Laboratory Studies of Main Component Composition of Hyperhaline Lakes

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Introduction. Composition of water is an important hydrochemical characteristic of a salt water body. It is very important in shaping the conditions for the ecosystem functioning. This factor should be taken into account in determining water salinity since salinity measurements carried out by the standard oceanographic equipment using electrical conductivity in the water where the ion ratio is different from that in the oceanic water results in significant errors.
Data and methods. The present paper describes the analytical methods for laboratory determining the chlorides, sulfates, calcium, magnesium and total dissolved inorganic carbon concentrations using potentiometric titration, the potassium content – by the gravimetric method. These methods are adapted for hyperhaline waters having the different ion-salt composition as compared with the oceanic one. The method's error (relative deviation) did not exceed 1.7% for halogens, 4% for sulfates, 1.5% for carbonate ions, 0.7% for bicarbonate ions, 4% for calcium ions, 3.2% for magnesium and 1.3% for potassium.
Results. The components of main chemical composition of the hyperhaline reservoirs, namely the Aral and Dead seas, and Lake Urmia were obtained. Salinity of these water bodies represented by total amount of the basic ions were determined.
Discussion and conclusion. The natural basins under study represent the terminal lakes characterized by high water salinity, which is many times higher than that of the ocean water. The ratios of the main ions in the sources under study differ from each other significantly as well as from the similar ratios in the world ocean.

Keywords: ion composition, basic ions, automatic potentiometric titrator, Metrohm Titrando 905, hyperhaline lakes, the Aral Sea, the Dead Sea, the Lake Urmia.

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Introduction

The ion (component, chemical and salt) composition of water is an important hydrochemical characteristic of a salt water body. It plays an important role in shaping the conditions for the ecosystem functioning. The study of the ion composition is especially important in the economic use of water. This factor should be taken into account in determining water salinity since salinity measurements carried out by the standard oceanographic equipment using electrical conductivity in the water where the ion ratio is different from that in the oceanic water results in significant errors.

In some cases, the necessity of analyzing the composition of the waters of hyperhaline natural objects appears. These are lakes or other water bodies having mineralization (salinity) many times higher than the values characteristic of the ocean and its seas. Laboratory study of such waters has its own features.

History of the physicochemical state variations of the considered hyperhaline lakes have been studied by scientists for a long time. The results of these observations were published in a number of scientific papers. Historic records on the main component composition of the Aral Sea waters from 1952 to 1985 are given in the study [1, p. 102−103], for 2002−2009 – in [2, p. 78−79], the Dead Sea waters from 1959 to 1979 – in [3, p. 481] and for 2002 – in the report* and Lake Urmia for 2002 and 2008 – in [4, 5].

Based upon the available literature, the potentiometric method has not been previously used to analyze the ion-salt composition of hyperhaline reservoirs. The present paper represents the methods for determining the components of the ion-salt water composition when applying potentiometric titration, adapted to the study of water samples of hyperhaline reservoirs, using the example of the Aral Sea (western basin of the Southern Aral), the Dead Sea (northern basin) and Lake Urmia (northern part). The existing techniques modified to reflect the high salinity and characteristics of the salt composition of the studied samples were taken as the basis. Salinity of the analyzed samples taken during expeditions in 2017 ranged from 140 to 328 g/kg. The main advantages of potentiometric titration are high sensitivity and accuracy, ease of use, selectivity, the minimum amount of reagents required, as well as the quickness of the analysis. Potassium ions were measured by the gravimetric method. Concentration of sodium ions was established by calculating the difference between known amounts of anions and cations [6]. Comparative description of the considered lakes was also carried out. The data obtained was compared with the literature data of the ionic composition of the Standard Seawater [7, p. 60].

1. Equipment

The high-end potentiometric titrator *Metrohm* 905 *Titrando* (Switzerland) was applied to determine the ion composition. It is completed with indicator electrodes that record the change in the electrode potential at the equivalence point (the end point of the titration) during the titration process**. Electrodes are selected according to the type of the reaction and the ion to be detected. The measuring system allows carrying out any potentiometric titration, measuring the pH, electrode potential and temperature of the sample, as well as determining the concentration of anions and cations with high accuracy.

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* Esakov, S., ed., 2011. *Dead Sea Study: Final Report*. Tel Aviv, pp. 31-36. Available at: http://siteresources.worldbank.org/INTREDSEADEADSEA/Resources/Dead_Sea_Study_Final_August_2011.pdf [Accessed: 14 January 2019].

** Kreshkov, A.P., 1971. *Osnovy Analiticheskoy Khimii. Teoreticheskie Osnovy. Kolichestvennyy Analiz* [Analytical Chemistry Fundamentals. Theoretical Basis. Quantitative Analysis]. Moscow: Khimiya, p. 416.

The mass of the sample under analysis was measured by weighing on a laboratory analytical balance of the first accuracy class with an error of 0.001 g. Deionized water was used to dilute all reagents and samples. It was obtained using a laboratory deionizer. The conductivity of this water is less than 0.2 µS/cm. The reaction medium of the solutions during the analysis was monitored using a *Metrohm* combined pH electrode.

2. Methods

The existing methods for determining ions in sea and drinking water were modified based on the chemical composition of the waters of the considered water bodies: the samples were diluted with different proportions – by deionized water, concentrations of reagents were increased, reagents or procedures recommended by the basic method were excluded or replaced. The optimal sample volume for each analysis was determined empirically depending on the sample salinity.

2.1. Chlorinity determination

During the titration, poorly soluble compounds of silver halides are formed, the sum of which is called chlorinity (Cl). To determine the content of chlorides in drinking water (in a neutral or slightly alkaline environment), precipitation titration is done using indicators to determine the end point of the titration. Samples with the content of chlorine ion above 10 mg/dm^3 are titrated with silver nitrate in the presence of potassium chromate, while those with the content of chlorine ion below 10 mg/dm^3, with mercury nitrate in the presence of diphenylcarbazone indicator *. To determine the chlorinity of seawater, titration with silver nitrate in the presence of potassium chromate ** is used. In the work of foreign authors [8], the end determination point description of the titration potentiometric method is given.

