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Quantitative Analysis of The Seasonal Changes of Traces of Copper(II) in Mineral Water

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A selective, sensitive and simple kinetic method for the determination of trace amounts of Cu^{2+} in mineral water was developed. The method is based on the catalytic effect of Cu^{2+} on the reaction of sodium pyrogallol-5-sulphonate (PS) with hydrogen peroxide in the presence of 2,2'-bipyridyl. The calibration graph is linear in the concentration range of 0.25-5.00 ng mL^{-1}. Investigation of the seasonal changes of Cu^{2+} ions in mineral water of Glavno Vrelo and Skolska Cesma in Niska Banja revealed that rainfalls and surface drainage of water after rain showers and snow melting increase the content of this ion in mineral water of this area.

Key Words: Copper(II), Seasonal changes, Mineral water, Kinetic method, Atomic absorption spectrometry.

INTRODUCTION

Mineral water is water containing minerals or other dissolved substances that alter its taste or give it therapeutic value. They have biologically active properties and show physiological effect on the human organism. Salts, sulfur compounds, radioactive components, organic matter and gases are among the substances that can be dissolved in water[1]. It is very complex and complicated to study these components because of their specific properties due to the various hydro-chemical anomalies which cause unusual concentrations of elements in natural water and therefore, consequently in mineral water[2].

In mineral water inorganic materials appear in various forms. If an element moves together with the water it is either in a soluble form or a constituent of a stable suspension. All minerals are more or less soluble, even in pure water the presence of dissolved oxygen, carbon dioxide and humus compounds increases to a great extent the corrosive ability of mineral waters. The speed of water movement

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through the stratum pervaded oxidation processes also has significant influence on the intensity of hydro-chemical anomalies. If water moves slowly, there is more time for transmission of decomposition products of minerals in the water. As a result the element solubility depends also on a presence of other ions in the mineral water.

The intensity of hydro-chemical anomalies also changes depending of hydrometeorological conditions. In stability of hydro-chemical water anomalies caused by these changes is one of the most serious problems in the water analysis studies.

Atmospheric sediments and water surface outflow have a significant influence on the intensity of hydro-chemical anomalies, especially under climatic conditions characterized by a strong seasonal change in the rainfall characteristics. The composition of subterraneous water is stable in periods of drought. When it rains after a period of drought, two factors are important. The first one consists of simple dilution of water and the other one comprises washing out soluble salts accumulated in the soil during the previous drought period. As a consequence salt concentration in the water is raised.

The aim of this study is to establish the seasonal hydro-chemical anomalies changes in terms of the Cu^{2+} contents in the mineral water of Niska Banja. Copper, as a biogen microelement, has a big role in process of blood formation. It stimulates synthesis of hemoglobin, growing of cells and activity of some enzymes. By food and water we take in the necessary amounts of cooper. Therefore, it is very important to follow and determinate the contents of copper in water. In order to determinate small changes of this ion in mineral water, an analytical method not only high sensitive but also selective enough is required. In addition measurements should be carried out as simple as possible without use of sophisticated equipment. All of these conditions are satisfied by kinetic methods of analysis based on the direct or indirect measurement of the reaction rate of species, which in turn involves measuring the change in the reactant or product concentration as a function of time[3].

Many analytical methods have been developed for the determination of copper, but the majority of them suffer from poor selectivity. Among these methods are spectrophotometry[4], ion chromatography[5,6] and atomic absorption spectrophotometry[7,8]. Anodic stripping voltametry[9,10] and high performance liquid chromatography[11,12] have also been used for the determination of copper with high sensitivity and selectivity, but suffer from more or less time consuming procedure and/or expensive and complicated instrumentation[9,12]. A few catalytic kinetic methods for the Cu^{2+} determination at trace levels have been published using various types of indicator reaction[13,14]. Some of these methods are based on the oxidation of various reagents with H_2O_2. Most of these kinetic methods have a narrow dynamic range of determination and are applicable to microgram amounts[15,16]. Besides, to improve sensitivity, the reactions are carried out at elevated temperatures[17]. In the order to overcome these problems a successful attempt was made at developing and validating a rapid, sensitive and selective kinetic method for the trace determination of Cu^{2+}.

