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Effect of Potable Water Afterpurification by Ozonization and Incomplete Freezing

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Abstract

Using the methods of mass spectrometry and gas-liquid chromatography it has been demonstrated that potable water fed into water supply systems contains a number of hazardous trace microelements and chloroorganic substances in the concentration close to the maximum permissible concentration (MPC) value (except for iron and manganese). It is established that the treatment of potable water by ozone, with subsequent filtering through a coal filter (an Ozonide-Rodnik household device) and freezing at −18 °C under domestic conditions could provide an efficient afterpurification. The purified water does not contain carcinogenic chloroorganic substances, whereas the content of hazardous microelements (As, Cd, Ni, Cr, Pb, Se, V, Sb, and Hg) exhibits a 1.5- to 4.5-fold decrease, the decrease for Fe, Mn, and Al being from 2- to 15-fold.

Key words: purification methods, potable water, ozonization, freezing, analysis, mass spectrometry, gas-liquid chromatography, chloroorganic substances, microelements

INTRODUCTION

The problem of potable water quality will always be of urgent importance in connection with the proceeding environmental contamination, first of all of water reservoirs and water sources, by the products of man-caused origin.

It is known, that water purification at water-treatment plants before feeding into water supply systems includes a number of stages: rough impurities filtration, dispersed impurities coagulation, water precipitation with the subsequent filtration and disinfection with the help of chlorine and chlorine-containing compounds [1–4]. The use of chlorine during the process of water treatment is mandatory, since chlorine content in potable water is regulated by water disinfection standards, notwithstanding the fact that it could result in the formation of much more hazardous chloroorganic substances. In this connection there is a problem of potable water afterpurification under household conditions, which problem is usually solved via employing filters with activated coal or with a chelate absorbent. It is well known that the adsorption of chloroorganic substances on activated coal results in the efficiency of water purification up to 90–95 % [5, 6]. However, it is not possible to purify water completely from chloroorganic substances some of them exhibit carcinogenic properties.

It is also known that ozone is effectively applied to disinfection and purification from many trace pollutants such as metal cations as well as chloroorganic substances. This method of purification is used abroad and in some cities of Russia. Moreover, ozone exerts bactericidal and antiviral effects [7]. Ozonization under household conditions can be carried out with the help of such household electrical devices as ozonizers.

Another efficient method for water treatment from disperse impurities is presented by freezing [8]. However, the author of [9] did not succeed in achieving any positive result in his attempt to purify water from excess calcium carbonate, since the conditions of freezing provided for entire water bulk being transformed into ice.

In order to perform water quality control one should apply sensitive methods of analysis those allow determining of nanogram amounts of substances. So, for example, the method of mass spectrometry is known to be used for determining the microelemental composition of potable water [10]. The authors of this work determined a number of toxic impurity elements in water (As, Be, Cd, Cr, Hg, Ni, Pb, Sb, Se, V, and Tl), whose content in drinking water should be reduced to a minimum. As far as the Sanitary-and-Epidemiologic Regulations and Standards “Potable Water Quality Control” [11] is concerned, the ions of such wide-spread occurred chemical elements as Al, Ba, Be, B, Fe, Cd, Mn, Cu, Mo, As, Ni, Hg, Pb, Se, Sr, Cr, and Zn are distinguished and regulated as hazardous with respect to human health. In this connection our investigation was aimed at water purification from the mentioned chemical elements. In order to analyze the content of chloroorganic compounds we used a gas-liquid chromatography technique as the most efficient method [12].

In the estimation of water quality according to the Sanitary Regulations and Standards (SanPin) as well as in the case of detecting several (hazard class 1 and 2) chemical substances in potable water, the sum of all the individual concentration-to-MPC ratios (those are calculated for each pollutant) should not exceed 1. The calculation is performed according to the formula

$$\frac{C^1_{\text{fact}}}{A^1_{\text{MPC}}} + \frac{C^2_{\text{fact}}}{A^2_{\text{MPC}}} + \ldots + \frac{C^n_{\text{fact}}}{A^n_{\text{MPC}}} \le 1$$

where C^1_{fact}, C^2_{fact}, C^n_{fact} are the concentrations of individual chemical substances of the 1st and 2nd class of hazard; A^1_{MPC}, A^2_{MPC}, A^n_{MPC} are the values of MPC for the chemical substances of the 1st and 2nd class of hazard.

