"Green" method for monitoring the mineral composition of spring waters based on the results of double measurement of specific electrical conductivity

A E Vasyukov¹, K K Surinov¹, N R Zinoviev¹, S N Nikulina² and T A Chudakova²

¹Kaluga State University named after K.E. Tsiolkovsky, Kaluga, Russia
²Kaluga branch of the Moscow State Technical University named after N.E. Bauman, Kaluga, Russia

E-mail: Voinsveta579@mail.ru

Abstract. The "green" method of conductometric determination of the double dilution coefficients has been tested according to the results of monthly measurements during the year of the specific electrical conductivity of undiluted and twice diluted underground water from 4 springs. The first coefficient characterizes the ratio of mono- and divalent cations and anions in the water under study, the second one characterizes the content of dissolved salts in mg-eq/dm³, which makes it possible to establish the hydrochemical type of the water under study. The technique can be classified as environmentally friendly since natural diluted distilled water serves as waste.

1. Introduction
The main goal of green chemistry, which is a fundamentally new innovative approach to reducing or completely eliminating the use of hazardous and toxic chemicals, is to prevent pollution in the process of creating chemical products or processes, i.e. prevention of pollution at the very early stages of planning and implementation of chemical processes [1]. Chemical processes should also include chemical analysis of environmental objects for the content of pollutants. From a green chemistry perspective, the choice of analytical method for determining the analysis in the analytical control object should be made with an emphasis on preventing contamination in the very early stages of sampling and performing chemical analysis.

The main approaches are highlighted that ensure a decrease in the negative impact on the environment in the implementation of chemical analyzes [2]:

- Complete elimination of sample preparation through the use of direct determinations.
- Analysis automation.
- The consumption of reagents and the mass of the analyzed objects is reduced, as well as energy for the implementation of processes.
- Applying chemometric approaches to data processing to extract more information even when few measurements have been made.

Let us consider these approaches for controlling the mineral composition of natural waters using the example of spring water, the release of groundwater and deep groundwater to the surface. Mineralization
is an integral parameter that reflects the total content of salts dissolved in water without dividing them into groups or classes. Analytical monitoring of the mineralization of spring waters in time makes it possible to obtain an ecological assessment of the constancy of their mineral composition, for example, over a year.

To determine mineralization, gravimetry is most often used, [3], rarely - conductometry [4]. From the standpoint of "green" chemistry, conductometry has a number of undeniable advantages over gravimetry. In addition, the method of direct conductometry determines the specific electrical conductivity (EEC) of the investigated mineral water diluted with distilled water n times and calculates the identification coefficient of the chemical composition of waters as the tangent of the slope of the dependence of the inverse EEC on the degree of dilution, which has a strictly defined value for a given mineral composition investigated aqueous solution [5].

UEP characterizes the total value of the ionic composition of waters, i.e. mineralization, and, in addition, gives an approximate idea of the concentration of some components and the ratio between them in the solution, which is important for the characterization and classification of natural waters [4].

The most promising for the purposes of "green" chemistry are studies in which, according to the results of a double measurement of the UEP of water (χ₁ - undiluted and χ₂ - diluted 2 times), one can get an idea of the type and total salinity of this water by the values of the dilution coefficients k₁ = χ₂/(χ₁ - χ₂) and k₂ = χ₁ × χ₂/(χ₁ - χ₂). The graph compiled in the coordinates k₁ - k₂ makes it possible to identify chloride-sodium and sulfate-calcium-magnesium waters [4].

Purpose of the work: to show the possibilities of the "green" method - two-fold measurement of UEP (χ₁ - undiluted and χ₂ - diluted 2 times) - for the ecological assessment of the mineral composition of groundwater using the example of spring waters.

2. Devices, reagents, objects and research methods
UEP measurements were carried out using a conductometer - liquid analyzer of the laboratory series Anion 4100 model A4155 (K-A4155). The operability of the measuring channels was checked according to the operating manual K-A4155 [6] in the course of performing the current definitions of the comparison and analysis of the results of measurements of the UEP of distilled water and standard KCl solutions.