In this paper a sensitive and sample kinetic method for the determination of Cu^{2+} is proposed. The oxidation of sodium pyrogallol-5-sulphonate (PS) by hydrogen peroxide in acidic medium gives a yellow oxidation product at 437 nm. It was observed that small amounts of Cu^{2+} strongly catalyzed this reaction. This fact was used for the kinetic determination of Cu^{2+}. As a continuation of our studies it was also observed that small amounts of 2,2'-bipyridyl enhances the sensitivity of the copper catalyzed oxidation reaction. This fact was used as the basis of the kinetic method for the determination of nanogram amounts of Cu^{2+}.

EXPERIMENTAL

The reaction rate of the oxidation of sodium pyrogallol-5-sulphonate by hydrogen peroxide was followed spectrophotometrically. The absorbance of the solution was measured at the wavelength of 437 nm, which corresponds to the maximum absorption of yellow oxidation product. The readings were done on a Perkin-Elmer Lambda 15 UV/V is spectrophotometer, connected to a thermocirculating bath.

pH measurements were carried out using Hanna instruments pH meter. The solutions were thermostated at 25.0 ± 0.1 ºC before the beginning of the reaction.

Sodium pyrogallol-5-sulphonate was synthesized by dissolving 3.7833 g of pyrogallol in 100.00 mL of the sulfuric acid (96 %)[18]. An 8.8×10^{-3} mol L^{-1} solution was prepared by appropriate dilution of the Merck p.a. reagent and standardized against potassium permanganate solution. The perchloric acid solution (0.12 mol L^{-1}) was prepared from the 70 % reagent. The copper(II) solution (1.0 g L^{-1}) was prepared by dilution of a copper sulfate solution and standardized iodimetrically. A standard copper solution (1.0×10^{-5} g L^{-1}) was prepared by diluting the stock copper solution with deionised water. The 2,2'-bipyridyl solution (1.0×10^{-2} mol L^{-1}) was prepared by dissolving 2,2'-dipyridil in 25.00 mL of ethanol and diluting the solution to 100.00 mL with deionized water.

All the stock solutions were stored in polyethylene containers. The working solutions of Cu^{2+}, H_2O_2 and sodium pyrogallol-5-sulphonate were prepared immediately before the use.

Analytical grade chemicals (Merck) and deionised water (MicroMed high purity water system, TKA Wasseraufbereitungssysteme GmbH) were used for the preparation of all solutions. All the glassware used was washed with aqueous HCl (1:1) and then thoroughly rinsed with running, distilled water and then finally with deionized water.

Procedure

Determination of copper(II): Selected volumes of reactants were transferred into a 10.0 mL volumetric flask in the following order: sodium pyrogallol-5-sulphonate, perchloric acid, 2,2'-bipyridyl and catalyst. Water was added to give the predetermined volume. After the flask was thermostatted for 10 min the solution was made up to the mark with hydrogen peroxide and vigorously shaken. The spectrophotometer cell was rinsed well and then filled with the solution. The absorbance at 437 nm was measured every 30 s over a period of 3-8 min after the addition of hydrogen peroxide. The tangent method was used for the processing of the kinetic data. The rate of the reaction was obtained by measuring the slope of the linear part of the kinetic curves to the absorbance-time plot (from Beer's law $A = \varepsilon \cdot l \cdot c$, $\frac{dA}{dt} = \varepsilon \cdot l \cdot \frac{dc}{dt}$, $\frac{dc}{dt} = \frac{DA/dt}{\varepsilon \cdot l}$, slope = dA/dt , rate = dc/dt). The calibration graph was constructed by plotting the slope of the linear part of the kinetic curve, *versus* concentration of Cu^{2+}($c_{Cu^{2+}}$ ng mL^{-1}).

RESULTS AND DISCUSSION

In order to determine the lowest possible determinable concentration of Cu^{2+}, the working conditions needed to be optimized. The influence of 2,2'-bipyridyl, as activator, on the oxidation rate of sodium pyrogallol-5-sulphonate with hydrogen peroxide in presence of Cu^{2+} as a catalyst in acidic acid solution was investigated (Fig. 1). The 2,2'-bipyridyl enhances the sensitivity of the copper-catalyzed oxidation reaction about two orders of magnitude. It also catalyzed reaction in the absence of Cu^{2+} ions (Fig. 1, curve 2). The maximal difference between curves 1 and 2 appears at the 1.0×10^{-4} mol L^{-1} concentration of 2,2'-bipyridyl (Fig. 1, curve 3). For further work this concentration was selected.