The purpose of the present work consisted in the studies on the efficiency of potable water joint treatment via absorption on a coal filter, ozonization and freezing to reduce the content of hazardous microelements, with the use of techniques for trace impurity chemical analysis (such as mass spectrometry with inductively coupled plasma and gas-liquid chromatography).

EXPERIMENTAL

In the experiments we used tap water from the city cold water supply. Water was frozen during 7–12 h within a polyethylene vessel of 1.5 L volume capacity at the temperature of −18 °C in a refrigerator. The water freezing level ice fraction amounted to 50–70 %, *i. e.* the ice fraction after freezing amounted to 0.5–0.7 from total water volume. Water remained after freezing was removed, its volume was measured and then analyses were performed; ice was melt and also analyzed.

Prior to freezing, we treated water with ozone using an Ozonide-Rodnik household electrical device (Ufa city), which caused the content of ozone in water to be as much as 0.2 mg/L. The time of treatment by ozone sufficient for completing the process of disinfection and oxidation amounted to 12 min. Water purification from residual ozone and polluting substances within the device was carried out *via* filtering water through a Rodnik-7 coal filter.

After thawing ice, we analyzed water for the content of all the cations including uranium elements, with the use of a mass spectrometry technique with inductively coupled plasma (ICP-MS, ELAN-9000 spectrometer). The samples under analysis were acidified by nitric acid purified via a sub-boiling distillation technique using a BSB-939-JR apparatus (Berghof) according to the requirements imposed upon sample preparing for ICP-MS [13]. The account of spectral noise was carried out with the help of software. The detection limit (DL) was calculated according to the formula DL = $3\sigma_{\text{bg}}/D$, where σ_{bg} is the stability of background at the given mass (the standard deviation); D is the sensitivity coefficient equal to the ratio between the change in the intensity of an elemental isotope analytical signal and the change in the isotope concentration ($D = \text{d}I/\text{d}c$).

Analytical data for water samples were presented taking into account the detection limit. In order to plot calibration curves we used multi-element standard solutions certified according to ISO 9001 (Perkin-Elmer Instruments). For correction of the spectrometer drift we used the internal standard element ^{115}In (certificate No. 9300124, prepared basing on NIST SRM 3124a, Perkin-Elmer Instruments). The determination of microelemental composition was carried out according to NSAM No. 480-x "The technique for determining the elemental composition of natural and potable water by ICP-MS method". The content of chemical elements in water was determined with averaging the results of three parallel experiments.

In order to determine chloroorganic substances we used a gas-liquid chromatography assay (Tsvet-550 chromatograph with an electron capture detector; the stationary phase of column packing was presented by SE-30 sorbent (10 %) on chromatone with the grain size of 0.16–0.20 μm). Isothermal mode was employed; the temperature of column thermostat amounted to 60 °C, the evaporator and detector temperature was equal to 150 and 300 °C, respectively; the gas-water mixture was fed with the flow rate of 0.2 mL/h. The detection limit for chloroorganic substances amounted to 1 μg/L.

RESULTS AND DISCUSSION

In the experiments, the following samples of water were obtained and analyzed: 1) initial water; 2) the initial water filtered with 0.25 L/min flow rate through a Rodnik type coal filter; 3) water treated with ozone and filtered through a Rodnik-7 filter (included in an Ozonide-Rodnik household electrical device); 4) initial water exposed to freezing and thawing without ozonization (thaw water); 5) water processed by ozone and filtered through the Rodnik-7 filter (within an Ozonide-Rodnik household electrical device) and exposed to freezing and thawing, *i. e.* ozonized thaw water.

From data presented in Table 1 one can see that in the tap water under investigation only the content of iron, manganese and mercury exceeds the MPC standards. However even the minimal content of heavy metal cations in potable water is undesirable. The initial tape water contains also chloroform and other chloroorganic compounds, in the springtime the contamination level of water exhibiting an increase.

