INVESTIGATION OF CHEMICAL COMPOSITION OF THE ARAL SEA WATER IN AUTUMN SEASONS OF 2012 AND 2013

Abstract. The water level in the Aral Sea started drastically decreasing from the 1960s onward. The reduction in the volume and area of the sea has led to significant changes in the hydrological, chemical and natural biological structure of the water. Regular observations of the chemical composition of the Aral Sea stopped in the early 90s. There were practically no observations of biogenic elements and the oxygen regime of water (the so-called "first day" analyses).

In September 2012 and October 2013, a complex of hydrochemical observations, including the measurement of the content of biogenic elements, dissolved oxygen, the concentration of hydrogen sulfide and components of the carbonate equilibrium, was carried out within the framework of international expeditions. The determinations were carried out directly on the seashore in a temporary laboratory. The main purpose of the work was to determine the content of nutrients in the water of the Aral Sea and to develop methods for hydrochemical studies in conditions of increased salinity (mineralization) of water. In addition, samples were collected to determine the total mineralization of water and the content of dissolved and suspended forms of metals. It was shown that the small depth of the sea and the high intensity of the processes of vertical transport of substances allowed that seasonal changes in the chemical composition affected the entire vertical water. Deeper than 18-30 meters in water, there was hydrogen sulfide. The presence of anaerobic conditions in the deep part of the sea affected all hydrochemical parameters. Some research results are given in the article.

Key words: the Aral Sea, biogenic elements, oxygen.

Introduction. After a fairly long break, starting from 2002, the annual complex oceanographic studies of the Aral Sea was resumed by the Federal state budgetary institution of science of the IO RAS (Russia) and Khoja Akhmet Yassawi International Kazakh-Turkish University (Kazakhstan), together with the Institute of Geology and Geophysics named after Kh. M. Abdullaev (Academy of Sciences of Uzbekistan), Nukus State Pedagogical Institute named after Azhiniyaz (Uzbekistan) of Karakalpak State University named after Berdakh [1-3].

The study of the hydrochemical conditions of the reservoirs at such a stage of degradation as now the Aral Sea presents a unique opportunity for studying the catastrophic consequences of both anthropogenic impact and climate change. In this case, the Aral Sea can be considered as a unique natural laboratory as it does not sound cynical.

The correct determination of the content of biogenic elements practically excludes long-term transport of samples. The sooner the tests are performed, the more reliable the results are obtained. The permissible storage time for samples under different manuals is determined from 6 to 12 hours after the selection [3-5]. The conservation of samples naturally increases the risk of obtaining unreliable results. So, with the widespread procedure of sample freezing, it is possible to form a sparingly soluble precipitation or sorption of carbonates on the inner surface with a vial, which is especially manifested under conditions of increased mineralization. For this reason, analyses of the phosphate, nitrate, nitrite and ammonium nitrogen, as well as pH values are sometimes called "the first day analyzes". Therefore, in expeditions
Figure 1 – Scheme of location of stations where hydro-chemical observations were carried out in 2012 and 2013

hydrochemical studies were carried out directly on the seashore in 2012 and 2013. At the meteorological station Aktumsuk Uzhdromet (figure 1), located 8 km from the modern coastline on the Ustyurt plateau, a temporary hydrochemical laboratory was deployed.

In 2012-2013, the content of biogenic elements in the water of the Aral Sea was measured and the methods of hydrochemical studies were tested in conditions of extremely high salinity (mineralization) of water. Perhaps the complex of hydrochemical works, including the determination of dissolved oxygen, hydrogen sulfide, pH values and total alkalinity, the content of dissolved inorganic phosphorus, silicon, nitrogen in nitrate, nitrite and ammonium forms was performed on the Aral Sea shore for the first time since the beginning of the 1990s. The filtration and conservation of the samples for the subsequent determination of metals, suspended substances and general mineralization in stationary laboratories were also carried out.