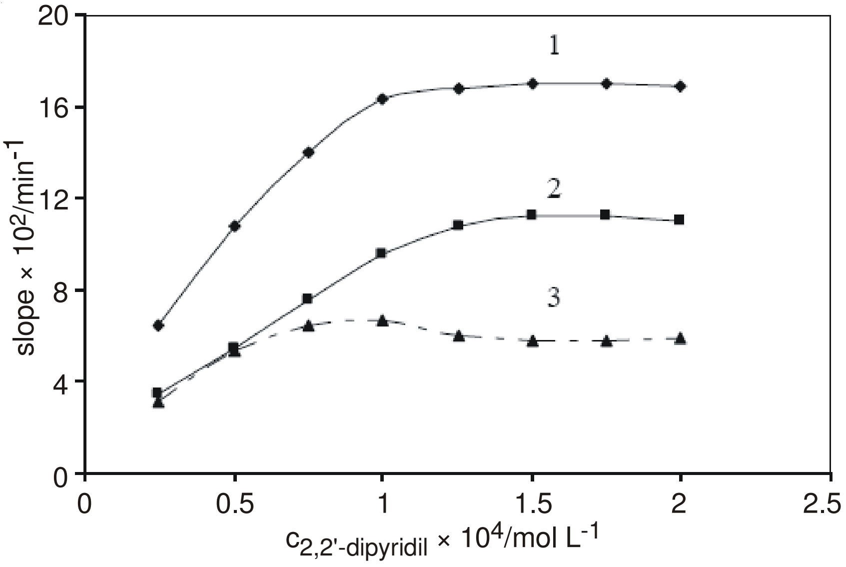

Fig. 1. Dependence of the rate of the catalytic (1) and uncatalytic (2) reaction on the 2,2'-bipyridyl concentration. Initial concentrations: $c_{PS} = 8.8 \times 10^{-4}$ mol L^{-1}, $c_{H_2O_2} = 0.16$ mol L^{-1}, $c_{HClO_4} = 1.2 \times 10^{-3}$ mol L^{-1}, $c_{Cu^{2+}} = 5.0$ ng mL^{-1}, $t = 25.0 \pm 0.1$ °C

Calibration graph: The tangent method was used to calculate the rate of catalyzed reaction in the presence a constant (1.0×10^{-4} mol L^{-1}) 2,2'-bipyridyl concentration, which was plotted as a function of the copper concentration. The fixed time and the fixed absorbance (variable time) method were also used[19]. For the fixed time method, measurements were made after 4 min. For the fixed absorbance method, the inverse of time necessary to obtain an absorbance of 0.300 was plotted against the copper concentration. In all cases, the calibration graph is linear in the concentration range indicated in Table-1. The accuracy and precision of the three methods applied for a Cu^{2+} concentration of 3.0 ng mL^{-1} is also included in Table-1. It can be concluded that the fixed absorbance method has a positive systematic error ($t'_{exp} > t$), whereas the tangent method is more precise. Although the fixed time method is accurate and precise, the permissible concentration range is slightly narrower than the tangent method. Therefore, the tangent method is recommended.

TABLE-1
LINEAR CONCENTRATION RANGE, ACCURACY AND PRECISION OF THE KINETIC METHOD FOR THE DETERMINATION OF Cu^{2+} IN THE PRESENCE OF 2,2'-BIPYRIDYL AS AN ACTIVATOR

Method	Concentration range $c_{Cu^{2+}}$, ng mL^{-1}	RSD* (%)	t'_{exp}**
Tangent	0.25-5.00	2.0	0.95
Fixed time	0.75-5.00	3.4	1.82
Fixed absorbance	1.00-5.00	3.5	3.28

*Relative standard deviation, mean of five measurements.
**t = 2.77.

The least square's equation (y = bx + a, where b and a are slope and intercept, respectively) for the calibration graph and correlation coefficient (r)[20] for the determination of Cu^{2+} in the interval 0.25 to 5.00 ng mL^{-1} (Fig. 2) under the optimal reaction conditions ($c_{PS} = 8.8 \times 10^{-4}$ mol L^{-1}, $c_{HClO_4} = 1.2 \times 10^{-3}$ mol L^{-1}, $c_{H_2O_2} = 0.16$ mol L^{-1}, $c_{2,2'\text{-bipyridyl}} = 1.0 \times 10^{-4}$ mol L^{-1}, t = 25.0 ± 0.1 ºC) were calculated:

$$\text{slope} = 0.0125 \times c_{Cu^{2+}} + 0.0968 \qquad r = 0.998$$

where slope is the slope of the linear part of the kinetic curve to the absorbance-time plot (slope = $dA/dt = \varepsilon \cdot l \cdot dc/dt$, Beer's law) and $c_{Cu^{2+}}$ is the copper concentration expressed in ng mL^{-1}.

