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DETERMINATION OF CHLORIDE CONTENT IN BOTTLED MINERAL WATER

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Abstract

Mineral waters from different sources have different contents, because each source has its own individual physical and chemical characteristics. Chlorides appear in natural waters because of the dissolution of minerals from sediments, but also because of anthropogenic influence. In this paper, Mohr's method of chloride content determination was used. Natural mineral waters “aqua viva” and “ELEMENT” were used for testing. Determination by Mohr’s method was performed in water samples without the addition of standard and with the addition of standard, as well as in the standards themselves. In water samples without the addition of standards, much higher chloride content values were obtained than those given by the declaration. The results of the Recovery test obtained after the determination of chloride content in the samples with the addition of the standard confirmed the applied method for the used concentration range. Based on the difference in the chloride content in the samples with the addition of standard and the standards themselves, the values of the chloride content in the sample were determined and they were closer to the values stated on the declaration. Given the results of the performed analyses, it can be concluded that they are in agreement with literature data, i.e. Mohr’s method is more suitable for determination in samples with high chloride concentrations. In samples containing low concentrations of chloride, a tendency towards increased results was recorded, which was also the case in this research.

Keywords: mineral waters, chlorides, Mohr’s method, standard addition method, method confirmation

INTRODUCTION

The availability of drinking water is one of the most important problems of today’s world, because the growing demand for water exceeds the supply possibilities (Vučijak *et al.*, 2011). Recently, bottled drinking water has been increasingly used. Bottled water, which is available in the market, is a unique product with a protected name and hydrogeological origin of unique quality. The quality of this water depends on the quality of its source, the filling and disinfection technology, the quality of the water filtration plant, or the bottle distribution system.

Various Directives for natural mineral water, spring water and bottled drinking water (Videnović, 2018) regulate the quality of bottled water currently in circulation in the European Union. In our country, the Rulebook on Health Safety of Drinking Water regulates potable water, natural mineral and natural spring water reliability (Official Gazette of the Republic of Srpska, 75/15).

Mineral waters from different sources have different contents, because each source has its own individual physical and chemical characteristics. Sulphates, chlorides, hydrogen carbonates and carbonates, nitrogen compounds, iron compounds, silicic acid and silicates, trace elements, phosphorus compounds, radioactive substances, colloids can be present in the water (Blagojević, 2007). Chlorides appear in natural waters because of the dissolution of minerals from sediments (Đuković *et al.*, 2000). Almost all natural waters contain chlorides mainly in the form of calcium, magnesium and sodium salts. Natural water samples from different sources differ in their chloride content (Wu *et al.*, 2021). When rainwater and snow fall to the ground, evaporation and evapotranspiration tend to concentrate chlorides in soil water at levels ten or more times the original concentration (Kelly *et al.*, 2012). Increased chloride concentrations can also occur as a result of anthropogenic factors, such as contamination of sewage water, use of water softeners, use of sodium chloride as a preservative, disposal of livestock waste, use of synthetic fertilizers (primarily KCl) and salt runoff from roads in snowy periods (Hunt *et al.*, 2012; Kelly *et al.*, 2012).

Chlorides themselves are not toxic to humans; therefore, the World Health Organization has not prescribed a maximum permissible concentration based on their effects on health. The US Environmental Protection Agency (US EPA) has prescribed a secondary maximum level of 250 mg/L. At concentrations higher than mentioned, chlorides cause a salty taste in water (Laketić *et al.*, 2014).

Some of the methods used to determine chloride in water are: ion chromatography (Bekić, 2019), application of ion-selective electrodes (Bratovcic and Odobasic, 2011), conductometric method (Flueraru *et al.*, 2014), spectrophotometric method (Coll ,1957; Maya *et al.*, 2008), turbidimetric method (Mesquita *et al.*, 2002), volumetric sedimentation method according to Mohr (Bitar, 2016, Shukla and Arya, 2018), titration with mercury (II)-nitrate (Thomas, 1954), etc.

In this paper, Mohr's method of chloride determination was used. This volumetric method belongs to the group of direct sedimentation methods with the use of indicators (Vindakijević and Sladojević, 2005). It is used to determine chloride ions in a neutral or weakly base environment (pH=6.5-9). A standard silver nitrate solution is used as a titration agent, and a sodium chromate or potassium chromate solution is used as an indicator (Blagojević, 2021). First, a white precipitate of silver chloride is deposited, and when the precipitation of the primary precipitate is completed, i.e. when the equivalence point is reached (TE), the precipitation of a secondary red-brown precipitate of silver-chromate begins. The appearance of this precipitate is a sign that the end of the titration has been reached (ZTT).

