

# Investigation of Hardness and Permanganate Oxidation Value in Water Systems by a New Methodical Approach

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**Abstract:** The quality of the waters of the rivers of the Lake Sevan catchment basin was assessed by the investigation of water hardness, pH and permanganate oxidation (PO) value. The measurement of the hardness of the waters by the settling of salts and the determination of PO value in the water samples before and after the settling of salts gave an opportunity to separate the possible impact of salts on PO value and to assess the quality of the waters more precisely. The investigations have been clarified that PO value isn't directly related to the level of hardness in water, and it is influenced by the qualitative nature of salts dissolved in water.

Key words: water hardness, permanganate oxidation, water quality

## 1. Introduction

More than a few thousand types of organic matters exist in natural waters, the huge quantity of which is quite unstable and undergoes transformation incessantly. That is why the direct determination of organic matter concentration is quite difficult, and its content is characterized by an indirect method -permanganate oxidation or dichromate oxidation for highly polluted waters. The integral value of permanganate oxidation (PO) characterizes the content of organic and some mineral matters in water which can be oxidized by a strong oxidant potassium permanganate. In case of high content of some chemical compounds, for instance  $Fe^{2+} >$ 0.1-0.2 mg/l,  $NO_2^- > 0.1$  mg/l,  $H_2S > 0.1-0.2$  mg/l,  $Mn^{2+} > 0.5$  mg/l and so forth, their impact on PO degree should be taken into consideration to characterize organic matter content as precise as possible. To take into consideration the impact of salt ions on PO degree means to determine their content in water samples in advance and to recalculate PO

value, which is done in practice. For skipping this difficulty and for characterizing organic matter content precisely, we tried to reveal the integral portion of salts in PO value by determining PO value before and after the assessment of the total hardness of waters by a chemical method based on the settling of salts in water samples [1].

For assessing the quality of waters, hydrogen index (pH) and hardness types measured by different methods were also investigated.

## 2. Materials and Methods

The water samples taken from the midstream of the Masrik, Karchaghbyur (Maqenis), Argichi, Vardenis, Arpa, Lichq, Gavaraget and Dzknaget rivers of the Lake Sevan catchment basin and the 2 coastal sites of Lake Sevan (Chkalovka (1) and Karmir village (2)) were investigated in June-October, 2012. Water pH was measured by a laboratory pH-2 meter. The types of the hardness of the waters were determined by the standard methods [2]. The same time, total hardness in the water samples was also determined according to our innovation — the chemical method based on the settling of salts [1]. Permanganate oxidation (PO)

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value in the waters was determined by the Kubel method [3]. PO value in the water samples was determined before and after the settling of salts by the chemical method.

The water samples were taken by plastic bottles of 1 or 1.5 litres which were intended for drinking water.

## 3. Results and Discussion

The pH values of the rivers show that this parameter values fluctuated widely: 7.0 (Dzknaget) – 8.5 (Arpa), but mean values were in shorter interval - 7.4 (Lichq) – 7.9 (Karchaghbyur, Vardenis), which is typical for the acidity of good quality waters (Table 1). The only exception was observed in the Masrik

river, the unusually high pH value (8.7) of which was registered in October, and mean pH value was 8.3 (Table 1).

It is necessary to mention that the only bizarre result was registered in the Masrik river in October: water hardness of 6.0 meq/l, and the same time high basicidy (pH = 8.7) (Table 1). This was the only deviation from regularity, and such a result was never registered in the water samples. This result was observed in the conditions of PO value of 2.32 mgO<sub>2</sub>/l in the Masrik river. Apparently it was conditioned by the entrance of industrial discharges (Zod mine or other industrial wastewaters) into the river.

Table 1The values of pH, Temporary and Total Hardness in the Waters of the Rivers of the Lake Sevan Catchment Basin inJune-October, 2012

Date (2012) Object	pH				Temporary hardness meq/l			Total hardness meq/l					
								Compleximetric method			Salt settling method		
	03.0 6	20.0 8	01.1 0	Mean value	03.06	20.0 8	01.1 0	03.06	20.0 8	01.1 0	03.06	20.0 8	01.1 0
Masrik	8.3	7.9	8.7	8.3	1.6	1.2	3.9	2.05	2.5	6.0	2.0	2.4	5.9
Karchaghbyur	7.9	7.5	8.3	7.9	1.7	1.2	0.8	0.8	1.5	1.0	0.9	1.5	1.0
Argichi	7.9	7.3	7.4	7.6	1.0	1.8	1.2	1.0	2.3	1.5	1.0	2.3	1.5
Vardenis	8.2	7.5	-	7.9	0.2	2.1	-	0.4	2.6	-	0.4	2.5	-
Arpa	7.4	8.5	7.7	7.9	0.6	3.9	2.5	0.8	4.1	3.0	0.7	4.0	3.0
Lichq	7.6	7.4	7.2	7.4	1.6	1.6	1.5	1.6	1.8	1.7	1.7	1.8	1.8
Gavaraget	7.8	7.6	7.4	7.6	1.5	1.8	1.9	1.6	2.4	2.4	1.5	2.5	2.4
Dzknaget	8.2	8.2	7.0	7.8	0.9	2.0	1.8	1.0	2.1	2.0	0.9	2.1	1.9
Sevan-1	8.9	-	8.9	8.9	4.9	-	5.0	5.2	-	5.2	5.2	-	5.4
Sevan-2	8.9	-	8.9	8.9	4.9	-	5.0	5.2	-	5.3	5.2	-	5.3

Note: "-" - absence of data

According to the data in Table 2, PO value in the water samples before the settling of salts by the chemical method fluctuated widely:  $0.56 \text{ mgO}_2/\text{l}$  (Lichq) –  $3.52 \text{ mgO}_2/\text{l}$  (Dzknaget), and any common regularity wasn't revealed during the investigation period. However, PO values and particularly their mean values characterized the degree of organic pollution in each river, according to which, the most polluted river was Dzknaget (2.74 mgO\_2/l), and the cleanest river was Lichq (0.67 mgO\_2/l) (Table 2).

