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SOME CHEMICAL CHARACTERISTICS OF NATURAL WATERS FROM PROBIŠTIP AREA

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ИЗВАДОК

Јордановска В., Димески М. (1985): Некои хемиски карактеристики на природни води од Пробиштипска околија.
Год. зб. Фарм. фак., Скопје.

Извршена е хемиска анализа на 12 примероци вода за пиење од Пробиштипска околија. Определени се количествата на: F^- , Cl^- , I^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} ; потоа карбонатната, постојаната и вкупната тврдина како и рН во земените примероци. Користени се потенциометриската метода со примена на соодветни јон-селективни електроди и волуметриски методи. Од добиените резултати е установено дека повеќето од водите ги задоволуваат пропишаните хигиено-технички норми за водите за пиење но мал дел од нив не ги задоволуваат.

ABSTRACT

Jordanovska V., Dimeski M. (1985): Some chemical characteristics of natural waters from probishtip area.
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Twelve samples of drinking water from Probištíp area were analysed. The quantities of: F^- , Cl^- , I^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , and carbonate, permanent and total hardness and pH values were determined. For this purpose potentiometric methods with corresponding ion-selective electrodes and volumetric methods were used.

The results have shown that more of the samples are convenient to use as drinking waters.

The accurate determination of the concentration in natural water of Cl^- , F^- , I^- , Ca^{2+} , Mg^{2+} , SO_4^{2-} , as well as carbonate, permanent and total hardness is essential to use the water in the industry and drinking water.

Sulfate salts are widely distributed in nature and may be present in natural waters in concentrations up to several thousand mg/dm^3 , but a recommended limit in potable waters is up to $250 mg/dm^3$.

Total hardness of potable water should be up to $20^{\circ}DH$, the concentration of Ca^{2+} up to $150 mg/dm^3$ and Mg^{2+} up to $150 mg/dm^3$.

The optimal amount of F^- in potable water should be $1 mg/dm^3$. The higher concentration causes Fluorosa and the lower Carias.

The present work is concerning the results of the determination of amounts of Cl^- , F^- , I^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} , pH, carbonate, permanent and total hardness in natural waters from Probištip area.

The total hardness and concentration of Ca^{2+} and Mg^{2+} are determined by complexometric titration (1, 2, 3); the carbonate hardness by acidimetric titration (1, 2, 3); the amounts of F^- and I^- with ion-selective electrodes (4, 5); Cl^- with classical volumetric method with AgNO_3 standard solution. and pH values with pH-meter.

There are a lot of methods for the determination of sulfates in natural water. The gravimetric determination of sulfate (6) is the most accurate method but is time-consuming too. Therefore other numerous methods have been proposed: exchange of chloranilate anion from insoluble barium chloranilate by sulfate in partially nonaqueous solution (7), diazotization and coupling of benzidine from precipitate benzidinium sulfate to form an azo dye (8, 9), reaction of benzidine precipitated by sulfate with phosphotungstomolibdic acid to produce a colored compound (10), ultraviolet absorption of the $(\text{FeSO}_4)^+$ complex cation (11), ultraviolet absorption of excess 4-amino-4'-chlorodiphenyl not precipitated by sulfate (12), and exchange of chromate from insoluble barium chromate by sulfate followed by spectrophotometric or titrimetric determination of the anion (13-15), reduction of sulfate to sulfide and colorimetric determination of the sulfide (16-18), nephelometric determination of sulfate (19), colorimetric determination of sulfate by alizarin sodium sulfonate (21), direct titrimetric determination of sulfate with $\text{Pb}(\text{NO}_3)_2$ using diphenylcarbazone as indicator (22), x-ray spectrometric determination of sulfate (23), precipitation of sulfate as PbSO_4 and after dissolving PbSO_4 , titration with EDTA by dimethylphenol orange as indicator (24).

We have adopted the complexometric determination of sulfate to natural waters proposed by Babačev (25). The principle of the method is to precipitate sulfate with a standard solution of BaCl_2 as BaSO_4 and excess of Ba^{2+} determine by titration with standard solution of complexon III by eriochromblack-T as indicator. Interferences of cations can be eliminated by passing the water sample through a cation exchange column.

EXPERIMENTAL

Apparatus and reagents

Fluoride ion-selective electrode, No 9409 Orion
Single junction reference electrode, No 9001 Orion
Iodide ion-selective electrode, No 94-53 Orion
Orion Specific Ionmeter 404
Glass electrode
Calomel electrode

All solutions are prepared of analytical grade reagents and with demineralized water.