During the titration, the following reactions take place:

3. $Ag^+ + Cl^- \rightleftarrows AgCl_{(s)}$ TE
4. $2Ag^+ + CrO_4^{2-} \rightleftarrows Ag_2CrO_{4\,(s)}$ ZTT

When determining chloride argentometrically, anions must not be present in the solution, which together with the Ag^+-ion give hard-to-dissolve precipitates (CO_3^{2-}, S^{2-}, SO_3^{2-}, PO_4^{3-}, AsO_4^{3-}). Cations that with chromate ions give hardly soluble precipitates, such as Pb^{2+} or Ba^{2+}-ions, must not be present either (Sladojević, 2016).

MATERIALS AND METHODS

For determining the chloride content, “aqua viva” and “ELEMENT” bottled waters were used.

According to the data stated on the declaration, “aqua viva” water belongs to the group of natural mineral waters with low mineralization (dry residue less than 500 mg/L) with chemical content listed in Table 1.

Table 1. Chemical composition of “aqua viva” bottled mineral water

Chemical substance	**(mg/L)**
Calcium (Ca^{2+})	88
Magnesium (Mg^{2+})	13
Natrium (Na^+)	10.5
Potassium (K^+)	1.5
Iron ($Fe^{2+/3+}$)	< 0.05
Hydrogen carbonates (HCO_3^-)	317
Sulfates (SO_4^{2-})	22
Chlorides (Cl^-)	11.7
Fluorides (F^-)	0.14
Dry residue (at 180°C)	355

“ELEMENT” water also belongs to the group of natural low-mineralized waters, and its chemical content is given in Table 2.

Table 2. Chemical composition of “ELEMENT” bottled mineral water

Chemical substance	**(mg/L)**
Calcium (Ca^{2+})	33.82
Magnesium (Mg^{2+})	10.56
Natrium (Na^+)	1.605
Potassium (K^+)	0.402
Hydrogen carbonates (HCO_3^-)	134.2
Sulfates (SO_4^{2-})	8.81
Chlorides (Cl^-)	3.8
Dry residue (at 180°C)	134

To determine the chloride content by Mohr’s method, two methods of determination were used: determination of chloride without the addition of standard and determination of chloride with the addition of standard.

For experimental work, the following solutions, dishes and utensils were used:

Solutions:

- Standard solution $AgNO_3$, $c(AgNO_3)=0.1$ mol/L, $F(AgNO_3)=0.9996$,
- Standard solution NaCl, $c(NaCl)=0.05$ mol/L, F (NaCl)=1.0000,
- Solution K_2CrO_4 (5%).

Dishes and utensils:

- Erlenmeyer flasks of 300 mL,
- Volumetric flasks of 500 mL,
- Measured pipettes of 5, 10, 15 и 25 and 100 mL,
- Propipeta,
- Beakers,
- Burette of 50 mL,
- Graduated Cylinder of 5 mL.

In the first case, 100 mL of the tested mineral water sample was measured and transferred into three Erlenmeyer flasks. 2 mL of indicator (5% K_2CrO_4 solution) was added and the samples were titrated with standard $AgNO_3$ solution until the color changed from yellow to ocher. From the burette, the used volume of $AgNO_3$ solution was read and the chloride content was calculated as follows:

$n(Cl^{-})/100\ mL= n(AgNO_3) = V(AgNO_3) \cdot c(AgNO_3) \cdot F(AgNO_3)$

$m\ (Cl^{-})/1000\ mL = n(Cl^{-})/100\ mL \cdot M(Cl^{-}) \cdot 1000/100$

In the second method, in order to determine the applicability of the method and the validity of the obtained results, the standard addition method was used. This technique consists in adding a known amount of analyte to a sample, then analyzing such a sample and determining whether the added amount is obtained experimentally. For this purpose, the analytical yield is calculated, i.e. the Recovery test, according to the pattern:

$$R = \frac{Q_A(O+S) - Q_A(O)}{Q_A(S)} \cdot 100\%,$$ where are:

$Q_A(S)$–the quantity of analyte A added,

$Q_A(O+S)$–the quantity of analyte A recovered from the sample with added analyte,

$Q_A(O)$–the quantity of analyte A from the original sample (Burns *et al.*, 2002).