Table 2 demonstrates data concerning the total water contamination factor, a water quality parameter determined according to the formula (1). According to [11], for the calculation we took into account only the substances of 1st and 2nd class of hazard. The contamination factor for tap water during the winter period is equal to 2, whereas in the springtime this parameter exceeds 3, which is connected with snow thawing resulted in water pollution. The minimal total factor (0.08) was observed for water samples preliminary processed with ozone those were then frozen and thawed. At the same time this parameter for the samples of water processed by ozone with the subsequent filtration through a coal filter amounted to 1.0, whereas for the samples of thaw water without ozonization it was equal to 0.12. When taking into account the substances of 3rd class of hazard in the formula (1), this factor would increase due to the increased concentration of manganese in tap water flowed through the coal filter.

The efficient water purification is achieved with use of the two methods such as water processing with ozone and water freezing. Ozone, being the strongest oxidizer, a number oxidation-reduction processes to occur with the subsequent sorption onto the filter. For example, the oxidation of iron and manganese could proceed according to the following equations:

$$2FeSO_4 + O_3 + H_2O \rightarrow Fe_2(OH)_2(SO_4)_2\downarrow + O_2 \quad (2)$$

$$MnSO_4 + O_3 + H_2O \rightarrow MnO_2\downarrow + O_2 + H_2SO_4 \quad (3)$$

The joint application of the two purification methods such as the treatment by ozone and the freezing results in reducing the contamination factor. To all appearance, the ozonization results in the oxidation of many variable-valency microelements to occur as well as a more complete adsorption at the activated coal, whereas under slow water freezing one can observe the formation the ice crystal structure which does not contain microelemental cations. Many impurity microelements remain in the liquid phase, *i. e.* in non-frozen water. The sequence of processing could be opposite, *i. e.* water is first of all exposed to freezing, and then it is ozonized. However, in this case there could be

TABLE 1

Results of determining trace microelements and chloroorganic substances in water samples (during winter period), mg/L