According to Perez-Bendito and Silva[19], Mottola[21] and Thomsen[22] the following expressions are used to evaluate limit of detection (LOD) and limit of quantification (LOQ):

$$LOD = 3.3\ S_0/b = 0.05 \text{ ng ml}^{-1}$$
$$LOQ = 10\ S_0/b = 0.16 \text{ ng ml}^{-1}$$

where S_0 and b are standard deviation of the blank and slope (analytical sensitivity) of the calibration curve, respectively.

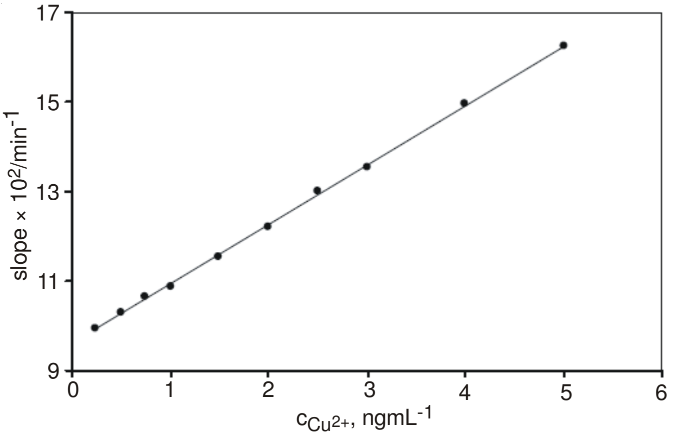

Fig. 2. Calibration graph. Optimal reaction conditions: $c_{PS} = 8.8 \times 10^{-4}$ mol L^{-1}, $c_{H_2O_2}$ = 0.16 mol L^{-1}, $c_{HClO_4} = 1.2 \times 10^{-3}$ mol L^{-1}, $c_{2,2'\text{-bipyridyl}} = 1.0 \times 10^{-4}$ mol L^{-1}, t = 25.0 ± 0.1 °C

The precision and accuracy of the above system were studied by performing the experiment 5 times for different concentrations of copper(II)[23]. The relative error ranges from 0.4 to 4.7 % for the copper concentration of 5.00-0.25 ng mL^{-1}.

Interference studies: The interference of several foreign ions on the determination for a constant Cu^{2+} concentration of 3.0 ng mL^{-1} in the presence a constant 2,2'-bipyridyl concentration of a 1.0×10^{-4} mol L^{-1} was investigated by 2S (S-standard deviation) criteria[24]. Tolerance levels of anions and cations usually found in real samples are presented in Table-2. Many of the cations and anions do not interfere at a ratio of foreign ion to Cu^{2+} of 1000:1 and 100:1, respectively. Positive interference was observed for Fe^{3+}, I^- and Cr^{6+}, because they also act as catalysts of the oxidation reaction. Masking with fluoride could successfully eliminate the interference of Fe^{3+}. Nevertheless, interferences due to presence of Cr^{6+} and I^- are noticeable at the same concentration level as the Cu^{2+}.

TABLE-2
TOLERANCE RATIO FOR FOREIGN SPECIES IN THE DETERMINATION Of 3.0 ng mL^{-1} OF Cu^{2+}

Ion added*	Tolerance level (ng mL^{-1} interferent/ng mL^{-1} $c_{Cu^{2+}}$)
Ca^{2+}, Sr^{2+}, Mg^{2+}, Ba^{2+}, $S_2O_3^{2-}$, Sn^{2+}, Se^{4+}, VO_3^-, S^{2-}, Br^-, CN^-, F^-	1000**
Cd^{2+}, Ni^{2+}, Al^{3+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, WO_4^-, SO_4^{2-}, PO_4^{3-}, SCN^-	500
Co^{2+}, MoO_4^{2-}, AsO_3^{2-}, acetate, citrate, tartarate	100
I^-, Cr^{6+} (catalyzed)	10
Fe^{3+} (catalyzed)	5

*Cations added as chlorides or nitrates, anions as sodium or potassium salts
**Maximum concentration studied

Applications: The method was directly applied for the determination of copper in mineral water without any separation. A 2 mL of the mineral water sample was used for the recommended procedure.

The results obtained by an interpolation of calibration graph are given in Table-3. The results found by the proposed method and atomic absorption spectrophotometry (AAS) were compared. The values obtained by both methods are in good agreement. From these results, the proposed kinetic method seems to be applicable to the determination of Cu^{2+} in mineral water.