Here, standard NaCl solution was used as a source of a known amount of chloride. 5, 10 and 15 mL of the prepared standard sodium chloride solution were transferred to three 50 mL volumetric flasks. Then 25 mL of the tested mineral water sample was transferred to each flask. The flasks were filled up to the mark with distilled water. The entire contents of the volumetric flasks were transferred into three labeled Erlenmeyer flasks. 2 mL of 5% K_2CrO_4 solution were added, after which the content of each Erlenmeyer flask was titrated with a standard $AgNO_3$ solution until the color changed from yellow to ocher. The used volume of the AgNO3 solution was read (U+S). The described procedure was repeated for both mineral waters tested. In the same way, as in the first case, based on the used volume of $AgNO_3$ solution, the calculation of the experimentally obtained chloride values in samples with the addition of standard was performed (E).

After that, standards for titration were prepared by transferring 5, 10 and 15 mL of the standard with measuring pipettes into three 50 mL volumetric flasks and diluting to the mark with distilled water. The entire content of each flask was transferred to three labeled

Erlenmeyer flasks, after which the titration was performed in the manner already described. The volume of $AgNO_3$ solution used was recorded and the calculation of the chloride content was carried out, as in the previous two cases.

Based on the data obtained, the chloride content in the samples (U) was determined, as follows:

$$m(Cl^-)/1000\ mL_{\text{sample}}\ (U) = m(Cl^-)/1000\ mL_{\text{sample with standard}} - m(Cl^-)/1000\ mL_{\text{standard}}$$

RESULTS AND DISCUSSION

Table 3 shows the results of determining the chloride content in the “aqua viva” bottled mineral water, and Table 4 shows the results for the “ELEMENT” bottled mineral water. The presented results refer to the determination of chloride without the addition of standard.

Table 3. Results of determination of chloride content in the “aqua viva” bottled mineral water

Sample	$V(AgNO_3)$ (mL)	Cl^- content (mg/L)
1	0.5	17.72
2	0.5	17.72
3	0.5	17.72
Cl^- content according to the declaration		11.70

Table 4. Results of determination of chloride content in the “ELEMENT” bottled mineral water

Sample	$V(AgNO_3)$ (mL)	Cl^- content (mg/L)
1	0.2	7.09
2	0.2	7.09
3	0.2	7.09
Cl^- content according to the declaration		3.80

For all three titrations, in the case of “aqua viva” water samples, the same volume of silver nitrate solution was used, so it can be said that the titration was carried out precisely. Equal volumes were also recorded during the titration of “ELEMENT” water samples. Nevertheless, regardless of the accuracy, it can be noted that with both tested waters, elevated values of chloride content were obtained compared to the values given in the declaration.

The obtained results are in accordance with the literature data, where it is stated that high accuracy of experimental results obtained by the Mohr’s method can be expected only when chloride ions in the sample are present in concentrations higher than 50 mg/L, when the pH of the sample is higher than 4 and the content of heavy of metals is relatively low

(Bulgariu *et al.*, 2007). Other authors, who determined chlorides in snow samples, state that the Mohr's method is applicable in neutral environments and for chloride concentration levels higher than 30 mg/L. The general tendency of elevated results in samples with low chloride concentrations has been pointed out, as well as the fact that, compared to the spectrophotometric method, the results have been approximately twice as high (Iacoban and Macoveanu, 2005).

Also, the accuracy of chloride content determination by the Mohr's method is affected by the presence of some heavy metals, such as Pb^{2+}, Ba^{2+}, Fe^{3+}, Zn^{2+} or Ca^{2+}-ions, which cause serious interferences, especially in higher concentrations (more than 250 mg/L). In that case, it is recommended to determine chloride by the conductometric method (for higher chloride concentrations) and the turbidimetric method for samples containing trace amounts of chloride (Flueraru *et al.*, 2014). As stated on the declaration, Ca^{2+}-ions are present in the "aqua viva" water in a concentration of 88 mg/L, and in the "ELEMENT" water in a concentration of 33.82 mg/L. Although these concentrations are significantly lower than the stated critical value (250 mg/L), they are still many times higher compared to the concentration of chloride ions, which could also be the cause of the elevated results of the analysis.

Table 5 shows the results of chloride determination by Mohr with the addition of standard in "aqua viva" water samples, and Table 6 shows the results for "ELEMENT" water samples. In the first column of tables are given the values of the chloride content contained in the added 5, 10 and 15 mL of standard NaCl solution (respectively).

