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DETERMINATION OF THE CONTENT OF MINERAL SUBSTANCES APPLYING DIFFERENT METHODS OF CHEMICAL ANALYSIS

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Abstract: In the course of this study, we have determined the content of mineral matter of calcium, chlorides, sodium and potassium, by means of volumetric and instrumental analysis methods in infusion solutions. Infusion solutions that we used for analysis were purchased commercially in pharmacies in the Republic of Srpska. We have used volumetric methods, complexometry to determine calcium and Mohr method to determine chloride. Sodium and potassium were determined instrumentally, by flame photometry. Calcium was also determined by this method. The aim of the study was to demonstrate that the concentration of the aforementioned elements in infusion solutions corresponds to concentrations indicated on the label. Obtained results for content of sodium and chlorides do not deviate for more than allowed $\pm 5\%$, in all three samples. Deviations occurred when content of calcium and potassium, was determined by flame photometry.

Keywords: Calcium, Chlorides, Sodium, Potassium, Infusion solutions, Complexometry, Mohr method, Flame photometry.

Introduction

Effects of mineral substances on the properties of food and their effects on human body are complex. Many mineral elements are an important component of enzyme, therefore have influence on various physiological processes and they are needed for growth and maintenance of bones and tissues. Some of minerals are needed for the maintenance of a human body and play an important role in the functioning of bodily fluids. Among all mineral substances only 17 of them are the essential components of food. Carbon, oxygen, hydrogen, and nitrogen grade tissues. Eight macro elements (calcium, phosphorus, sodium, potassium, chlorine, sulfur, magnesium and silicon) and 9 of trace elements (iron, zinc, copper, cobalt, iodine, manganese, chromium, molybdenum and selenium) also are essential elements (Grujić et al. 2014).

The presence of different mineral substances in food is analyzed using a large number of analytical methods. Determination of content of different metals is conducted for various purposes: determining the nutritional value of foods, toxicological safety assessment of foods, assessment of the degree to satisfy the applicable regulations and/or quality assurance of food products. In addition, based on the mineral composition, the authenticity of and/or geographical origin of the analyzed products can be determined (Murphy, 2002; Berg and Licht, 2002).

The content of some mineral substances in food is different and is determined by applying chemicals, photometric, ion - selective and spectroscopic methods (Grujić et al. 2007).

Volumetric methods are quantitative methods of chemical analyzes based on determination of known concentrations of the volume of reagent required for complete reaction with the test substance (Rajković et al., 2000). Volumetric methods are among the most important methods of quantitative chemical analysis.

They are generally fast, they do not require complicated equipment, they are simple to perform and enable the determination of a large number of different substances in a wide range of concentration (Vindakijević and Sladojević, 2005). Titrimetric determination is regulated by the Yugoslavian Pharmacopoeia (Jugoslovenska Farmakopeja) IV (Ph.jug.IV).

Instrumental methods of analysis are used to conduct measurements of physical properties of a substance to determine its chemical composition. In recent years, instrumental methods in analytical determinations have been increasingly applied, since almost every physical property of an element or compound can serve as the basis for the development of instrumental methods. Analysts apply the instrumental method of determining to achieve a savings in time, in order to avoid chemical separation in or to achieve greater accuracy during operation and analyze very small amounts of sample. There are, of course, other reasons with more or less specific nature for individual instrumental methods.

Saving of time comes to the fore during routine analysis or in cases when it is necessary to conduct a large number of uniform determination. Instrumental methods applied in these cases usually require standardized or calibration procedures to determine the relationship between the measured values of the physical properties and chemical composition of the test substance. In certain cases, this relationship can be obtained from tables or literature, otherwise it must be determined experimentally. So, when it comes to just a few samples to be analyzed, less time is lost if classical chemical analysis are applied, such as gravimetric or volumetric methods. However, in routine work, the time required for the initial standardization is negligible to the saving that can be achieved in a further embodiment of a large number of analyzes by some instrumental methods.