**Materials and methods.** In 2012, selection of samples was conducted during outages at sea: 26, 27, 28 September. In 2013, it was carried out on 30, 31 October and 2 November. The sampling was conducted by a 5-liter plastic bottle of Niskin with the help of a hand winch mounted on an inflatable boat. The selection was preceded by sounding with an STD probe (SBE19plus). On the board after selecting, the samples were fixed for oxygen, hydrogen sulfide and ammonium nitrogen. The samples were taken in plastic bottles. Considering the need for conducting methodological work, a significant number of parallel determinations were performed by the use of various methods of analysis and sample preparation. The determination of biogenic elements was carried out in filtered water. The filtration was conducted through nuclear filters with a diameter of 47 mm with a pore size of 0.4 mm. The determination of hydrochemical parameters was carried out according to generally accepted methods [4-7].

With the onset of the sea level drop in the 1960s, the mineralization (the salinity) of the Aral Sea increased from about 10 to 100 g/kg or more in the western basin, while in the eastern basin, according to the data of the year 2008, the mineralization exceeded 200 g/kg [1]. Naturally, as for other hyperhaline reservoirs, the adaptation of existing methods to the conditions of increased salinity was a serious problem [2, 8].

As mentioned above, the question of the applicability of standard methods of hydrochemical work under conditions of high mineralization and the specific ionic composition of the Aral Sea waters was one of the basic for the hydrochemical group. The simplest reliable solution to this problem in the temporary laboratory was the dilution of samples. A part of the samples with colorimetric determinations was measured, both in natural samples and with varying degrees of dilution with distilled water.

The samples were diluted in a proportion of 1:4 and 1:3, which approximated their mineralization to the ocean salinity. Each series of samples included the determination of the content of this component in distilled water in order to take into account the degree of its contamination by the component being tested. In the diluted samples, the content was calculated by the following formula:
\[ C = K \cdot ((D_\lambda - D_\lambda^0) - (D_{\text{tw}} - D_\lambda^0) \cdot (1 - St)) / St. \]

Where \( C \) is the concentration of the determined characteristic; \( D_\lambda \) is the optical density of the sample with the appropriate wavelength method; \( K \) and \( D_\lambda^0 \) are the coefficient of recalculation and blank correction for reagents, which was determined in a stationary laboratory when the method was calibrated; \( D_{\text{tw}} \) is the optical density of distilled water with reagents, which is determined simultaneously with a series of samples; \( St \) is the proportion of the Aral water in a colorimetric sample.

**Results of methodical work.** It was found that in the undiluted samples, methods for determining nitrite and nitrate nitrogen with a “single color reagent” and determination of phosphates by the Morphy-Riley method are not applicable. At high concentrations of phosphates and nitrite nitrogen (more than 1.5 and 0.1 \( \mu M \), respectively) in undiluted samples, discoloration practically ceases.

The method for the determination of the Silicon Queen in undiluted samples gave underestimated results, in comparison with the diluted ones, by an average of 9%, but this may be due to the fact that the empirical formula for the salinity correction [4] is not sufficiently correct for such a high mineralization of water. The determination of ammonium nitrogen by the phenol-hypochloride method is applicable only for dilution of samples, at least 4 times, the dilution of the sample with distilled water should be carried out when sampling from the bathometer before fixation.

The method for determining dissolved hydrogen sulfide as well as the Winkler method for determining oxygen normally works in undiluted samples. To determine the total titrated alkalinity by the method of direct titration by Bruyevich, the dilution of the sample is not required, the procedure has no limitation on the value of salinity. But for the convenience of the analysis (too large was the natural value of total alkalinity, up to 17 mg-equiv/l) and the reduction in the analysis time, we applied the dilution of samples 2-3 times immediately before the titration.

The processing of the collected samples was continued in the Institute of Oceanology Russian Academy of Science. In the laboratory conditions, the content of total dissolved nitrogen and phosphorus was determined and the weight determination of salinity (mineralization) was conducted. A reliable determination of the mineralization value is extremely important for correcting STD sounding data. The latest published data on the ion-salt composition of the Aral waters refer to 2009 [1]. To obtain reliable results on the mineralization of water, the works were carried out to determine the so-called dry residue [9-11]. A separate article will be devoted to the methodological work on determining the general mineralization of the Aral Sea waters and discussing the results of these definitions.