The most common method for determining in seawater is the method of precipitation titration with silver nitrate ($AgNO_3$) with potentiometric determination of the end point of titration [8, 9]. It was applied to determine the chlorinity content of water in samples of hyperhaline lakes. For fixation, a *Metrohm Ag Titrode* combined electrode was used. It contains a silver ring membrane and a pH electrode as a reference. *Metrohm Ag Titrode* is suitable for the titration of chlorides, bromides, iodides, sulfides, mercaptans and cyanides (at constant pH values), for example, with silver nitrate. Used reagents are listed in Tab. 1.

The required amount of water for the sample (for the Aral Sea — 1 g, for the Dead Sea and Lake Urmia — 0.2–0.45 g) was placed in a measuring glass beaker. The sample was weighed on an analytic balance and its weight was recorded. The sample was refilled with deionized water to the 100 ml mark and titrated with a solution of $AgNO_3$ with a molar concentration of 0.1 mol/l (M).

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* Gosstandart, 1994. *GOST 4245-72. Voda Pit'evaya. Metody Opredeleniya Soderzhaniya Khloridov* [State Standart 4245-72. Drinking Water. Methods for the Determination of Chloride Content]. Moscow: IPK Izdatel'stvo standartov, 5 p. (in Russian).

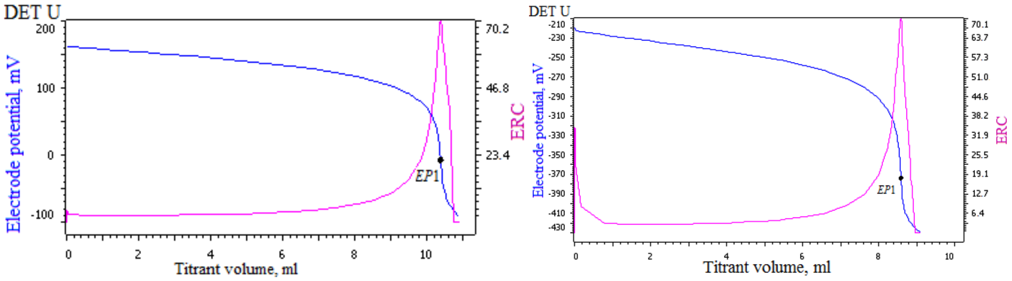
** Rosgidromet, 1993. *RD 52.10.243-92. Rukovodstvo po Khimicheskomu Analizu Morskikh Vod* [Guidance Document 52.10.243-92. Guidance on Chemical Analysis of Sea Waters]. Saint Petersburg: Gidrometeoizdat, 127 p. (in Russian).

Table 1

Concentrations of the reagent solutions for chlorinity determining

Name of reagent	Solution concentration
$AgNO_3$	0.1 mol/l
Standard volumetric solution HCl	0.1 mol/l
Analytical standard (AS) of composition of chloride-ion solution	1 mg/ml
Deionized water, conductivity is lower than 0.2 µkS/cm	

Fig. 1 shows an example of a titration curve illustrating the dependence of the electrode potential (U, mV) on the volume of titrant added (V, ml). The end point (equivalence point) $EP1$, marked on the graph, which is determined by the maximum of the first derivative of the titration function. An Equivalence point recognition criterion (*ERC*) value is a criterion for recognizing an equivalence point.



a *b*

F i g. 1. Titration graphs at determining chlorinity content with the end point *EP*1: *a* − 0.1M HCl solution; *b* − water sample from the Aral Sea. Blue line denotes the titration curve (change of the electrode potential); red line – the *ERC* titration function derivative

The result was calculated by the following formula

$$C_{\mathrm{Cl}} = \frac{V_{EP1} C_{\mathrm{AgNO_3}} M_{\mathrm{Cl}} K}{m},$$

where C_{Cl} is halogen ion concentration (chlorinity), g/kg; V_{EP1} is the volume of titrant, followed by titration to the *EP1* determination point, ml; $C_{\mathrm{AgNO_3}}$ is the titrant concentration, mol/l; M_{Cl} is Cl^- ion molar mass; m is the considered sample mass, g; K is the correction factor. The correction factor for the solution of the $AgNO_3$ titrant concentration of 0.1 mol/l was determined by the hydrochloric acid (HCl) solution titration of the same molar concentration*.

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* Gosstandart, 1994. *GOST 4245-72. Voda Pit'evaya. Metody Opredeleniya Soderzhaniya Khloridov* [State Standart 4245-72. Drinking Water. Methods for the Determination of Chloride Content]. Moscow: IPK Izdatel'stvo standartov, 5 p. (in Russian); Rosgidromet, 1993. *RD 52.10.243-92. Rukovodstvo po Khimicheskomu Analizu Morskikh Vod* [Guidance Document 52.10.243-92. Guidance on Chemical Analysis of Sea Waters]. Saint Petersburg: Gidrometeoizdat, 127 p. (in Russian).

It was experimentally established that the pH value of the solution during the titration within the required volume (10 ml) varies slightly (by 0.05) and linearly. Therefore, a change in pH does not have a significant effect on determining the equivalence point based on the maximum of the derivative of the titration function. NaCl or KCl can also be used to determine the titer correction.

2.2. Determination of sulfates

The classical methods for determining sulfates in standard sea water are the gravimetric method [8], based on precipitating sulfate ions by barium chloride and by weighing the resulting barium sulfate sediment, the chromatographic method and the potentiometric method of the back titration of excess barium ions after precipitation as $BaSO_4$. In drinking water, the concentration of sulfate ions is determined by titration with Trilon B (EDTA) in the measurement range from 25 to 500 mg/dm^3, barium chloride in the measurement range from 10 to 2500 mg/dm^3 and by turbidimetry in the measurement range from 2 to 50 mg/dm^3*, as well as by the method of back titration of excess barium ions using complexometric titration with Trilon B (EDTA)**.

In this work, the barium chloride direct titration method was applied to determine the content of sulfate ions in the samples under study with the registration of the end point of the titration with a potentiometric ion-selective membrane electrode *ECOM-Va**** produced by RPP *Econix* (Russian Federation) in combination with a reference electrode. At the equivalence point, if an excess of barium ions occurs in the solution, the electrode potential sharply rises, which is fixed by the electrode.