In classical analytical procedures it often happens that the presence of one or more elements (substances) interfere with the detection or determination of another element. In such cases it is necessary to pre-dry separation of one element from another, which requires appropriate and effective methods, use of time, with the constant presence of danger to increase the possibility of errors in the determination. On the other hand, a number of instrumental methods, according to their nature, is specific for some substances to be determined, so the need for chemical separation is eliminated.

The accuracy of the instrumental methods of analysis is typically less than the accuracy that is achieved by analytical techniques when the concentration of the test substances is greater than 1%. However, the fact that in physical measurements, constant relative error is maintained (rather than absolute) allows increased accuracy in the determination of small amounts of test substances (under 1%). It should be noted that accuracy, which is achieved by an instrumental method depends on the accuracy with which a conventional chemical analysis can be accomplished, so called wet process. Therefore, improvement of classical methods of analysis at the same time represents the improvement of accuracy of instrumental methods.

There are several different instrumental methods such as separation method, optical analysis methods, electroanalytical methods, radioisotope methods and manometric methods (Marjanović and Krstić, 1998).

Flame photometry is one of the many simple and applied techniques for quantitative analysis of elements whose atoms can be excited by the energy of flame and in returning from the excited to the ground state they emit electromagnetic radiation in the range of wavelengths from 200 to 850 nm. Due to easy excitation and wavelength of visible light, it is usually used for the determination of alkali and alkaline earth metals (Li, Na, K, Ca, Sr, Ba) (Marjanović and Krstić, 1998).

Materials and Methods

The samples that were used in determining Ca, Cl, Na and K in the infusion solutions were bought in a pharmacy in the Republic of Srpska.

Sample 1. Sodium chloride infundibile-solution for infusion

1000.00 ml solution contains: Sodium chloride 9.0000g, Na⁺ 154.0000 mmol/l, Cl⁻ 154.0000 mmol/l

Excipients: hydrochloric acid, concentrated, sodium hydroxide, water for injection.

Manufacturer and marketing authorization holder: Hemofarm limited partnership, Banja Luka, Bosnia and Herzegovina

Serial number: A402896; Date of manufacture: November, 2014; Shelf life: November, 2017.

Sample 2. Hartmann's solution-solution for infusion

1000.00 ml of solution contains: Sodium chloride 6.0200 g, Potassium chloride 0.3730 g, Calcium chloride 0.2940 g, Sodium Lactate 6.2760 g, Water for injections up to 1000.00 ml

Na⁺ 131.0000 mmol/l, K⁺ 5.0000 mmol/l, Ca²⁺ 2.0000 mmol/l, Cl⁻ 112.0000 mmol/l, Lactate³⁺ 28.0000 mmol/l

Excipients: hydrochloric acid, concentrated, water for injections.

Manufacturer and marketing authorization holder: Hemofarm- limited partnership, Banja Luka, Bosnia and Herzegovina

Serial number: A402361; Date of manufacture: September, 2014; Shelf life: September, 2017.

Sample 3. Sodium Chloride infundibile compositum (Ringer's solution) - solution for infusion

1000.00 ml of solution contains: Sodium chloride 8.6000g, Calcium Chloride 0.3300g, Potassium chloride 0.3000g, Na⁺ 147.0000 mmol/l, K⁺ 4.0000 mmol/l, Ca²⁺ 2.2500 mmol/l, Cl⁻ 155.6000 mmol/l

Excipients: hydrochloric acid, concentrated, sodium hydroxide, Water for injection.

Manufacturer and marketing authorization holder: Hemofarm - limited partnership, Banja Luka, Bosnia and Herzegovina

Serial number: A403139; Date of manufacture: December, 2014; Shelf life: December, 2017.