Standard KCl solutions (GOST 4234-77, reagent grade) were prepared from a fixed channel. We used distilled water in accordance with GOST 6709-72 [7] with an ECE less than 5 µS/cm.

Figure 1. Map-diagram of the location of the studied springs.
Objects of research: The objects of research were groundwaters of four springs (figure 1): spring no. 1 - Berezuevsky ravine; spring No. 2 - a platform near the St. Laurentian Monastery; spring No. 3 - intersection of Vygonaya and Sadovaya streets; spring number 4 - Azarov region, right slope of the river. Terepets. Spring water was collected monthly from October 2017 to October 2018.

The characteristics of error and reproducibility were determined in accordance with the requirements of GOST R 51672-2000 [13].

The experimental procedure included measuring the UEP of a 40 ml aliquot of the test water, adding to this aliquot 40 ml of distilled water from the burette to achieve two-fold dilution, and measuring the UEP of the resulting solution after 1 minute, during which the test solution was stirred on a magnetic stirrer.

3. Research results and their discussion

The experimental procedure included measuring the UEP of a 40 ml aliquot of the test water, adding to this aliquot 40 ml of distilled water from the burette to achieve two-fold dilution, and measuring the UEP of the resulting solution after 1 minute, during which the test solution was stirred on a magnetic stirrer.

Table 1. Results of measurement of UEP (mcm/cm) of the studied spring waters and diluted twice with distilled water (n=3, t=25°C).

| Month selection | Spring number 1 | Spring number 2 | Spring number 3 | Spring number 4 |
|----------------|----------------|----------------|----------------|----------------|
|                | $\chi_1$ | $\chi_2$ | $\chi_1$ | $\chi_2$ | $\chi_1$ | $\chi_2$ | $\chi_1$ | $\chi_2$ |
| Oct 17         | 993.1     | 516.3        | 835.2         | 426.0        | -           | -           | 550.0       | 288.9       |
| Nov 17         | 1007.6    | 513.6        | 842.4         | 428.2        | -           | -           | 542.2       | 289.8       |
| Dec 17         | 1032.8    | 529.4        | 864.2         | 437.1        | 941.1       | 503.4       | 554.3       | 299.0       |
| Jan 18         | 1020.4    | 534.8        | 872.5         | 444.6        | 943.4       | 499.0       | 562.8       | 299.0       |
| Feb 18         | 1039.6    | 552.5        | 896.3         | 454.5        | 964.7       | 502.7       | 573.5       | 301.0       |
| Mar 18         | 1048.2    | 549.4        | 898.7         | 466.4        | 965.1       | 505.2       | 568.5       | 304.9       |
| Apr 18         | 1057.4    | 554.5        | 916.5         | 469.3        | 966.1       | 503.9       | 578.0       | 305.0       |
| May 18         | 1040.9    | 547.9        | 928.9         | 474.4        | 971.8       | 500.8       | 571.5       | 304.3       |
| Jun 18         | 1042.0    | 553.5        | 949.6         | 489.0        | 972.8       | 502.7       | 578.1       | 305.6       |
| Jul 18         | 1034.0    | 553.9        | 954.2         | 489.5        | 972.0       | 505.1       | 578.8       | 302.5       |
| Aug 18         | 1033.0    | 533.0        | 951.7         | 489.5        | 971.3       | 501.7       | 578.3       | 302.5       |
| Sept 18        | 1009.2    | 528.8        | 922.4         | 470.4        | 950.7       | 497.4       | 560.3       | 296.3       |
| Oct 18         | 1015.9    | 531.9        | 916.4         | 467.3        | 961.2       | 503.1       | 571.0       | 302.1       |
| Max            | 1057.4    | 554.5        | 954.2         | 489.5        | 972.8       | 505.2       | 578.8       | 305.6       |
| Min            | 993.1     | 513.6        | 835.2         | 426.0        | 941.1       | 497.4       | 542.2       | 288.9       |
| The average    | 1034      | 543          | 916           | 468          | 962         | 502.3       | 571         | 302.0       |