To form a stable barium sulfate sediment, the titration was carried out in an aqueous-alcoholic and acidic medium with pH = 2. The reagents used for the determination of sulfate ions and their concentrations are listed in Tab. 2

The correction factor (titer) was determined to bring the concentration of barium chloride solution to 0.1 mol/l by titration with a solution-of the magnesium sulfate ($MgSO_4$) with a molar concentration of 0.1 mol/l. The titer was set for each new solution of titrant. This correction was used when calculating the result according to GOST 31940-2012. Preparation of water samples for titration was carried out according to this GOST requirements. The Aral Sea water samples of 1–5 g, the Dead Sea and Lake Urmia of 0.5 g were placed in a measuring beaker. The sample was weighed on a laboratory analytic balance and its mass was recorded. 20 ml of ethyl alcohol was added to the sample and adjusted with 0.1M hydrochloric acid with a volume of 1–2 ml to pH = 2. Then it was topped up with 80 ml of deionized water and titrated with constant mixing to the equivalence point. The equivalence point was determined using a barium selective electrode.

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* Gosstandart, 2013. *GOST 31940-2012. Voda Pit'evaya. Metody Opredeleniya Soderzhaniya Sul'fatov* [State Standart 31940-2012. Drinking Water. Methods for Determination of Sulfate Content]. Moscow: Standartinform, 16 p. (in Russian).

** Metrohm, 2004. Food PAC 6.6055.003. *Methods for the Titrimetric/Potentiometric Analysis of Foodstuffs : Application File*.

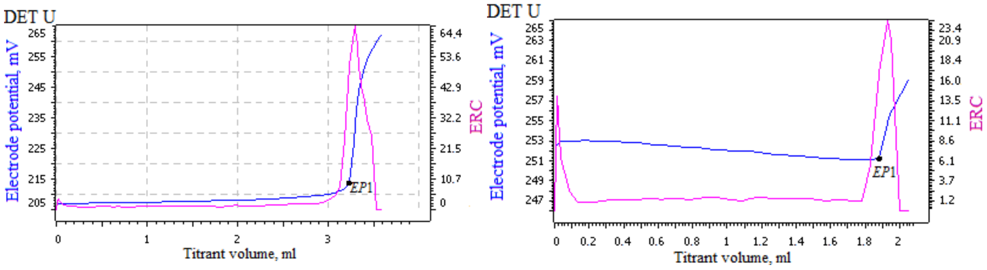
*** NPP Ekoniks, 2007. *Metodika Vypolneniya Izmereniy Massovoy Kontsentratsii Sul'fat-Ionov v Vode i Vodnykh Rastvorakh Potentsiometricheskim Metodom s Pomoshch'yu Ionoselektivnykh Elektrodov «EKOM-Va»* [Methods for Measuring the Mass Concentration of Sulfate Ions in Water and Aqueous Solutions by Potentiometric Method Using Ion-Selective Electrodes "ECOM-VA"]. Attestation Cert. 35-07 dated 11.05.2007. Moscow, 2007. 7 p. (in Russian).

Table 2

Concentrations of the reagent solutions for determining sulfates

Name of reagent	Solution concentration
2-water Barium chloride ($BaCl_2 \cdot 2H_2O$)	0.1 mol/l
Standard volumetric solution HCl	0.1 mol/l
Magnesium sulphate (standard titer) $MgSO_4$	0.1 mol/
Analytical standard (AS) of composition of chloride-ion solution	1mg/ml
Ethyl alcohol	95%
Deionized water, conductivity is lower than 0.2 μkS/cm	

Fig. 2 shows an example of a titration curve for a 0.1 M solution of $MgSO_4$ with the determination of the end point (equivalence point) *EP1*, which is determined by the maximum of the first derivative of the titration function and shows that the number of equivalents of the added EDTA titrant is equal to the number of equivalents of sulfate ions.



a *b*

F i g. 2. Titration graphs with the end point (*EP*1): *a* − 0.1M $MgSO_4$ solution; *b* − water sample from the Urmia Lake. Blue line denotes titration curve (change of the electrode potential); red line – derivative of the *ERC* titration function

The sulfate ion concentration was calculated by the following formula

$$C_{SO_4^{2-}} = \frac{V_{EP1} \cdot C_{BaCl_2} \cdot M_{SO_4^{2-}} \cdot K}{m}, \qquad (2)$$

where $C_{SO_4^{2-}}$ is the sulfate ion concentration; V_{EP1} is the volume of titrant, followed by titration to the point of determination, ml; C_{BaCl_2} is the barium chloride titrant concentration, mol/l; $M_{SO_4^{2-}}$ is the sulfate ion molar mass; m is the studied sample mass, g; K is the correction factor.

2.3. Determination of calcium and magnesium

The method of complexometric titration with a solution of EDTA (Trilon B, ethylene diamine tetraacetic acid disodium salt $Na_2H_2Y_2H_{20}$) in an alkaline medium at pH = 10 was used to determine calcium and magnesium. The basis of the titration is complexation, which results in the formation of sufficiently stable complexes [10, p. 49]. Since the Ca^{2+} and Mg^{2+} ions have different stability factors*, first complexones with calcium and then with magnesium with the appearance of two equivalence points are formed. The points were determined using a *Metrohm* calcium-selective membrane electrode. The advantage of this method is that it allows both calcium and magnesium to be determined with great accuracy in a single titration process. The reagents used are presented in Tab. 3

Table 3

Concentrations of the reagent solutions for determining calcium and magnesium

Name of reagent	Solution concentration
Trilon B (EDTA)	0.1 mol/l
Standard volumetric solution HCl	0.1 mol/l
Magnesium sulfate (standard-titer) $MgSO_4$	0.1 mol/l
Ammonia buffer ($NH_4Cl + NH_4OH$)	pH = 10
AS of composition of calcium ion water solution (Ca^{2+})	1 mg/ml
AS of composition of magnesium ion water solution (Mg^{2+})	1 mg/ml
Deionized water, conductivity is lower than 0.2 μkS/cm	

The correction factor (titer) to bring the concentration of the EDTA solution to 0.1 mol/l was determined by titrating the $MgSO_4$ solution with a molar concentration of 0.1 mol/l prepared from standard titer**. The titer was taken into account when calculating the result.