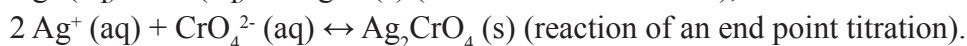
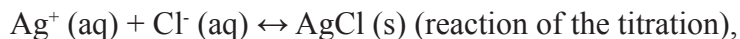


Figure 1. The analyzed infusion solutions - Ringer's solution, Sodium Chloride infundibile and Hartmann's solution

Determination of calcium and chlorine in infusion solutions were conducted by volumetric methods of analysis. Complexometric method was used to determine calcium while chlorides were determined by depositional volumetric, Mohr method. Contents of sodium and potassium were determined by using instrumental methods with the help of a flame photometer. Calcium content was also determined by instrumental methods of analysis.

For complexometric determination of calcium, murexide was used as an indicator. The sensitivity of the reaction is high, so even concentration of the order of 10^{-5} mol/l can be determined. Titration with murexide is conducted in strongly alkaline medium, at pH = 11-13, EDTA solution, with concentration of 0.0010 mol/l is used. Change of the color of the indicator from red-purple to blue-violet is easy to perceive. In sufficiently alkaline medium color transition is not sharp, and too alkaline medium gives too low results (Rajković et al. 2000). Complexometric titration was performed on the samples 2 and 3.

Titration of chlorides is performed by standard solution of silver nitrate, and soluble chromate salts are used as an indicator. When the deposition of chloride is complete, the first excess silver ions react with chromate ions, building a reddish precipitate of silver chromate:



Determination of the final point at Mohr method is based on the construction of another precipitate of characteristic color (Rajković et al. 2000). In all three samples, chlorides were determined by Mohr method.

On the flame photometer, the content of Na^+ in all three samples, as well as the content of Ca^{2+} and K^+ in samples 2 and 3. All samples were diluted before measurements on flame photometer. An analysis were conducted on the flame photometer SOLAR S4, Thermo Electron Corporation.

Results and discussion

During the experimental determination of calcium, chloride, sodium and potassium in the infusion solutions of Hemofarm, using volumetric and instrumental methods of analysis, contents of the above mentioned elements in real samples were determined, values of their content are compared with the values which were indicated on the package by the manufacturer, the Recovery values were obtained for each performed analysis.

$$\text{Recovery (\%)} = \frac{m_{\text{calculated}}}{m_{\text{theoretical}}} \cdot 100\%$$

Table 1. The chloride content of the sample 1 - *Sodium Chloride infundibile*, using volumetric methods of analysis

Volume of consumed AgNO_3 for titration	$V_1=15.60$ ml	$V_2=15.50$ ml	$V_3=15.50$ ml	$V_{\text{aver.}}=15.50$ ml
The declaration prescribed amount of Cl in 1000.00 ml	154 mmol			
Experimentally determined amounts of Cl ⁻ in 1000.00 ml	154.69 mmol			
Recovery value	1.0045			

On the label: $n_{(\text{Cl}^-)} = 154$ mmol in 1000.00 ml of the sample,

$n_{(\text{Cl}^-)} = c_{(\text{AgNO}_3)} \cdot f_{\text{AgNO}_3} \cdot V_{\text{Sr}(\text{AgNO}_3)}$ in 10.00 ml of the sample

$n_{(\text{Cl}^-)} = 0.1 \text{ mmol/ml} \cdot 15.50 \text{ ml} \cdot 0.998 = 1.5469$ mmol in 10.00 ml of the sample

$n_{(\text{Cl}^-)} = 1.5469 \text{ mmol} \cdot 100 = 154.69$ mmol in 1000.00 ml of the sample

Recovery = $154.69 \text{ mmol} / 154 \text{ mmol} = 1.0045$

As the permissible deviation of $\pm 5\%$ is acceptable (Savić and Savić, 1989), the tested composition is in accordance with the label and contains a sufficient amount of chloride in the composition. Since, the sample 1 is consisted just of sodium chloride and water for injection, according to the reaction:



it can be concluded that $n_{(\text{Cl}^-)} = n_{(\text{Na}^+)}$ and indirectly determine the sodium via chloride solution. From this it follows that:

$n_{(\text{Cl}^-)} = n_{(\text{Na}^+)} = 154.69$ mmol in 1000.00 ml of the sample on the basis of experimental results. Declaration on the sample prescribes 154 mmol Na^+ in 1000.00 ml of the sample. Recovery value for Na^+ is 1.0045, as well as Cl^- . Since the allowed tolerance of $\pm 5\%$ (Savić and Savić, 1989), we see that the preparation is in accordance with the declaration and that it contains a sufficient amount of sodium in the preparation.