Comparison of the average SEC values, taking into account the standard deviation (Sr), shows that, according to the decrease in the mineralization of the studied waters, a sequence is observed: spring no. 1 - (1034 ± 11) μS/cm, spring no. 3 - (962 ± 9) μS/cm, spring no. 2 - (916 ± 24) μS/cm, spring no. 4 - (571 ± 7) μS/cm. It should be noted that, in terms of mineral composition, the spring waters differ significantly from each other, since the ranges of oscillations of the SEC ($\chi_1 \pm Sr$) of the studied waters do not overlap. The numerical value of Sr for the UEP of groundwater of the investigated springs is within (1.0-2.6) %, which corresponds to the error of direct conductometric measurements and does not make it possible to speak under static conditions and significant changes in the mineral composition of spring waters during the period under study [8, nine].

A much larger amount of information can be obtained by knowing the numerical values of the double dilution coefficients of the investigated spring waters presented in table 2.
Results of calculating the double dilution coefficients of the studied spring waters.

| Month | Spring number 1 | | Spring number 2 | | Spring number 3 | | Spring number 4 | |
|-------|----------------|---|----------------|---|----------------|---|----------------|---|
|       | k₁ | k₂ | S/cm | k₁ | k₂ | S/cm | k₁ | k₂ | S/cm | k₁ | k₂ | S/cm |
| Oct17 | 1.083 | 10.8 | 1.041 | 8.69 | - | - | - | 1.106 | 6.09 |
| Nov17 | 1.040 | 10.5 | 1.034 | 8.71 | - | - | 1.148 | 6.23 |
| Dec17 | 1.052 | 10.9 | 1.023 | 8.84 | 1.150 | 10.8 | 1.171 | 6.49 |
| Jan18 | 1.101 | 11.2 | 1.039 | 9.07 | 1.123 | 10.6 | 1.133 | 6.38 |
| Feb18 | 1.134 | 11.8 | 1.029 | 9.22 | 1.088 | 10.5 | 1.105 | 6.33 |
| Mar18 | 1.101 | 11.5 | 1.079 | 9.70 | 1.098 | 10.6 | 1.157 | 6.58 |
| Apr18 | 1.103 | 11.7 | 1.049 | 9.62 | 1.090 | 10.5 | 1.117 | 6.46 |
| May18 | 1.111 | 11.6 | 1.044 | 9.70 | 1.063 | 10.3 | 1.139 | 6.51 |
| Jun18 | 1.133 | 11.8 | 1.062 | 10.1 | 1.069 | 10.4 | 1.121 | 6.48 |
| Jul18 | 1.154 | 11.9 | 1.053 | 10.1 | 1.082 | 10.5 | 1.095 | 6.34 |
| Aug18 | 1.066 | 11.0 | 1.059 | 10.1 | 1.068 | 10.4 | 1.097 | 6.34 |
| Sept18 | 1.101 | 11.1 | 1.041 | 9.60 | 1.097 | 10.4 | 1.123 | 6.29 |
| Oct18 | 1.099 | 11.2 | 1.041 | 9.54 | 1.098 | 10.6 | 1.123 | 6.41 |
| Max | 1.154 | 11.9 | 1.079 | 10.1 | 1.150 | 10.8 | 1.171 | 6.58 |
| Min | 1.040 | 10.5 | 1.023 | 8.69 | 1.063 | 10.3 | 1.095 | 6.09 |
| The | 1.105 | 11.4 | 1.047 | 9.6 | 1.093 | 10.5 | 1.125 | 6.42 |

Coefficient k₁ is dimensionless, it does not depend on the concentration of ions in the test solution, its physical meaning is associated with the ratio of mono- and divalent ions in the studied natural water. Since the UEP of solutions of salts consisting of monovalent cations and anions of ions (chlorides, sodium ions) is on average 50% higher than the UEP of solutions of salts, with their divalent cations and anions (sulfates, magnesium and calcium ions) [4], the numerical value k₁ of natural water with a predominance of sodium chloride will be lower than the k₁ value of natural sulphate water with high hardness. Therefore, the coefficient k₁ can be conventionally called "valence".