Ammonia buffer with pH = 10 was prepared by introducing into a volumetric flask with a volume of 1000 ml 20 g of ammonium chloride, 100 ml of deionized water and 100 ml of a solution of an aqueous ammonia with a mass fraction of 25%***.

For the Aral Sea samples, a sample of 1 g was taken, for the Dead Sea and Lake Urmia – of 0.5 g. A sample of 3 ml of ammonia buffer was added to maintain pH = 10 and topped up with deionized water up to a volume of 80 ml. The pH of the finished sample was measured and titrated with EDTA solution with a concentration of 0.1 mol/l to the second equivalence point. For fixing the end point, a combined *Metrohm scION Tip Ca* ion-selective polymembrane electrode, equipped with interchangeable tips in combination with a reference electrode, was used. The result for ion concentration was calculated by the formulas below

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* Yakovlev, K.I. and Stetsenko, A.I., eds., 2003. Kompleksonometricheskoe Titrovanie [Complexometric Titration]. In: *Metodicheskie Ukazaniya k Vypolneniyu Laboratornykh Rabot po Kursu Kolichestvennogo Khimicheskogo Analiza* [Methodical Instructions for Laboratory Work in the Course of Quantitative Chemical Analysis]. Saint Petersburg: SPKHFA, pp. 8-39.

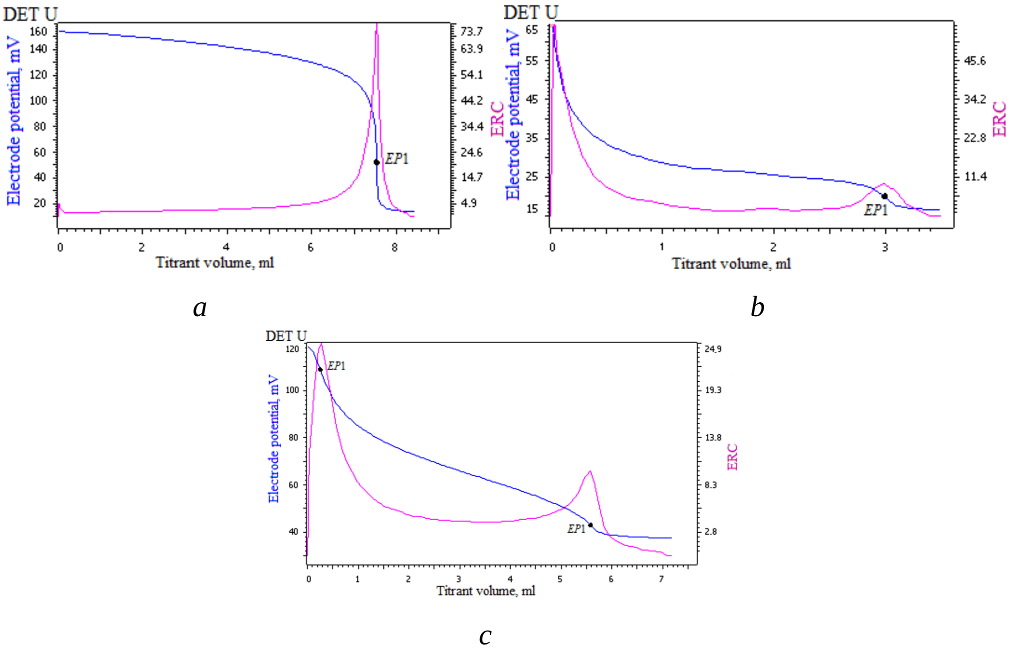
** Metrohm, 2004. Food PAC 6.6055.003. *Methods for the Titrimetric/Potentiometric Analysis of Foodstuffs : Application File*.

*** Gosstandart, 2013. *GOST 31940-2012. Voda Pit'evaya. Metody Opredeleniya Soderzhaniya Sul'fatov* [State Standart 31940-2012. Drinking Water. Methods for Determination of Sulfate Content]. Moscow: Standartinform, 16 p. (in Russian).

$$C_{\mathrm{Mg}^{2+}} = \frac{(V_{EP2} - V_{EP1}) \cdot C_{\text{ЭДТА}} \cdot M_{\mathrm{Mg}^{2+}} \cdot K}{m} \qquad (3)$$

$$C_{\mathrm{Ca}^{2+}} = \frac{V_{EP1} \cdot C_{\text{ЭДТА}} \cdot M_{\mathrm{Ca}^{2+}} \cdot K}{m}, \qquad (4)$$

where $C_{\mathrm{Ca}^{2+}}$, $C_{\mathrm{Mg}^{2+}}$ are the concentrations of calcium and magnesium; V_{EP1} is the volume of titrant, followed by titration to the first point of determination, ml; V_{EP2} is the volume of titrant, followed by titration to the second point of determination, ml; C_{EDTA} is the EDTA (titrant) concentration, mol/l; $M_{\mathrm{Ca}^{2+}}$, $M_{\mathrm{Mg}^{2+}}$ is the molar mass of calcium and magnesium ions; m is the sample mass, g; K is the correction factor.



a *b*

c

F i g. 3. Determination of the end points of calcium *EP*1 and magnesium *EP*2 by the example of titration: *a* – AS of composition of the calcium ion water solution (Ca^{2+}); *b* – AS of composition of the magnesium ion water solution (Mg^{2+}); *c* – water sample from the Aral Sea. Blue line denotes titration curve (change of the electrode potential); red line – derivative of the *ERC* titration function

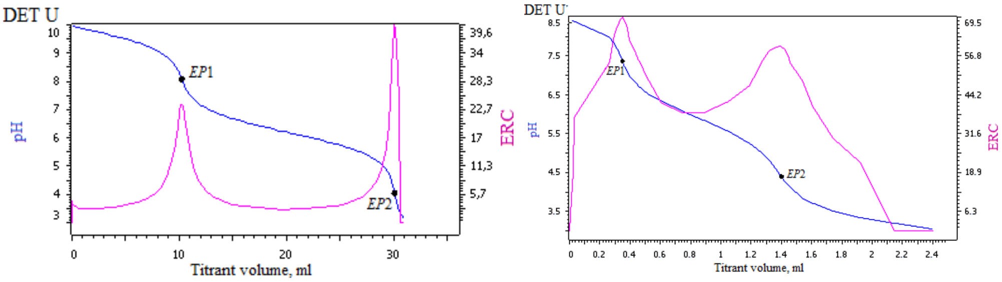
Fig. 3*c* shows an example of a titration curve of the Aral Sea sample with end points *EP*1 and *EP*2, which are determined from the maximum of the first derivative of the titration function.