**Results of the work**

In 2012 and 2013, hydrochemical work was carried out, mainly on a section passing through the Western basin (figure 1). A significant difference was that in 2012 observations were made in the autumn period, and in 2013 later, in the conditions of transition from autumn to winter. Naturally, seasonal changes strongly affected the content of biogenic elements and other hydrochemical parameters (table 1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
<th>Limits</th>
<th>Average</th>
<th>Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2012</td>
<td></td>
<td>2013</td>
</tr>
<tr>
<td>Oxygen (ml/l)</td>
<td>3.28</td>
<td>0 - 3.38</td>
<td>2.22</td>
<td>0 - 3.51</td>
</tr>
<tr>
<td>Oxygen (%)</td>
<td>111.3</td>
<td>0 - 115.8</td>
<td>58.8</td>
<td>0 - 92.8</td>
</tr>
<tr>
<td>pH, NBS</td>
<td>8.11</td>
<td>8.05 - 8.16</td>
<td>8.11</td>
<td>8.01 - 8.15</td>
</tr>
<tr>
<td>Alk, meq/L</td>
<td>11.26</td>
<td>11.109 - 11.448</td>
<td>11.49</td>
<td>11.16 - 12.78</td>
</tr>
<tr>
<td>P-PO₄ μg-at/l</td>
<td>1.80</td>
<td>0.24 - 8.96</td>
<td>6.92</td>
<td>0.79 - 14.59</td>
</tr>
<tr>
<td>P_total μg-at/l</td>
<td>3.55</td>
<td>1.43 - 17.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N-NO₂ υg-at/l</td>
<td>0.09</td>
<td>0 - 0.24</td>
<td>0.53</td>
<td>0.23 - 0.98</td>
</tr>
<tr>
<td>N-NO₂ υg-at/l</td>
<td>6.35</td>
<td>1.27 - 11.34</td>
<td>1.26</td>
<td>0.00 - 2.70</td>
</tr>
<tr>
<td>N-NO₃ μg-at/l</td>
<td></td>
<td></td>
<td>70.93</td>
<td>12.70 - 255.6</td>
</tr>
<tr>
<td>N_organic μg-at/l</td>
<td>276.6</td>
<td>209.1 - 424.0</td>
<td>516.1</td>
<td>317.1 - 651.7</td>
</tr>
<tr>
<td>Si - SiO₂ μg-at/l</td>
<td>43.44</td>
<td>39.42 - 46.39</td>
<td>33.59</td>
<td>17.27 - 120.27</td>
</tr>
<tr>
<td>H₂S</td>
<td></td>
<td></td>
<td>22.78</td>
<td>0.00 - 48.19</td>
</tr>
</tbody>
</table>
In addition to the seasonal course, a significant effect on the distribution of hydrochemical parameters was apparently also due to a change in the salinity profile observed in recent years. The smoothing of the vertical profile of mineralization caused a weakening of the stratification of waters and an increase in vertical exchange. The presence of anaerobic conditions in deep waters also has a significant effect on the hydrochemical regime. According to the literature [1], hydrogen sulfide in the deep waters of the Aral Sea was discovered in 2002, but, possibly, hydrogen sulfide contamination of water was presented even earlier, data on water chemistry between 1991 and 2002 are absent. The evidence, relating to the begin-ning of the twentieth century, about the presence of a smell of hydrogen sulfide in sediments and in the bottom layer of water was mentioned in the book by L. K. Blinov [12]. In the middle of the XX century, it was believed that the Aral waters were well aerated, due to vertical mixing and the development of photosynthetic processes throughout the water column [12-15].