Table 5. Results of determination of chloride content by Mohr with the addition of standard in "aqua viva" bottled mineral water

Added standard (Cl^-) (mg/L)	**$V(AgNO_3)$(S) (mL)**	**$V(AgNO_3)$ (U+S) (mL)**	**Cl^- content (E) (mg/L)**	**Recovery (R) (%)**	**Cl^- content (U) (mg/L)**
177.27	2.55	2.70	191.37	101.35	10.63
354.54	5.10	5.25	372.11	101.65	10.63
531.81	7.55	7.70	545.76	99.67	10.63
$\underline{\boldsymbol{x}}$					10.63
Cl^- content according to the declaration					11.70

Table 6. Results of determination of chloride content by Mohr with the addition of standard in "ELEMENT" bottled mineral water

Added standard (Cl^-) (mg/L)	**$V(AgNO_3)$ (S) (mL)**	**$V(AgNO_3)$ (U+S) (mL)**	**Cl^- content (E) (mg/L)**	**Recovery (R) (%)**	**Cl^- content (U) (mg/L)**
177.27	2.55	2.60	184.28	101.81	3.54
354.54	5.10	5.15	365.02	101.88	3.54
531.81	7.55	7.60	538.67	100.58	3.52
$\underline{\boldsymbol{x}}$					3.53

Cl$^-$content according to the declaration					3.80

As already mentioned, one way of confirming the method is to examine the samples to which a known amount of analyte has been added and determine the yield percentage. Recovery is the measured amount of analyte (expressed in %) in relation to the added amount of analyte in a sample that does not contain the given analyte or contains it in an amount not greater than 30% of the added amount (Rajković *et al.*, 2019). The method is considered accurate if the R value is within the range of 95–105% (Matijević, 2013).

The obtained Recovery test values show that this method gives good results for samples with standard addition, i.e. the yield is within acceptable limits, thus confirming the method and the obtained results for the concentration range used.

Based on the difference in the chloride content in the samples with added standard and the standards themselves, the values of the chloride content in the sample were determined. For the “aqua viva” water sample, the value of 10.63 mg/L was obtained, which is much closer to the value stated on the declaration (11.7 mg/L), than was the case for samples without the addition of standards (17.72 mg/L). A similar thing can be observed with the “ELEMENT” water sample, where, with the addition of the standard, the chloride content of 3.53 mg/L was determined, which is also closer to the value stated on the declaration (3.8 mg/L) compared to the specified value in the samples without standard (7.09 mg/L).

CONCLUSION

In this paper, the results of the determination of chloride in “aqua viva” and “ELEMENT” bottled mineral waters by the Mohr’s method are presented. The determination was made in water samples without the addition of standard and with the addition of standard, which verified the method and validity of the results. Chloride was also determined in the standards themselves. According to the declaration, both waters belong to the group of low-mineralized waters. “Aqua Viva” water contains 11.7 mg/L of chloride ions, and “ELEMENT” water contains 3.8 mg/L. Of the other ions, calcium and hydrogen carbonate ions can be distinguished by their content. When determining chloride without the addition of standard, higher values were obtained compared to the values given in the declaration, namely 17.72 mg/L for “aqua viva” water and 7.09 mg/L for “ELEMENT” water. Both waters contain Ca^{2+}-ions, and although the concentrations listed on the declaration are significantly lower than the interfering value for determination by the Mohr’s method (250 mg/L), they are still many times higher than the concentration of chloride ions, which could be the cause of the elevated results of the analysis.

Based on the difference in the chloride content in the samples with the addition of standard and the standards themselves, the values of the chloride content in the sample were determined and they were closer to the values stated on the declaration. For the “aqua viva” water sample, the value of 10.63 mg/L was obtained, and in the “ELEMENT” water sample, the content of 3.53 mg/L was determined. The results of the Recovery test obtained after the determination of chloride content in the samples with the addition of standard confirmed the applied method for the concentration range used.

Taking into account the results of the performed analyses, one can say that they agree with literature data, mentioned in the paper, i.e. the Mohr's method is more suitable for determination in samples with higher chloride concentrations. In samples with low concentrations, a tendency towards increased results was recorded, which was also the case in this research. In addition, according to literature data, it is recommended to use the turbidimetric method for samples with low concentrations of chloride and, in general, to select the method by which chlorides will be determined according to the type of sample.

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