2.4. Determination of total inorganic dissolved carbon and total alkalinity

In order to determine the contribution of total dissolved carbon (T_{CO2}) to the main component composition of water in hyperhaline lakes, its content in samples was measured. The obtained value was calculated as HCO_3, since the proportion of bicarbonate ions in the carbonate system of seawater is about 90% [6].

To characterize the components of the carbonate system in seawater, it is necessary to measure at least two of the four parameters (pH, total alkalinity, total dissolved inorganic carbon and partial pressure of carbon dioxide (pCO_2) [6].

In the samples under study, total dissolved carbon and total alkalinity (A_T) were determined by acid-base titration. Total carbon was measured in mmol/kg and calculated in g/kg as a bicarbonate ion. The method is based on the titration of the sample with a strong acid without removing the carbon dioxide produced [6, p. 274–276] until two equivalence points appear. In the process of direct titration of the sample with a solution of hydrochloric acid, a change in the concentration of hydrogen ions [H+] or pH occurs. This change is fixed by the pH indicator electrode (Fig. 4).



a *b*

F i g. 4. Determination of the end points *EP*1 and *EP*2 by the example of titration of the samples: *a* – made of the standard-titers of 0.1M solution K_2CO_3 + 0,1M $NaHCO_3$; *b* – from the Aral Sea. Blue line denotes titration curve (change of the electrode potential); red line – derivative of the titration function *ERC*

The reagents used to determine T_{CO2} and A_T are listed in Tab.4. In the case of preparing the HCl solution from concentrated acid (not from a standard-titer), it is necessary to determine the correction factor*.

Table 4

Concentrations of the reagent solutions used for determining total dissolved carbon and total alkalinity during titration

Name of reagent	Solution concentration
Standard volumetric solution HCl	0.1 mol/l
$NaHCO_3$	0.1 mol/l
Standard volumetric solution K_2CO_3	0.1 mol/l
Deionized water, conductivity is lower than 0.2 µkS/cm	

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[*] Rosgidromet, 1993. *RD 52.10.243-92. Rukovodstvo po Khimicheskomu Analizu Morskikh Vod* [Guidance Document 52.10.243-92. Guidance on Chemical Analysis of Sea Waters]. Saint Petersburg: Gidrometeoizdat, 127 p. (in Russian). Available at: http://oceanography.ru/images/stories/lmz/docs/rd_52_10_243-92.pdf (accessed 14 January 2019).

For the Aral and Dead Seas, a 10 ml water sample was taken while Lake Urmia sample was not analyzed. The sample was weighed on an analytic balance and its weight was recorded, then it was topped up with deionized water to a volume of 100 ml and titrated with a solution of 0.1M HCl to the second equivalence point. The points were determined using a *Metrohm* pH electrode calibrated according to the instruction manual for the electrode. Total alkalinity was calculated by the following formula

$$A_{\mathrm{T}} = \frac{(V_{EP2} \cdot C_{\mathrm{HCl}})}{m}, \tag{5}$$

total carbon content - according to the formulas [6, p. 276]

$$C_{T\mathrm{CO}_2} = \frac{(V_{EP2} - V_{EP1}) \cdot C_{\mathrm{HCl}}}{m}, \tag{6}$$

$$m_{T\mathrm{CO}_2} = C_{T\mathrm{CO}_2} \cdot M_{\mathrm{HCO}_3^-}, \tag{7}$$

where A_{T} is the total alkalinity, mmol/kg; T_{CO2} is the total carbon concentration, mmol/kg; $m_{T\mathrm{CO}_2}$ is the total carbon mass, expressed by HCO_3^- equivalent, g/kg; V_{EP1} is the volume of titrant that went to the titration to the first point, ml V_{EP2} is the volume of titrant that went to the titration to the second point, ml; C_{HCl} is HCl (titrant) concentration, mol/l; $M_{\mathrm{HCO}_3^-}$ is the molar mass of bicarbonate ion; m is the sample mass in grams.

It should be noted that borate alkalinity ($B(OH)_4$), being 2.9% of the total alkalinity in sea water, is also titrated to the first point [6]. The results of determining the total alkalinity and total carbon are presented in Tab. 7

2.5. Determination of potassium

The potassium concentration in the considered samples was determined by the gravimetric (weight) method described in GOST 23268.7-78*, as well as in [8, 9], based on the subsidence of potassium ions with sodium tetraphenyl borate $Na[B(C_6H_5)_4]$. It allows determining the concentration of potassium ions in the sample with great accuracy. A list of reagents and their concentrations are given in Tab.5.

Table 5

Concentrations of the reagent solutions used for determining potassium by the gravimetric method

Name of reagent	Solution concentration
Sodium tetrapheniylborate solution	3%
Standard volumetric solution HCl	0.1 mol/l
AS of composition of potassium ion water solution	0.1 mol/l
Deionized water, conductivity is lower than 0.2 μkS/cm	

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* Gosstandart, 2003. *GOST 23268.7-78. Vody Mineral'nye Pit'evye Lechebnye, Lechebno-Stolovye i Prirodnye Stolovye. Metody Opredeleniya Ionov Kaliya* [State Standart 23268.7-78. Mineral Drinking Medicinal Water, Medical Table and Natural Table. Methods for the Determination of Potassium Ions]. Moscow: IPK Izdatel'stvo standartov, 4 p. (in Russian).