As mentioned in the methodical section, the total hardness of the waters was determined by the 2 independent methods — well-known compleximetric method and the chemical method based on the settling of salts [1]. The study results obtained by the 2 methods are given in Table 1 which shows that they coincide with each other and reveal the existence of mediate maximum. In all the rivers, a drastic increase in total hardness value was observed in August, then slight fall was registered till October. The same regularity was observed in temporary hardness value.

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Apparently a decisive factor was water temperature: it being higher in August (20°C) than in June (14°C) and October (12°C) stimulated higher intensity of chemical reactions according to the river flow. In the conditions of an increase in water temperature, the level of the solubility of bottom mineral matters in water increases.

Table 2Permanganate Oxidation (PO) Values in the Rivers of the Lake Sevan Catchment Basin before and after the Settlingof Salts

Date (2012) Object	PO	settling of salts	PO	PO value (mgO <sub>2</sub> /l) after settling of salts					
	03.06	20.08	01.10	Mean value	03.06	20.08	01.10	Mean value	г
Masrik	2.72	1.76	2.32	2.26	2.50	1.70	1.68	1.96	3.0
Karchaghbyur	2.00	0.80	1.76	1.52	1.92	0.72	1.52	1.39	1.3
Argichi	2.56	1.64	0.80	1.67	2.16	1.60	0.48	1.41	2.6
Vardenis	1.76	3.24	-	2.50	1.70	3.20	-	2.45	0.5
Arpa	1.92	3.08	0.48	1.83	1.90	3.00	0.32	1.74	0.9
Lichq	0.80	0.56	0.64	0.67	0.80	0.52	0.32	0.55	1.2
Gavaraget	1.44	1.04	1.44	1.31	1.40	1.00	1.12	1.17	1.4
Dzknaget	3.52	2.88	1.84	2.74	2.80	2.32	1.04	2.05	6.9
Sevan-1	-	-	2.88	2.84	-	-	2.56	2.44	4.0
Sevan-2	-	-	2.80	2.84	-	-	2.32	2.44	4.0
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Note: "-" - the absence of data; "F" - the reliability coefficient of the difference of mean PO values before and after the settling of salts.

The values of the same parameters in the water samples taken from the 2 coastal sites of Lake Sevan are given in Table 1. Water pH was stable and equal to 8.90. The total and temporary hardness was also quite stable and equal to 5.25 meq/l and 5.00 meq/l respectively. According to Table 2, the mean PO values (2.96 mgO<sub>2</sub>/l and 3.36 mgO<sub>2</sub>/l) were very close to the same parameter value of the lake in 1982 (3.9 mgO<sub>2</sub>/l) [4].

It is necessary to mention that the determination of water hardness by the method based on the settling of salts has such a big advantage that allows to determine PO value in desalted water after recording hardness value by settled salts and compare it to PO value measured in a water sample before the settling of salts. The comparative results of PO value study implemented by this scheme are given in Table 2. As the results show, in the water samples, PO values after the settling of salts. It is obvious that this difference should be attributed to PO values obtained by the degradation of salts. The calculation of the reliability coefficient (F) of the difference of mean PO values showed that this difference was statistically reliable (F > 2.4) in the

Masrik, Argichi, Dzknaget rivers and Lake Sevan [5]. The comparative analysis of these results didn't reveal any comparative relation with water hardness values (Table 1). It is possible to conclude that water hardness level doesn't affect PO value, and it is influenced by the qualitative nature of salts dissolved in water. Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mn<sup>4+</sup>, S<sup>6+</sup>, Cu<sup>2+</sup>, the salts of nitric acid can be considered as oxidant ions in water samples that affect PO value [6]. Instead of the quantitative determination of these matters, the calculation of oxygen consumption corresponding to their quantities and subtracting it from PO value, by the abovementioned method, we are able to separate integral PO values depleted on salts and to assess organic matter level in waters more precisely.

For example, according to Table 2, if before the settling of salts, the Dzknaget river was the most polluted with organic matters (2.74 mgO<sub>2</sub>/l), so after the settling of salts, the Vardenis river became the most polluted (2.45 mgO<sub>2</sub>/l), and the Dzknaget and Masrik rivers became almost equal to each other — 2.05 mgO<sub>2</sub>/l and 1.96 mgO<sub>2</sub>/l respectively. During the investigation period, low PO values measured by the 2 methods were recorded in the Lichq river.

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## 4. Conclusion

In all the investigated rivers, water acidity (pH) values were typical for good quality waters. In the investigated rivers and lake, the determination of the hardness of the waters by the salt settling and compleximetric methods gave completely coincident results recording an increase in August which apparently was conditioned by an increase in the level of the solubility of bottom mineral matters in water in the condition of high temperature. For taking into consideration the integral influence of salts on PO value, a new methodical approach was applied: the determination of PO value before and after the settling of salts as a result of which it is possible to separate integral PO values depleted on salts and to assess the level of organic matters in water more precisely. The

investigations have been clarified that PO value isn't directly related to the level of hardness in water.

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