Impurities	Water samples					Detection limit	MPC^a	Class of hazard^b
	I	II	III	IV	V			
Li	0.007981	0.014544	0.002244	0.007694	0.0022	0.000024	0.03	2
Be	n/d	n/d	n/d	n/d	n/d	0.000003	0.0002	1
B	0.013647	0.00934	n/d	0.013436	n/d	0.000119	0.5	2
Na	6.289983	6.289983	3.256065	6.136198	3.23	0.000082	200.0	2
Mg	6.212002	6.300368	4.365235	5.887544	4.367	0.000011	40.0	
Al	0.017158	0.008945	n/d	0.001209	0.00667	0.000023	0.5	2
Si	0.728024	0.870242	n/d	0.730627	n/d	0.000310	10.0	3
P	0.024601	0.029814	0.023853	0.051634	0.023	0.001113	3.5	3
Ca	14.55967	17.51015	8.599875	13.9402	8.580	0.000795	180.0	
Sc	0.001311	0.000727	0.000763	0.001297	n/d	0.000074		
Ti	0.000809	0.000685	0.000315	0.000805	0.0003	0.000051		
V	0.000228	0.000137	0.000129	0.000170	n/d	0.000028	0.1	2
Cr	0.001729	0.000672	0.000975	0.001792	n/d	0.000032	0.05	3
Mn	0.227627	0.194549	0.025641	0.19772	0.025600	0.000003	0.1	3
Fe	0.332889	0.065989	n/d	0.015911	0.035342	0.000020	0.3	3
Co	0.000113	0.000072	0.000048	0.000072	0.000028	0.0000002	0.1	
Ni	0.002219	0.001329	0.000788	0.001145	0.000565	0.000023	0.1	3
Cu	0.00165	0.000571	0.000398	0.0005	0.000924	0.000002	1.0	3
Zn	0.021039	0.00526	0.003664	0.00612	0.012085	0.000008	5.0	
Ga	n/d	0.00001	n/d	n/d	n/d	0.000001		
Ge	n/d	0.000003	n/d	0.000002	n/d	0.000005	0.05	2
As	0.000482	0.000405	n/d	0.000344	0.000075	0.000023	0.01	2
Se	n/d	0.000119	n/d	n/d	n/d	0.000090	0.1	2
Rb	0.001379	0.003062	0.000851	0.001391	0.000331	0.0000002	7.0	2
Sr	0.089715	0.107478	0.041044	0.089023	0.020810	0.000003		
Y	0.000001	0.000002	n/d	0.000002	n/d	0.0000002	0.07	
Zr	0.000004	n/d	0.000002	0.000009	n/d	0.000001	0.01	2
Nb	n/d	n/d	0.000004	n/d	0.000003	0.00000011	0.25	2
Mo	0.000219	0.000322	0.00019	0.000141	0.000106	0.000008	0.05	2
Ag	0.000004	0.01935	n/d	0.001004	0.001711	0.0000005	0.001	2
Cd	0.000013	0.000007	n/d	0.000006	0.000009	0.0000002		
Sn	n/d	n/d	0.000739	n/d	0.000036	0.000003	0.05	2
Sb	0.000155	0.006315	0.000064	0.000139	0.000047	0.000001	0.01	2
Te	n/d	0.000003	n/d	n/d	0.000007	0.000014		
Cs	n/d	0.000004	n/d	n/d	0.000001	0.0000004	0.10	2
Ba	0.014614	0.044072	0.015463	0.019869	0.003745	0.0000001		
La	0.000001	0.000001	n/d	0.000001	0.000001	0.000001		
Ce	n/d	0.000001	n/d	n/d	0.000001	0.000001		
Pr	n/d	n/d	n/d	n/d	n/d	0.0000004	0.024	
Nd	n/d	0.000001	n/d	n/d	n/d	0.0000004		
Sm	n/d	0.000001	n/d	n/d	n/d	0.000001		
Eu	n/d	n/d	n/d	n/d	n/d	0.000001		
Gd	n/d	n/d	n/d	n/d	n/d	0.0000001		
Tb	n/d	n/d	n/d	n/d	n/d	0.0000001		
Dy	n/d	n/d	n/d	n/d	n/d	0.0000003		
Ho	n/d	n/d	n/d	n/d	n/d	0.0000004		
Er	n/d	n/d	n/d	n/d	n/d	0.0000003		
Tm	n/d	n/d	n/d	n/d	n/d	0.00000001		
Yb	n/d	n/d	n/d	n/d	n/d	0.00000003		
Lu	n/d	n/d	n/d	n/d	n/d	0.0000001		
Hf	n/d	0.000001	n/d	n/d	n/d	0.0000001		
Ta	n/d	n/d	n/d	n/d	n/d	0.0000001	0.0001	1
W	n/d	0.000007	n/d	n/d	n/d	0.0000001	0.05	2
Hg	0.0008	n/d	n/d	0.000293	n/d	0.000041		
Tl	n/d	n/d	n/d	n/d	n/d	0.0000003		
Pb	0.000348	0.000255	n/d	n/d	0.000104	0.000015		
Bi	n/d	n/do	n/d	n/d	n/d	0.000001		
Th	0.000001	n/d	n/d	n/d	0.000001	0.00000001		
U	0.000003	0.000001	n/d	n/d	n/d	0.0000004		
$CHCl_3$	0.080	0.014	n/d	n/d	n/d	0.001		
$CHBrCl_2$	0.007	0.0012	n/d	n/d	n/d	0.001		

Notes. 1. Water samples: I – tap water; II – water filtered through a Rodnik coal filter; III – water processed by ozone exposed to thawing; IV – water processed by ozone; V – water exposed to thawing. 2. Standard deviation for determining the elements with averaging over three parallel experiments amounted to $0.2 \cdot 10^{-7}$; 3. n/d – not detected.

[a] Drinking water, SanPiN 2.1.4.1074-01.

[b] SanPiN 2.1.4.1074-01.

TABLE 2

Values of total contamination factor (water quality parameter K) for water samples

Water sample	*K*	S^{2*}
Initial water (winter)	2.0	0.04
Filtered through a coal filter («Rodnik»)	1.0	0.05
Processed with ozone using an Ozonide-Rodnik household device	1.0	0.05
Thaw water obtained after freezing 50–70 % of entire water volume	0.12	0.03
Processed with ozone using an Ozonide-Rodnik household device with the subsequent freezing	0.08	0.01

*Standard deviation.

active oxygen complexes remained in water those, however, use to decompose under boiling and freezing. Nevertheless, thaw water is considered to be more useful for a living organism.