3 to 10 ml of the analyzed water was taken in a way that it contained 20–40 mg of potassium ions. A sample of the Aral Sea water was taken with a volume of 10 ml, the Dead Sea one – 4 ml and one of Lake Urmia – 3 ml. The sample was weighed, and its weight was recorded on an electronic balance. The sample volume was topped up to 100 ml with deionized water, 4 ml of 1M HCl solution was added. The resulting sample was cooled to 0−2°C. Then 15 ml of 3% sodium tetraphenyl borate solution was added dropwise with stirring. Then it was cooled again to 0−2°C for 10 min to form a more stable sediment. The sediment formed was filtered through crucible filter No. 3 or No. 4, previously weighed to constant weight. The crucible filters with the sediment were dried at 110°C, cooled in a desiccator and weighed to constant weight [8]. Measurements for each sample were carried out at least two times. The absolute deviation did not exceed 4%. The concentration calculations were carried out according to the following formula

$$C_{\mathrm{K}^+} = \frac{m_{\text{осд}} \cdot 0{,}109 \cdot 1000}{m}, \tag{8}$$

where C_{K^+} is the potassium concentration, g/kg; $m_{\text{осд}}$ is the sediment mass, g; 0.109 is the conversion factor for potassium; m is the sample mass, g.

2.6. Determination of sodium

Sodium was determined as the difference between the sum of anions and cations in mole equivalents [6] and then recalculated in g/kg according to the formula below

$$C_{\mathrm{Na}^+} = M_{\mathrm{Na}^+} \cdot cM_{\mathrm{Na}^+}, \tag{9}$$

where C_{Na^+} is the ion concentration, g/kg; M_{Na^+} is the ion molar mass; cM_{Na^+} is the sodium ion concentration, mole equivalent.

2.7. Testing of the accuracy of basic ions determination methods By potentiometric titration and gravimetric method for potassium

The methods described above were tested on state standard reference samples (AS) and standard titers by the potentiometric titration and by the gravimetric method for potassium. The results of the tests (error evaluation) are presented in Tab. 6. Measurements of the standard titres were carried out at least three times, the SRS measurements – 1–3 times. Standardization of the pH electrode was carried out on buffer samples according to the instruction manual of the electrode. The standard deviation between measurements did not exceed 0.02 g/l. The permissible error of the SRS specified by the manufacturer is ± 0.02 g/l.

Table 6

Results of testing the methods used for determining the ions by measurements of the corresponding standard titers and as of the corresponding ions

Assessment of errors	Ions						
	Cl^-	SO_4^{2-}	CO_3^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	K^+
when measuring standard titers							
Absolute deviation, g/l	< 0.23	< 0.06	< 0.09	< 0.04	< 0.16	< 0.03	< 0.05
Relative divergence, %	< 0.65	< 0.58	< 1.49	< 0.70	< 4.00	< 1.16	< 1.30
when measuring AS							
Absolute deviation, g/l	< 0.02	< 0.06	< 0.09	< 0.04	< 0.06	< 0.03	<0.05
Relative divergence, %	< 1.70	< 4.00	< 1.50	< 0.70	< 4.00	< 3.20	< 1.30

3. Application of ion determination methods to study Chemical composition of water of hyperhaline reservoirs

As noted above, the methods were used to study the ionic composition of the following water bodies: the Aral Sea, the Dead Sea and Lake Urmia. Samples of their water were obtained in 2017. The Aral Sea water samples were taken in the western basin of the Big Aral (Uzbekistan) at the end of October 2017 (two samples from the surface and one from a maximum depth of 29 m), the Dead Sea water samples (Israel) – in the northern part from the surface of the water body (one on 02.08.2017 and two on 8.10.2017). A sample of Lake Urmia (Iran) water was obtained from the reservoir surface in its northern part on 28.08.2017. Sampling and storage of samples was carried out in accordance with GOST 17.1.5.04-81 *, GOST 17.1.5.05-85 **, DD 52.10.743-2010 ***. Samples were delivered to the laboratory within 2–3 days. The results of the analysis of the main ions of the considered lakes, calculated as average for five measurements, are presented in Tab. 7. Fig. 5 shows examples of ion concentrations as a percentage of the total salinity of the samples and their sulfate-chloride ratios.

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* Gosstandart, 2003. GOST 17.1.5.04-81. *Okhrana Prirody (SSOP). Gidrosfera. Pribory i Ustroystva dlya Otbora, Pervichnoy Obrabotki i Khraneniya Prob Prirodnykh Vod. Obshchie Tekhnicheskie Usloviya* [State Standart 17.1.5.04-81. Nature Conservation. Hydrosphere. Devices and Devices for the Selection, Primary Processing and Storage of Samples of Natural Waters. General Technical Conditions]. Moscow: IPK Izdatel'stvo standartov, 7 p. (in Russian).

** Gosstandart, 2003. GOST 17.1.5.05-85. *Okhrana Prirody (SSOP). Gidrosfera. Obshchie Trebovaniya k Otboru Prob Poverkhnostnykh i Morskikh Vod, L'da i Atmosfernykh Osadkov* [State Standart 17.1.5.05-85. Nature Conservation. Hydrosphere. General Requirements for Sampling Surface and Sea Waters, Ice and Precipitation]. Moscow: IPK Izdatel'stvo standartov, 12 p. (in Russian).

*** FGU GOIN, 2010. RD 52.10.743-2010. *Obshchaya Shchelochnost' Morskoy Vody. Metodika Izmereniy Titrimetricheskim Metodom* [Guidance Document 52.10.743-2010. Total Alkalinity of Sea Water. Measurement Method Titrimetric Method]. Moscow: FGU GOIN, 20 p. (in Russian).

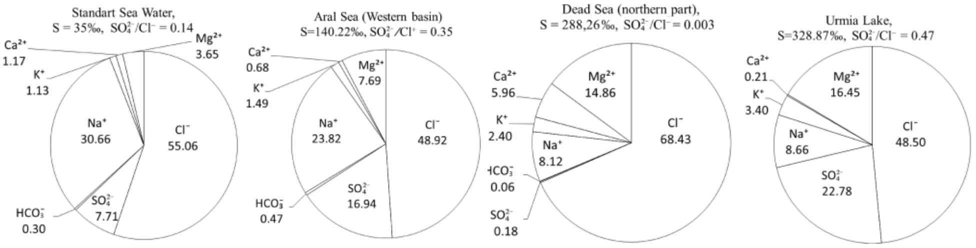
Table 7

Chemical composition of water in the hyperhaline basins and standard seawater (based on [7])