The depth of occurrence of hydrogen sulfide from 2002 to 2010 varied from 15 to 35 m. According to the data of work [1], the highest content of hydrogen sulfide (80 mg/l) was observed in 2003. In 2012, in samples with 30 m and deeper, the smell of hydrogen sulfide was distinctly felt and oxygen was completely absent. The reason for the occurrence of hydrogen sulfide contamination, firstly, is the existence of a stable density stratification of water, and secondly, the low oxygen contents (the solubility of oxygen decreases significantly with increasing salinity) with a high content of organic matter. In 2013, the upper limit of the detection of hydrogen sulfide rose higher, up to 18 m.

Considering the distribution of hydrochemical parameters on the section passing through the western basin at about 58 ounces, it can be said that the hydrochemical composition of surface waters (up to 15-20 m) is fairly uniform across the vertical, but considerable variation in the composition of the waters was observed from the east to the west shore. In 2012, for the period of observations, the processes of production of organic substances were actively going on, the intensity of oxidative processes, on the contrary, was very weak. The relative content of oxygen in surface waters was high. The degree of saturation of water on the surface is on average above 110%. In 2013, the work, on the contrary, was at a decline in biological activity; the saturation of water with oxygen on the surface did not exceed 90%, and in some cases decreased to 60% or less. In 2013, the content of dissolved oxygen and the degree of its saturation increased, from the western to the eastern shore. An increase in the absolute and relative oxygen content of the western shore was observed in the entire upper layer (figure 2).

![Figure 2 - Distribution of the water saturation with dissolved oxygen (%) in the section on 58.5°c: min October 2013](image-url)

In both 2012 and 2013, the pH value varies not so much as dissolved oxygen, but falls from the west coast to the east, although the dynamics of these quantities are usually similar. In 2012, this may be due to an increase in the surface water temperature at the eastern shore, but the entire pH change cannot be explained solely by the difference in surface water temperature at the eastern and western shores. The range of surface water temperature changes was 1.26 °C, which is equivalent to a change in the pH value by 0.01-0.02 units of NBS [16, 17].
In 2013, the surface water temperature was practically the same in the section; the changes were only 0.47°C. Perhaps the pH increase in the western coast is related to the features of the functioning of aquatic biota, in particular, photosynthetic algae. The maximum pH value in the section in 2013 was noted in the 15-20 m layer near the western shore (figure 3). Such a distribution of the pH value is quite unexpected, since in this layer the oxidative conditions change to reducing ones, which, as a rule, is accompanied by a decrease in this value. In 2013, the pH value at the surface was slightly higher than in 2012, which is associated with a seasonal decrease in water temperature.

![Figure 3 – Distribution of the magnitude of pH in 2013](image)

For the total titrated alkalinity (Alk), a weak maximum in the central part of the sea was observed on the surface. In 2013, the value of Alk on the surface increased compared to 2012 by approximately 0.10 - 0.15 mg-eq/l. This is due to an increase in salinity from 105 to 114 g/l (Table 1). With depth, an increase in Alk, especially in anaerobic waters, is observed. According to the results of both surveys, a maximum of Alk was observed in the bottom waters of the deepest station A2 (figure 4).

![Figure 4 – Distribution of the magnitude of total titrated alkalinity in 2013](image)

In 2012, the phosphate content in surface waters rarely exceeded 1 mg-at/l. A significant increase in surface waters once noted at station A2 in 2012 may be due to the contamination of the sample, either during the selection process or during the transportation of samples to the onshore laboratory. In deep waters, below the layer of occurrence of hydrogen sulfide, the phosphate content increased to 8.96 mg-at/l.
In 2013, there was an increase in the phosphate content throughout the profile. The most growth was in the eastern, shallow part of the section. In the bottom waters, the phosphate content in 2013 also increased to 14.59 mg-at/l (figure 5).