Coefficient k₂ has the dimension of UEC and is directly related to the concentration of ions in the test solution. Numerous studies of natural waters have shown that the numerical value of the coefficient k² in most cases coincides with the salt content calculated from the results of chemical analysis in mg·eq/dm³ [4]. Therefore, the coefficient k₂ can be conditionally called "equivalent".

Comparison of the values of "valence" k₁ and "equivalent" k₂ of groundwater (table 2) shows that the investigated waters from springs No. 1, No. 2 and No. 3 are quite similar in mineral composition, but not completely identical. This is indicated by the coincidence or overlap of the ranges of k₁ values and rather close (9.59-11.4)×104 S/cm, but not the same average k₂ values.

Comparison of the obtained values of k₁ and k₂ of groundwater from springs No. 1, No. 2, and No. 3 with the literature data [4] shows that these waters can be attributed to the same sodium chloride type of water.

The data at table 2 show that according to the values of k₁ and k₂, the mineral composition of groundwater from spring No. 4 differs significantly from the mineral composition of groundwater from other investigated springs and, according to the literature data [4], is closest to the hydrocarbonate-calcium type.

The constancy of the numerical value of k₂ of spring water over time may indicate the stability of the release of groundwater and deep groundwater to the surface. Figure 2 shows the dynamics of the "equivalent" k₂ of the investigated spring waters in the period 2017-2018.

The results of the dynamic approach [8, 9] show the preservation of a stable mineral composition of groundwater in springs No. 3 and No. 4 during the entire period of research. At the same time, two periods can be distinguished for springs # 1 and # 2. The first from October 2017 to July 2018, when
the numerical value of $k_2$, equivalent to the amount of meq/dm$^3$ of salts in groundwater, increases by an average of 1.5-2.0% every month. Since September, such an increase stops and a decrease in the value of $k_2$ is observed, which may indicate the appearance during this period of factors, the belief of all natural ones, affecting the mineral composition of the release of groundwater and deep groundwater to the surface in the area of springs No. 1 and No. 2.

4. Conclusion
The method of conductometric determination of "valence" and "equivalent" coefficients of double dilution has been tested on the example of studying the mineral composition of groundwater in four springs.

The technique is extremely simple and includes a two-fold measurement of the UEP of undiluted and twice-diluted test water, followed by the calculation of the double dilution coefficients. This technique can be classified as environmentally friendly, since natural diluted distilled water serves as waste. The technique is fully consistent with the principles of "green" chemistry.

References
[1] Anastas P and Warner J C 1998 Green Chemistry: Theory and Practice Oxford University Press (New York) 30
[2] Zolotov Yu A 2013 "Green" Analytical Chemistry Journal of Analytical Chemistry 68(4) 315
[3] PNDF 14.1:2:4.261-2010 Methodology for measuring the mass concentration of dry and calcined residue in samples of drinking, natural and waste water by the gravimetric method
[4] Vorobiev I 1963 Application of measuring electrical conductivity for characterizing the chemical composition of natural waters (Moscow: Publishing house of the Academy of Sciences of the USSR) p 141
[5] Vasyukov A, Loboichenko V and Bushtec S 2016 Identification of bottled natural waters by using direct conductometry Ecology Environment and Conservation 22(3) 1171-6
[6] Liquid analyzers laboratory series Anion 4100 2011 Operation manual INFA.421522.002. RE LLC NPP "Infraspak-Analit" (Novosibirsk) p 86
[7] GOST 6709-72 Distilled water Technical conditions Retrieved from 01.01.1974
[8] Vasyukov A, Korzhavyi A and Nikulina S 2019 Static and dynamic approach to estimation of spring water mineralization stability as a factor of groundwater ecological safety Journal of Physics: Conference Series 1399(5)
[9] Vasyukov A, Korzhavyi A, Nikulina S and Zhukova Y 2019 Static and dynamic approach to estimation of spring water hardness cation content as a natural factor of groundwater formation Journal of Physics: Conference Series 1399(5)