Region and date of sampling	Depth and location of sampling	Anions, g/kg	Anions, g/kg			Cations, g/kg			Mg^{2+}	Alk, mmol/l
			Cl	SO_4^{2-}	HCO_3^-	Na^+	K^+	Ca^{2+}		
Standard seawater	-	35.165	19.350	2.712	0.105	10.781	0.399	0.412	1.284	2.300
Aral Sea, the western basin, 27.10.2017	0 m, by the coast	140.222	68.599	23.753	0.661	33.395	2.085	0.953	10.777	13.946
	0 m, station A2 [1]	140.060	68.517	23.875	0.568	33.235	2.082	0.914	10.871	14.249
	29 m, station A2	140.620	64.107	28.753	0.615	34.039	1.952	0.941	10.213	13.542
Dead Sea, the northern part, 02.08.2017, 08.10.2017	0 m, by the coast	267.686	182.772	0.627	0.104	22.228	6.382	16.488	39.085	5.198
	0 m, by the coast	288.050	197.248	0.515	0.162	22.957	6.913	17.177	43.078	5.146
	0.5 m, by the coast	297.373	200.699	0.305	0.162	30.347	6.605	16.231	43.025	5.085
Urmia Lake, the northern part, 28.08.2017	0 m, by the coast	328.870	159.506	74.920	no data	28.472	11.180	0.704	54.087	no data

Note. Station A2 [1] is the sampling station located in the deepest part of the lake.

The data on the ionic composition of standard seawater are taken from the work of F. Millero [7]. The data analysis revealed significant differences in the ratio of the concentrations of the main ions between the waters of different hyperhaline reservoirs and between the waters of hyperhaline lakes and standard sea water. The obtained data expands the available information on the hydrochemical characteristics of the studied natural water bodies and the processes occurring in them.



F i g. 5. Concentrations in percent and ratios of the main ions in the basins under study

4. Check of the accuracy of the determination of ions in the salt waters of natural sources

In waters with a complex hydrochemical composition, individual (interfering) ions may have an effect on the accuracy of determination of other components*. For example, orthophosphates and iron may interfere with the determination of chlorine ions. Calcium subsidence is possible during the sedimentation of sulfates [6]. The presence of a large amount of ions of iron, copper, cadmium, cobalt, lead, manganese (II), aluminum, zinc, cobalt, nickel, tin and increased turbidity** can lead to an overestimation of the determination of calcium and magnesium ions. During potentiometric titration, interfering ions can influence the value of the electrode potential.

In order to check how the interfering ions affect on the titration result, the following measurements were carried out. To the Aral Sea water samples with a previously determined content of ions under study solutions with a known content of the same ions were added. The samples were titrated. The results were compared with the calculated ones and expressed as percentages. This procedure was repeated five times. Similar measurements and calculations were carried out for standard sea water (SSW) with a salinity of 34.996‰ (*OSIL*).

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* Gosstandart, 1994. *GOST 4245-72. Voda Pit'evaya. Metody Opredeleniya Soderzhaniya Khloridov* [State Standart 4245-72. Drinking Water. Methods for the Determination of Chloride Content]. Moscow: IPK Izdatel'stvo standartov, 5 p. (in Russian).

** Gosstandart, 2013. *GOST 31940-2012. Voda Pit'evaya. Metody Opredeleniya Soderzhaniya Sul'fatov* [State Standart 31940-2012. Drinking Water. Methods for Determination of Sulfate Content]. Moscow: Standartinform, 16 p. (in Russian).

Tab. 8 shows the results of test measurements of chlorination titration, Tab. 9 – of sulfate ions, Tab. 10 – of calcium ions and in Tab. 11 – of magnesium ions.

Table 8

Calculation of accuracy of the chlorine content determination In the Aral Sea water sample and standard seawater

Type of a sample	Cl of a sample, mg	additional Cl, mg	Calculated Cl, mg	Titrated Cl, mg	Convergence, %
the Aral Sea Sample + HCl	64.9238	10.7538	75.6776	76.6559	98.7
	35.0230	11.5379	46.5609	46.5605	100.0
	33.4223	10.9489	44.3712	44.4043	99.9
SSW Sample + HCl	20.2981	10,7112	31.0093	31.0799	99.7
	20.1805	10.7219	30.9024	31.0406	99.5
	20.3178	11.3357	31.6535	31.4168	100.7

Table 9

Calculation of accuracy of the sulfate-ions determination In the Aral Sea water sample and standard seawater

Type of a sample	SO_4^{2-} of a sample, mg	Additional SO_4^{2-}, mg	Calculated SO_4^{2-}, mg	Titrated SO_4^{2-}, mg	Convergence, %
Aral Sea Sample + H_2SO_4	52.7372	28.9702	81.7074	81.2438	100.6
	52.9279	29.2442	82.1721	82.1854	100.0
	53.4760	28.8946	82.3706	82.2870	100.1
SSW Sample + H_2SO_4	8.7122	45.9610	54.6732	53.3922	102.4
	9.6614	15.4945	25.1559	24.4638	102.8
	6.9550	23.8355	30.7905	29.9401	102.8

Table 10

Calculation of accuracy of the calcium ions determination In the Aral Sea water sample and standard seawater

Type of a sample	Ca^{2+} of a sample, mg	Additional Ca^{2+}, mg	Calculated Ca^{2+}, mg	Titrated Ca^{2+}, mg	Convergence, %
The Aral Sea Sample + $CaCl_2$	0.9637	6.4016	7.3653	7.4501	98.9
	0.9246	6.4495	7.3741	7.4399	99.1
	0.9385	6.6605	7.5990	7.5493	100.7
SSW Sample + $CaCl_2$	0.9527	6,7340	7.6867	7.8544	97.9
	0.9583	6,5294	7.4877	7.5717	98.9
	0.9424	6,5518	7.4942	7.5868	98.8

Table 11

Calculation of accuracy of the magnesium ions determination In the Aral Sea water sample and standard seawater

Type of a sample	Mg^{2+} of a sample, mg	Additional Mg^{2+} , mg	Calculated Mg^{2+} , mg	Titrated Mg^{2+} , mg	Convergence , %
The Aral Sea Sample + $MgSO_4$	12.2240	7.6704	19.8944	20.0467	99.2
	12.2129	7.5657	19.7786	20.1216	98.3
	12.2018	7.9420	20.1438	20.0542	100.4
SSW Sample + $MgSO_4$	2.7416	7.6455	10.3870	10.2442	101.4
	2.7161	7.5308	10.2470	10.2657	99.8
	3.0212	7.5134	10.5346	10.4722	100.6

Tab. 12 shows an estimate of the accuracy of the testing measurements of ions, determined by potentiometric titration of natural sources in salt and hyperhaline water samples. The good convergence of the results measured with the calculated ones proves the insignificant effect of interfering ions.