![Figure 5](image1.png)

**Figure 5 – Distribution of the dissolved inorganic phosphorus content (mg-at/l) on 58.5°c.min October 2013**

For dissolved silicon on the surface, a small decrease in the silicon content in coastal waters can be noted in 2012, especially near the western shore. This may be due to the consumption of silicon by diatom algae, widely distributed in the sea waters [18]. The silicon content in surface waters varies little from the results of both surveys, from 21 to 26 mg-at/l. With depth, the silicon content increases, especially after the hydrogen sulfide occurrence boundary (figure 6). The maximum content of silicon reaches in the bottom waters.

![Figure 6](image2.png)

**Figure 6 – Distribution of the dissolved inorganic silicon content (mg-at/l) 58.5°c.min October 2013**

For nitrogen compounds in nitrate and nitrite forms in surface waters, a general drop in nitrate nitrogen to the eastern shore can be noted. The low content of nitrite nitrogen in 2012 indicates a weak intensity of the oxidation processes of organic substances, predominates synthesis processes that proclaim about the high saturation of water with oxygen. In 2013, on the contrary, the content of nitrite nitrogen on the surface is much higher than in 2013, and the content of nitrate nitrogen is much lower.

Taking into account the low saturation of water with oxygen, we can say that the processes of oxidation of organic substance prevailed in the upper, active layer of the water. The presence of anaerobic waters in the lower part of the profile led to the disappearance of oxidized forms of nitrogen. Because of this, a nitrate peak was formed in the 10-20 m layer, similar to what we observe in the aerobic waters of
the Black Sea [19]. A considerable part of the mineral dissolved nitrogen was contained in the form of an ammonium ion (up to 255.6 mg-at/l). The total content of dissolved nitrogen reached 434 and 652 mg-at/l (in 2012 and 2013, respectively). Such a large difference in the content of total dissolved nitrogen is most likely due to the fact that the position of the bottom bathometer was determined by the contact of the end load, and the depth of selection was fixed on the block of the counter. Technically, it was difficult to keep the boat in one place, and under these conditions, a change in the depth of selection of several meters could have a strong effect on the results of the analysis.

According to the data of 2013, it can be assumed that there was a "slip" of water along the western slope, caused by active cooling of the waters in the shallow part. This could be facilitated by the weakening of the stratification of waters. The descent of the waters along the slope is indicated by the bending of the isolines of the content of dissolved inorganic phosphorus and silicon, as well as the pH values (Figure). Perhaps this is due to the unusually high content of nitrate nitrogen and high pH values at the upper boundary of anaerobic waters.

**Conclusions.** Hydrochemical regime of the Aral Sea is characterized by sila variability in time. Seasonal changes in the chemical composition affect the entire vertical water. This contributes to the small depth of the sea and, probably, the high intensity of the processes of vertical transport of substances. But at the same time, vertical stratification of water was sufficient to preserve hydrogen sulfide contamination of the water. Despite the severe degradation of the marine ecosystem of the sea, the changes associated with the seasonal course of activity of aquatic biota remain significant. One cannot deny the existence of interannual changes associated with the continuing decline in the sea level and the penetration of waters from the eastern basin [20].

The presence of anaerobic waters in the lower part of the profile affected all hydrochemical parameters. In 2012, a sharp increase in the content of phosphorus and silicon was observed in a layer deeper than 30 m. Oxidized forms of nitrogen, on the contrary, disappeared. This led to the formation of a nitrate peak in the layer of 10-20 m. In 2013, the appearance of hydrogen sulfide was observed in the layer 18-19 m at all stations of the section. Deeper than 20 m, a significant increase in the content of dissolved phosphorus, silicon and ammonium nitrogen, the total alkalinity was observed.

An interesting and yet unexplained was the existence of a second maximum of the content of nitrate and nitrite nitrogen directly above the layer of hydrogen sulfide appearance. An increase in pH was observed in the upper part of the anaerobic layer. Perhaps this is due to the weakening of stratification and seasonal cooling of waters in coastal areas.

The smoothing of the vertical distribution profile of the mineralization of water during the transition from 2012 to 2013, naturally, caused a weakening of the stratification of waters and an increase in vertical exchange. But the hydrogen sulfide contamination of the water, in spite of this, remained, that is, even during the winter mixing of water, the bottom layer was not ventilated, despite a relatively small depth. And even a rise in the hydrogen sulfide occurrence limit was observed from 30 to 18 m. The latter, however, may be associated with a seasonal decrease in oxygen production in water.