TABLE-3
DETERMINATION OF Cu^{2+} IN MINERAL WATER SAMPLES

Water Sample		Found* ($\bar{x} \pm \overline{SD}$), ngmL^{-1}	
		Kinetic method	AAS**
Glavno Vrelo	Oct. ***	8.800 ± 0.21	8.760 ± 0.60
	Nov.	9.650 ± 0.23	9.420 ± 0.50
	Dec.	10.55 ± 0.18	10.60 ± 0.50
	Jan.	11.20 ± 0.25	11.52 ± 0.60
	Feb.	15.55 ± 0.19	15.32 ± 0.20
	Mar.	12.62 ± 0.31	12.32 ± 0.40
Skolska Cesma	Oct. ***	7.95 ± 0.25	8.05 ± 0.30
	Nov.	8.45 ± 0.32	8.56 ± 0.50
	Dec.	8.40 ± 0.18	8.50 ± 0.60
	Jan.	8.48 ± 0.23	8.50 ± 0.40
	Feb.	9.40 ± 0.32	9.58 ± 0.30
	Mar.	8.70 ± 0.20	8.90 ± 0.70

*Mean and standard deviation of three determinations and 95 % confidence
**At 324.8 nm
***Selected the every tenth in month (from October to March)

Conclusion

The greatest imperfection of the mineral water of Niska Banja is occasional turbidity and temperature decrease, which cause decrease in the therapeutics potential. It could be assumed that these turbidities are caused by water, which unfiltered from the surface of the terrain relatively quickly reaches, the thermal water. However, the mechanism of these turbidities is not simple and each spring a specific problem appears. A more detailed study of the thermal spring's position and geological circumstances of their closer environment are necessary for the explanation of these phenomena.

In order to establish the seasonal changes of the Cu^{2+} quantities in the mineral water of Niska Banja by observing the springs Glavno Vrelo and Skolska Cesma the atmospheric conditions in the period of 6 months (from October to March) were recorded. Quantitative determination of Cu^{2+} in the spring water samples was made by kinetic method. The data are given in Fig. 3 and Table-3. From Fig. 3 it could be seen that Cu^{2+} contents in the spring of Glavno Vrelo are unstable and significantly conditioned by the seasonal changes. The increase of the content of this ion in the periods of quick snow melting and heavy rains was recorded. It was also observed a slight muddling occurred as well as that a water temperature dropped from 31 to 25 ºC which also could cause changes of this ion in mineral water.

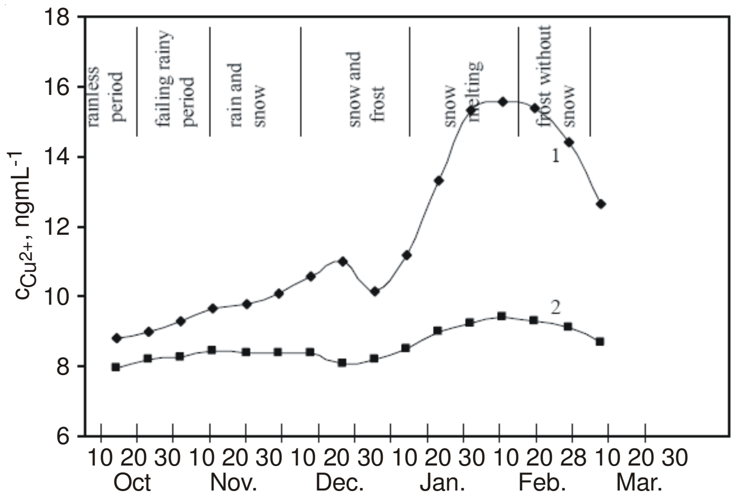

Fig. 3. Seasonal changes of the Cu^{2+} in the mineral water of Niska Banja from the springs Glavno Vrelo (1) and Skolska Cesma (2)

At the spring Glavno Vrelo slight muddling occurred, which was caused by the atmospheric water percolating through the crocks of limestone rocks and confluence into one of the 'veins' bringing water to Vrelo. This caused increase of the Cu^{2+} contents and decrease of the spring temperature.

On the other hand, water from the spring Skolska Cesma did not muddle and its temperature was almost stable, ranging from 17.5 to 17.2 ºC. From Fig. 3 (curve 2) a very small increase of the Cu^{2+} contents in the heavy rains period could be observed, therefore it can be concluded that the rocks around this spring are poorly permeable; therefore atmospheric water can not mix with the water from the spring.

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