The test results showed that determining the concentration of ions in standard water with a salinity of 35‰ applying the methods described above has an error of 1.4–2.8%, and in water of the Aral Sea sample with a salinity of 140‰ – of 0.6–1.7%.

Table 12

Results of testing accuracy in determining ions in the Aral Sea water sample and World ocean waters (%)

Type of a sample	Ions			
	Cl	SO_4^{2-}	Ca^{2+}	Mg^{2+}
The Aral Sea	< 1.3	< 0.6	< 1.1	< 1.7
Standard seawater	< 2.7	< 2.8	< 2.1	< 1.4

5. Comparative characteristics of reservoirs under study

The hyperhaline under study reservoirs are drainless lakes, and their waters are highly mineralized brines. These reservoirs are located in arid climatic zones and have a negative water balance. They are exposed to degradation mainly due to the human activity and partly due to natural processes. A level of the water bodies is steadily decreasing. Brines evolve and minerals precipitate.

But at the same time, there are many differences between the hyperhaline reservoirs. They have different depths and areas and are located at different heights relative to sea level. Until 1960s the Aral Sea level fluctuated at an altitude of about 53.5 m above sea level at a depth of 66 m [2, 11]; in 2017, the sea level dropped to 29.5 m. The Dead Sea is more than 400 m below sea level, and its depth is today about 400 m *. Highland Lake Urmia is located at an altitude of 1.250 m above sea level, and its average depth is 5 m [12].

The chemical composition study of these lakes revealed both significant differences in salinity, the ratio of the main ions between the lakes and their differences from similar characteristics of ocean water.

Despite the same set of basic ions in hyperhaline reservoirs, their ratio is different from the ratio of ions in the ocean (Fig. 5). In addition, it changes with time. Comparison of the data with previously published one allows estimating these changes for each reservoir (Fig. 6). The figure shows that the processes of deposition of the ions in lakes are different. They depend on many factors: on the initial chemical composition, which is affected by water inflow, ion concentrations, air humidity, temperature and evaporation rate [13]. This analysis can help in studying the processes of salt deposition.

The Aral Sea data for several previous years were taken for comparison from the study [2], for the Dead Sea one – for 1979 from the article [3] and for 2002 from the report **, for Lake Urmia for 1977 – from [14], for 2002 – from [4] and for 2008 – from [5].

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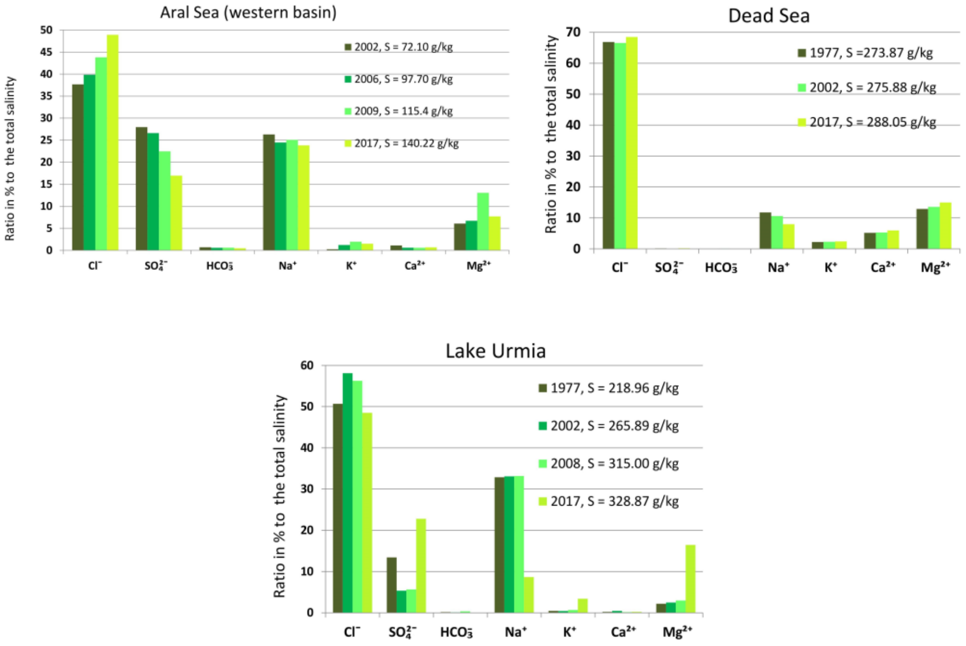
* Dead Sea study: Final report. Tel Aviv, 2011. P. 31–36.

** Ibid.



F i g. 6. Comparison (percentage wise to the sample total salinity) of the component composition of the hyperhaline lakes obtained in 2017 with the previously published data

6. Conclusions

The methods allowing determining the ionic composition of hyperhaline lakes using an automatic potentiometric titrator are given. The advantages of this approach are the use of a small amount of the sample and a significant reduction in the time of analysis. These methods can be applied to determine the ions in water bodies different according to the characteristics and to different concentrations of ions.

The concentrations of the main ions in the water samples of the Aral Sea, the Dead Sea and Lake Urmia were determined.

The values of salinity of the studied samples were established (as a sum of salts). Their measurement by standard hydrophysical equipment by electrical conductivity is not possible due to the different ratio of oceanic ions.

The determination and comparison of the ionic composition permitted to establish significant differences in the ratio of the main ions in the samples of hyperhaline reservoirs.

Verification measurements showed high accuracy in determining the main ions in the hyperhaline reservoirs by potentiometric titration using the methods proposed.

Comparison of our data with previously published data clearly demonstrates the evolution of the component composition over time, the differences in the physicochemical processes of salt deposition in the studied reservoirs.

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Pyotr O. Zavialov – problem statement, participation in field studies and sampling, development of approaches to the laboratory material analysis, participation in writing and editing the article text

All the authors have read and approved the final manuscript.

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