Table 2. The sodium content of the sample 1 - *Sodium Chloride infundibile*, using instrumental analysis methods

Content of Na^+ determined by flame photometer in 1000.00 ml	3.5000g
The calculated theoretical mass in 1000.00 ml of the sample on the declaration	3.5400g
Recovery value	0.9887

The calculated theoretical mass of Na in 1000.0 ml of the sample on the declaration:

$$m(\text{Na}) = n(\text{Na}) \cdot M(\text{Na}) = 154 \text{ mmol} \cdot 22.98 \text{ mmol/mg} = 3538.9200 \text{ mg, or } m(\text{Na}) = 3.5400 \text{ g}$$

Table 3. The content of chloride in a sample of 2 - *Hartmann's solution*, the use of volumetric analysis methods

Volume of consumed AgNO_3 for titration	$V_1=11.10$ ml	$V_2=11.20$ ml	$V_3=11.20$ ml	$V_{\text{aver.}}=11.20$ ml
The declaration prescribed amount of Cl in 1000.00 ml	112.00 mmol			
Experimentally determined amounts of Cl in 1000.00 ml	111.78 mmol			
Recovery value	0.9980			

Recovery value confirms that the content of chloride in the sample is in accordance with the prescribed declaration.

Table 4. Calcium content in the sample 2 - *Hartmann's solution*, using volumetric methods of analysis

The volume of consumed EDTA for titration	$V_1=19.30$ ml	$V_2=19.30$ ml	$V_3=19.30$ ml	$V_{\text{aver.}}=19.30$ ml
The declaration prescribed amount of calcium in 1000.00 ml	2.00 mmol			
Experimentally determined quantity of Ca in 1000.0 ml	1.98 mmol			
Recovery value	0.9900			

Recovery value confirms that the content of calcium in a sample is in accordance with the prescribed declaration.

Table 5. The content of calcium in the sample 2 - *Hartmann's solution*, using instrumental analysis methods

Content of Ca^{2+} determined by flame photometer in 1000.00 ml	0.0860 g
Theoretically calculated mass of Ca^{2+} in 1000.00 ml of the sample on declaration	0.0800 g
Recovery value	1.0750

Recovery value is 1.0750 (107.50%), which is not satisfactory, because it deviates from the allowable $\pm 5\%$ (Savić and Savić, 1989).

Table 6. The sodium content of the sample 2 - *Hartmann's solution*, the application of instrumental analysis methods

Content of Na^+ determined by flame photometer in 1000.00 ml	2.8800 g
Calculated theoretical mass of Na^+ in 1000.00 ml of the sample on declaration	3.0100 g
Recovery value	0.9568

Recovery value is satisfactory.

Table 7. Potassium content in the sample 2 - *Hartmann's solution*, using instrumental analysis methods

Content of K^+ determined by flame photometer in 1000.00 ml	0.1890 g
Theoretically calculated mass of K^+ in 1000.00 ml of the sample on declaration	0.1950 g
Recovery value	0.9692

Recovery value = 0.9692, which is in accordance with the allowed values of deviations.

Table 8. The chloride content of the sample 3 - *Ringer's solution*, using volumetric methods of analysis

Volume of consumed AgNO₃ for titration	V ₁ =15.50 ml	V ₂ = 15.60 ml	V ₃ =15.60 ml	V _{aver.} =15.60ml
The declaration prescribed amount of Cl in 1000.00 ml	155.60 mmol			
Experimentally determined amounts of Cl⁻ in 1000.0 ml	155.688 mmol			
Recovery value	1.0006			

Recovery = 155.688 mmol / 155.60 mmol = 1.0006 which confirms that the chloride content of the sample is in accordance with the prescribed declaration.