In the case of the only adsorption purification method with filtering (see Table 2) the total contamination factor amounts to 1 (without taking manganese into account). It should be noted that in this case the content of Fe, Co, Ni, Cu, Zn, chloroform and bromochloromethane decreases, though the purification from chloroorganic substances is not complete. The content of microelements, except for manganese, meets the requirements of the Russian Sanitary Regulations and Standards "SanPiN" 2.1.4.1074-01.

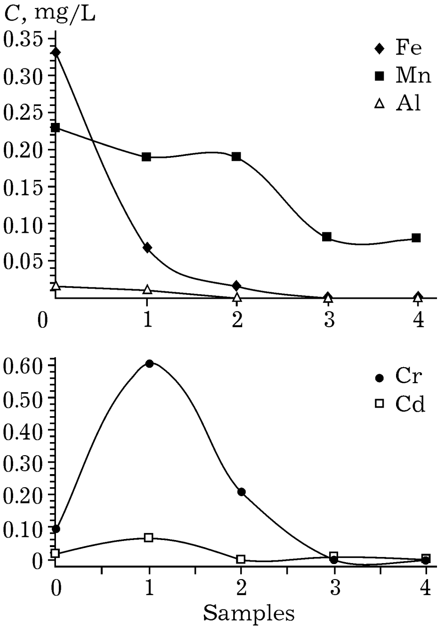

Fig. 1. Content of microelements in water depending on water treatment technique. Points on *X* axis are corresponding to: 0 – initial tap water; 1 – water filtered through a coal filter; 2 – water treated by ozone with the subsequent filtration through a coal filter; 3 – thaw water; 4 – water treated by ozone with the subsequent filtration through a coal filter and exposed to freezing (processed by ozone and thawed).

It is interesting to follow the dynamics of water purification with employing the aforementioned methods. So, the ozonization results in lowering the concentration of iron, manganese, aluminium, cadmium, chromium, copper, molybdenum, arsenic, nickel, mercury, lead, selenium, zinc, cobalt, whereas chloroorganic substances are completely removed.

During the following stage such as freezing, the further water purification proceeds, which is confirmed by the reduction of the total contamination factor (see Table 2, Fig. 1). In the course of water freezing (thaw water treated by ozone with the subsequent freezing) one can observe almost comprehensive water purification from iron and aluminium, whereas the content of manganese decreases down to <0.02 mg/L. It should be noted that the absence of aluminium, iron, arsenic, cadmium, lead, selenium, mercury is observed therein; water does not contain carcinogenic chloroorganic substances.

As far as many heavy metals are concerned, one can also conclude that the successive treatment by ozone and freezing results in profound water purification. Water purified in such a way is comparable with pure natural water (for example, the Baikal water) in the content of impurities. For comparison, data are presented concerning the content of some chemical elements in the Baikal water, μg/L: Al, Fe, Zn < 5; Pb, Mo, Cu, Ni < 2; As, Sb, Se < 1; Hg < 0.1; Sr 110 [10].

The process of ice formation, *i. e.* water crystallization should proceed slowly in such a way as the formation of ice crystal structure to occur with no capture of impurity cations. It has been experimentally established that this effect can be gained during 7.5–9.5 h. The freezing level in this case amounted to 0.5–0.7. With the increase in the freezing level the level of water purification exhibits a decrease, which could be explained by the capture of impurity cations. To all appearance, water purification by the freezing method with freezing level <0.5 is also efficient.

CONCLUSION

Thus, in order to obtain pure potable water one could efficiently employ the methods of purification via absorption water processing by ozone and the subsequent incomplete freezing it with thaw water obtaining. Following the mode of operation proposed one can obtain pure potable water with no chloroorganic substances, containing almost no hazardous microelements such as As, Cd, Ni, Cr, Pb, Se, V, Sb, Hg and less hazardous Fe, Al.

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