. Since $|t| > |t|_{crit.}$, then, with the risk of 5%, the hypothesis of equality of the arithmetic means of the two methods is rejected. It can be concluded that the ICP-OES method, with samples prepared with the same dilution, does not give the same mean value as the spectrophotometric method, i.e. it shows a systematic error.

After that, precision and accuracy verification was performed for the samples that were prepared with a different dilution (dilution 2).

In this case too, the null hypothesis about the equality of variances of the spectrophotometric and ICP-OES methods was tested. The value of $F=5.27$ was obtained.

The critical value of the one-way F-test at $\alpha=0.05$ $\nu_1=14$, $\nu_2=14$, is $F_{0.05;14,14}=2.49$. The calculated value is greater than the critical value, $F_{0.05;14,14}=2.49$, which means that even here, with a risk of 5%, the null hypothesis can be rejected and it can be concluded that there is a significant difference in the precision of the methods. The variance of the ICP-OES method is greater than the variance of the spectrophotometric method, based on which it can be concluded that the spectrophotometric method proved to be more precise in this case as well.

For a two-way F-test at $\alpha=0.05$, $\nu_1=14$, $\nu_2=14$, the critical value is $F_{0.05;14,14}=3.12$. The calculated value of the F-test is greater than the critical value of the two-way F-test, $F_{calc.}>F_{crit.}$, which means that the

standard deviations of the two methods differ significantly, so the accuracy check with the t-test is calculated in the same way. The following values were obtained: $t=1.311$ and $\nu=47.99$.

The critical value at $\alpha=0.05$, $\nu=48$ is $|t|=2.013$. As in this case $|t| < |t|_{crit.}$, one can accept the hypothesis of the equality of the arithmetic means of the two methods and conclude, with the risk of 5%, that the ICP-OES method does not show a systematic error when the samples are prepared with a different dilution, i.e. in terms of accuracy there is no significant difference between the two methods.

In previous research as well, the spectrophotometric method of determining iron with ortho-phenanthroline was used as a reference method against which the results obtained by the ICP-OES method were compared.

Thus, Wang et al. in their work [28] presented the results obtained by determining the iron content in water obtained from oil and gas fields. After eliminating the influence of individual cations on the determination of iron content (using the matching matrix method), the prepared samples were analyzed using ICP-OES and spectrophotometric methods. The relative error of the ICP-OES method compared to the spectrophotometric method of determining iron with ortho-phenanthroline was <5%, which showed that there was no significant difference between the methods. The accuracy of the method was checked by determining the iron yield (recovery) in the spiked samples, while the precision of the method was assessed based on the degree of dispersion of the results, i.e. based on the relative standard deviation (RSD). The recovery value ranged from 95%-105%, on the basis of which it was concluded that the ICP-OES method was accurate. The RSD value was <4%, which shows the high degree of precision of the results.

The importance of sample preparation in iron determination was pointed out by Costo et al. in their work [29]. In order to increase the reliability of determination of iron concentration in iron oxide nanoparticle suspensions, special attention was paid to sample preparation. The processes of digestion and dilution proved to be the most important steps for the determination of iron using the ICP-OES method and the spectrophotometric method with ortho-phenanthroline. Parallel trials were conducted in two separate institutions. The samples were prepared according to the established procedure in both institu-

tions, and then the ICP-OES analysis was performed in one institution, and the spectrophotometric analysis in the other institution. The agreement in the results between the two methods was greater when the samples were prepared and analyzed in the same institution, and in that case the uncertainty of the iron concentration measurement was on average 1.5% for both methods.

Although in the aforementioned research the results were not processed in the same manner as in this work, the observations are identical, the ICP-OES method can be considered accurate for determining the iron content, but depending the appropriate preparation of the sample, because it has been shown that this is a key step that affects the final result of the analysis.

4. CONCLUSION

The experimentally obtained results during the determination of iron content in water samples using ICP-OES and spectrophotometric methods were verified by using the G-test. The obtained values of this test were below the critical value, and therefore, with the risk of 5%, it was concluded that there were no outlier values. Precision was verified using the F-test. For samples that were prepared in identical manner, with identical dilution, F-test values were obtained based on which the null hypothesis of equality of variances was rejected with the risk of 5%. The variance of the ICP-OES method is greater than the variance of the spectrophotometric method, so it can be concluded that the spectrophotometric method is more precise. The difference in the precision of the methods was also shown in the samples that were prepared for measurement by the ICP-OES method with different dilutions compared to the samples analyzed by the spectrophotometric method. Here too, the null hypothesis of equality of variances was rejected with the risk of 5%. The spectrophotometric method proved to be more precise. Accuracy was verified by using the t-test. In the first case, with samples with identical dilution, the calculated value of the t-test was above the critical value, so the null hypothesis about the equality of the arithmetic means of the two methods was rejected with a risk of 5%. ICP-OES does not give the same mean value as the spectrophotometric method, i.e. it shows a systematic error. In the second case, with samples prepared for the two methods with different

dilutions, the value of the t-test was below the critical value, so the null hypothesis of equality of arithmetic means was accepted with the risk of 5%.

Based on the presented results, it can be concluded that for determining the iron content in Crni Guber natural mineral water samples, the ICP-OES method proved to be less precise than the spectrophotometric method, regardless of whether the samples for analysis using this method were prepared with identical or different dilution in relation to the samples for spectrophotometric analysis. However, the difference in sample preparation has a significant impact on accuracy. The two methods differ significantly in accuracy when dealing with samples with identical dilution, and in this case the ICP-OES method exhibits a systematic error. When the samples for measurement by the ICP-OES method are prepared with a different dilution, there is no statistically significant difference in accuracy compared to the spectrophotometric method. This means that the ICP-OES method can be considered accurate for the determination of iron content, but special attention must be paid to sample preparation, as it has been shown to be a key step that affects the final result of the analysis.

5. LITERATURE

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ОДРЕЂИВАЊЕ САДРЖАЈА ГВОЖЂА У ПРИРОДНОЈ МИНЕРАЛНОЈ ВОДИ: ПОРЕЂЕЊЕ ICP-OES И СПЕКТРОФОТОМЕТРИЈСКЕ МЕТОДЕ

Сажетак: Природна минерална вода Црни Губер спада у високоминерализоване гвожђевито-арсенске воде, која се може користити у терапеутске сврхе. У сврху одређивања прецизније и тачније методе за одређивање гвожђа, извршено је поређење ICP-OES и спектрофотометријске методе. За анализу ICP-OES методом, узорци воде су припремани са истим и са различитим разрјеђењем у односу на узорке за анализу спектрофотометријском методом. За провјеру постојања outlier вриједности добијених резултата кориштен је G-тест, а провјера прецизности и тачности методе извршена је употребом F-теста и t-теста. Наведени тестови су показали да се прецизнијом и тачнијом показала спектрофотометријска метода када су узорци припремани са истим разрјеђењем. Код анализе узорака са различитим разрјеђењем, прецизнијом се показала спектрофотометријска метода, док у погледу тачности није било статитистички значајне разлике између метода.

Кључне ријечи: ICP-OES метода, спектрофотометријска метода, гвожђе, природна минерална вода.