Table 9. Contents of calcium in the sample 3 - *Ringer's solution*, using volumetric methods of analysis

The volume of consumed EDTA for titration	V ₁ =21.90 ml	V ₂ = 21.90 ml	V ₃ = 21.90 ml	V _{aver.} =21.90ml
The declaration prescribed amount of calcium in 1000.00 ml	2.25 mmol			
Experimentally determined quantity of Ca in 1000.00 ml	2.24 mmol			
Recovery value	0.9956			

Calcium content is in accordance with the prescribed declaration.

Table 10. Calcium content in the sample 3 - *Ringer's solution*, using instrumental analysis methods

Content of Ca ²⁺ determined by flame photometer in 1000.00 ml	0.0860 g
Theoretically calculated mass of Ca ²⁺ in 1000.00 ml of the sample on declaration	0.0900 g
Recovery value	0.9556

Recovery value of 0.9556 is satisfactory.

Table 11. Sodium content in the sample 3 - *Ringer's solution*, using instrumental analysis methods

Content of Na ⁺ determined by flame photometer in 1000.00 ml	3.4700 g
Theoretically calculated mass of Na ⁺ in 1000.00 ml of the sample on declaration	3.3800 g
Recovery value	1.0266

Recovery value is satisfactory.

Table 12. Potassium content in the sample 3 - *Ringer's solution*, using instrumental analysis methods

Content of K ⁺ determined by flame photometer in 1000.00 ml	0.1390 g
Theoretically calculated mass of K ⁺ in 1000.00 ml of the sample on declaration	0.1560 g
Recovery value	0.8910

Recovery value of 0.8910 is not consistent with tolerance of $\pm 5\%$ (Savić and Savić, 1989).

Conclusions

- By direct determination of chloride, using depositional volumetric, Mohr's method, satisfactory results were obtained in all three samples, with recovery value amounted to 1.0045, 0.9980 and 1.0006. This confirms that Mohr's method is a reliable method to choose in the process of determining the chloride content in infusions.

- Determination of calcium using complexometric method, also provided good results, with recovery value 0.9900 and 0.9956 for samples 2 and 3, sucesively. On this basis, we can conclude that the applied volumetric methods of analysis can be used as a reliable method in the process of determining the content of calcium in infusion solutions.
- Determination of calcium content by flame photometry in samples 2 and 3 obtained Recovery values of 1.0750 and 0.9556. Recovery value for sample 2 deviates from the permitted values, or indicates higher calcium content in the sample than is required by the Declaration.
- Comparing the results related to the calcium content in the samples 2 and 3 using complexometry and flame photometry can be concluded that complexometry gave calcium content prescribed by the declaration on infusions within the permitted deviation of ± 5 (Savić and Savić, 1989) while the flame photometry identified deviation of 7.5% in the analyzed sample 2. It is necessary to carry out further examination of possibility of applying this instrumental method in the process of determining the calcium content in the tested solutions
- Sodium was determined in the sample 1 indirectly via the chloride and the following Recovery value was obtained 1.0045, that is, the possibility of applying the volumetric analytical method in the process of sodium determination in pure infusion solution was confirmed.
- In all three samples, sodium was determined by instruments, and the resulting Recovery values were 0.9887, 0.9568 and 1.0266. On this basis, we can conclude that the analysis of sodium in infusion solutions can be reliably performed also by using flame photometry.
- Recovery values related to the potassium content in the samples 2 and 3, using instrumental analysis methods, were 0.9692 and 0.8910. Deviations for sample 3 are 10.9%. Obtained results showed the lower content of potassium in the sample 3 than it was provided on a label, indicating the need for further investigation of the potential application of the instrumental method in the process of determining the potassium content in the tested solutions.

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