Summarizing the results of the methodological work, it can be said that the determination of biogenic elements (phosphorus, silicon, nitrogen forms) must be preceded by filtration and dilution of samples with distilled water to salinity values comparable to the average oceanic (about 4 to 5 times). The method for determining the dissolved oxygen content (Winkler method) and the titrometric determination of hydrogen sulfide and total alkalinity is quite applicable for the Aral waters. Accuracy in these conditions is not worse than 2-3%. To clarify the magnitude of the error, additional methodological work is required.

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2012 қыңы 2013 ғылдырдарға құзы ғылымға қызмет етеді
АРАЛ ТЕНЗІІ СУУНЫҢ ХИМИЯЛЫҚ КУРАМЫН ЗЕРТЕУ

Аннотация. 1960 жылының басынан бастап Араң төңілінін дәнегей түссе басталды. Тенздің колемі мез алдыңғы кыр қысымдары, сүйенің гидрологиялық, қырымдың жөне элбетте, биологиялық құрылыымының айырымы өзгеруіне алып келді. Араң суының қырымдың курамының үнемділігі байқалу 90-шы жылдардың басында тәкіттілді. Суының биологиялық элементтері мен өсірі регіноң байқалу тәжірбесі жүзінде тәлік дәлдік берді (алашық құның тәлдімділігі). 2012 жылының кырык-сентябрьында мен 2013 жылының қазыңда қылымсатын қурылысының өсірін тесікке арқылы ортада жатады, сондықтан кеңейте көрсетуі мүмкін. Қырымдың жөніндегі аудармалардың ерекшелігі, курылысының кеңейтілуі қырымдарының үнемділігіңің өзгеруін құрылысының үнемділігін қысымдарын анықтаудың кеңейтілуі құрылысының үнемділігін қысымдарын анықтаудың қажеттілігін анықтайды. Қырымдарының құрылысының үнемділігі құрылысының үнемділігін анықтаудың қажеттілігін анықтайды. Мұқтала зерттеулер нәтижелері ұсынылады.

Түнің сөзі: Араң тензді, биологиялық элементтер, оттярі.
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ИССЛЕДОВАНИЯ ХИМИЧЕСКОГО СОСТАВА ВОД АРАЛЬСКОГО МОРЯ ОСЕНЬЮ 2012 И 2013 Г.

Аннотация. С начала 1960-х годов началось падение уровня Аральского моря. Сокращение объема и площади моря привело к значительным изменениям гидрологической, химической и, естественно, биологической структуры вод. Регулярные наблюдения за химическим составом вод Арала прекратились в начале 90-х годов. Практически полностью отсутствовали наблюдения за биогенными элементами и кислородным режимом вод (так называемые анализы «первого дня»). В сентябре 2012-го и октябре 2013-го годов в рамках международных экспедиций был проведен комплекс гидрохимических наблюдений, включающий измерение содержания биогенных элементов, растворенного кислорода, концентрации сероводорода и компонентов карбонатного равновесия. Определения проводились непосредственно на берегу моря во временной лаборатории. Основной целью работ было определение содержания биогенных элементов в воде Аральского моря и отработка методов гидрохимических исследований в условиях повышенной солености (минерализации) воды. Кроме того был проведен сбор проб для определения общей минерализации вод и содержания растворенных и взвешенных форм металлов. Было показано, что небольшая глубина моря и высокая интенсивность процессов вертикального переноса вещества, делали возможным, что сезонные изменения химического состава сказывались во всех вертикалях вод. Глубже 18–30 м в воде присутствовал сероводород. Наличие аварийных условий в глубокой части моря отразилось на всех гидрохимических параметрах. В статье приводятся некоторые результаты исследований.

Ключевые слова: Аральское море, биогенные элементы, кислород.

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