Standard solution of complexon III /Na-salt of EDTA/, 0,05 mol/dm³.
Standard solution of BaCl_2 , 0,04977 mol/dm³.
Standard solution of MgCl_2 , 0,05158 mol/dm³.
Ammonia solution

Eriochromblack-T in NaCl /mass ratio 1 : 50/
 Standard solution of Na₂SO₄, 1mg (SO₄²⁻) / cm³
 Amberlit IR-120 in H⁺-form
 Ammonia buffer solution

General procedure for determination of SO₄ in drinking water

The filtered water is allowed to pass through a cation exchange resin. The first 40-50 cm³ of the passed water is ignored and from the rest of the water is taken a volume depending on the amounts of SO₄²⁻ /from 4-10 mg/ diluted with water to a volume of 200-250 cm³, neutralized with ammonia to pH 4 heated to boiling point and to the hot solution is added 5 cm³ of BaCl₂ solution. The reaction mixture is allowed to boil 4-5 minutes and placed in a boiling water bath for 4 hrs. After cooling the pH of the mixture is adjusted to 10 with ammonia buffer solution, add 5 cm³ MgCl₂ and eriochromblack-T then titrate with complexon III to change the colour to blue-violet. Comparative titration with complexon III was made with a known mixture of standard solutions of BaCl₂ and MgCl₂ /for 5 cm³ of each solution/.

The amount of SO₄²⁻ was obtained by this equation:

$$\text{mg (SO}_4^{2-})/\text{dm}^3 = \frac{a-b \times c / \text{complexon III} / \times 96 \times 1000}{\text{volume of water sample}}$$

where: **a** is volume of complexon III in cm³ used for standard mixture of BaCl₂ and MgCl₂; **b** is volume of complexon III used for known volume of water sample together with standard mixture of BaCl₂ and MgCl₂; **c** is concentration in mol/dm³; 96 is one mol of SO₄²⁻.

The results of complexometric titration of sulfate in standard solution of sodium sulfate are shown in Table 1. The results of complexometric determination of sulfate in natural waters together with the results of determined amounts of Cl⁻, I⁻, F⁻, Ca²⁺, Mg²⁺, carbonate, permanent and total hardness and the pH values are shown in Table 2. 12 samples of water from Probištip area were taken for analysis in October 1983.

RESULTS AND DISCUSSION

Table 1.
 Results of complexometric determination of sulfate in standard sodium sulfate solution (1mg SO₄²⁻/cm³)

added SO_4^{2-} in mg	determined SO_4^{2-} in mg	deviation in %
1	1.29	29.0
2	2.25	12.5
3	3.22	7.3
4	4.27	6.8
5	5.14	2.8
6	6.10	1.7
7	7.11	1.6
8	8.07	0.9
9	9.15	1.7
10	10.19	1.9

The accuracy is satisfactory for amounts higher than 4 mg SO_4^{2-} /250 cm³. So we have chosen the volume of water sample to correspond to 4-10 mg SO_4^{2-} and diluted to 250 cm³.

Based on the results in Table 2 it can be concluded that applying hygienic-chemical norms for the quality of the drinking water, the water samples from Probištíp area have the following characteristics: half of water samples have a total hardness bigger than allowed; the concentration of Mg^{2+} is within the allowed limit; most of the water samples /83%/ contain allowed concentration of Ca^{2+} , only 30% of the water samples have optimal concentration of F^- ; the pH values are within the allowed limits; the amount of SO_4^{2-} is up to the allowed limit, except in the water samples from Zarapinci and Gujanovci.

Table 2
The results of chemical analysis of waters samples from Probištip area

Location	total hardness DH°	carbon. hardness DH°	perman. hardness DH°	mgCa/dm ³	mgMg/dm ³	mgCl/dm ³	mgF/dm ³	mgI/dm ³	mgSO ₄ /dm ³	pH
Gujanovci, pump (A. Sandev)	38,19	26,07	12,12	215,99	34,58	112,53	0,40	0,0032	290,8	7,33
Bučišta, pump (Boris)	15,11	12,89	2,22	91,99	9,70	10,61	0,42	0,0010	35,5	7,18
Lezovo, pump (F. Jovančev)	19,02	17,10	1,92	96,99	23,66	22,85	0,66	0,0032	203,5	7,10
Petrašino, Bulina fountain	13,01	10,93	2,08	82,99	6,06	13,18	0,42	0,0055	18,5	7,25
Zarapinci (fountain water)	27,89	4,62	23,36	144,99	33,39	25,64	0,38	0,0030	528,8	6,41
Puzderci, (fountain water)	24,06	16,82	7,24	94,60	46,72	19,34	1,00	0,0050	120,1	7,16
Neokazi, fountain (C. Borova)	26,58	24,53	2,05	146,80	26,09	23,74	1,00	0,0040	174,6	7,10
Probištip, market fountain	7,27	5,60	1,67	41,90	6,06	7,03	0,26	0,0028	57,60	7,10
Ratavica, fountain (G. Jačev)	8,67	7,01	1,66	46,78	9,10	6,15	0,17	0,0030	49,9	7,20
Pišica (village fountain)	27,42	21,31	6,11	145,99	30,35	55,38	0,26	0,0077	189,9	7,07
Tripatnica (fountain)	16,79	15,42	1,37	68,50	30,94	114,29	0,45	0,0070	36,5	7,00
Zletovo, well (N. Ignatov)	32,46	22,85	9,61	154,99	46,72	80,88	0,66	0,0065	92,9	7,40

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