Development of a Standard Sample of Composition of Deep Baikalian Water

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Abstract

The possibility of creating a multielemental standard sample of deep water of Lake Baikal is substantiated. This is a new type of standard sample of natural waters balanced with respect to a wide range of macro- and trace elements. A standard sample reflects the specificity of matrix composition of hydrocarbonate-calcium waters to which waters of many world rivers and lakes and rain waters belong. Creation of a standard sample of Baikalian water has become possible as a result of substantiation of water composition at the depth of 500 m and development of sampling and water preparation technologies which ensure conservation of the primary composition of water and its absolute sterility. Experimental samples of Baikalian water in a special packing of polyethylene terephthalate poured out during 7 years have demonstrated stability with respect to the majority of parameters under storage. By the results of preliminary studies of the composition of deep Baikalian water, a set of items recommended for further attestation has been chosen, and their putative content has been estimated.

INTRODUCTION

Obtaining information about the chemical composition of water is of paramount importance for chemical and ecological monitoring of water bodies and for forecast of quality of potable water sources [1]. However, the widely used synthetic standard samples (SS) cannot fully reflect the specificity of the matrix water composition, which causes errors in the results of analysis. The currently existing synthetic SS of sea, sweet and rain water have been certified with respect to 6–10 elements, and these data are continuously specified and corrected. As for standard samples of composition of natural sweet waters with conservation of the natural chemical matrix, they have not so far been developed.

The idea of using Baikalian water for standardization of hydrochemical studies was put forward in [2, 3]. An attempt to create SS of Baikalian water was made in 1993 by the East Siberian Institute of Physicotechnical and Radiotechnical Measurements. However, in practice these projects have not been implemented. Creation of a standard sample of Baikalian water in accordance with international requirements to standard specimens of environmental objects was initiated by M. A. Grachev.

A standard sample of Baikalian water was first of all necessary for studies of Lake Baikal. As shown in the review [4], the discrepancy in the results of analysis of Baikalian water composition with respect to definite elements (*e. g.*, zinc) obtained by different authors is often as large as three orders. Incomparable data do not make it possible to give a reliable estimate of tendencies in the time course of the composition of Baikalian water and of the role of anthropogenous factors in this process.

Sweet water bodies and rivers, as well as rain waters, are close to Baikalian water by their matrix (Fig. 1); for this reason, a multielemental standard sample of Baikalian water may be used in monitoring studies.

The tendency in the change of water quality standard criteria in the world and separate

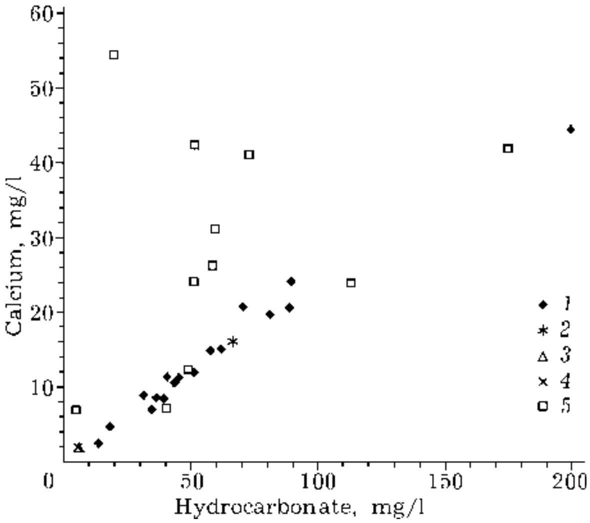


Fig. 1. Proportion of calcium (Ca^{2+}) and hydrocarbonate (HCO_3^-) ions content of natural aquatic objects: *1* – river water [11], *2* – Baikal water, *3* – lake water [10], *4* – rain water [10], *5* – snow water [10].

countries (Table 1) shows that as water changes from harmless for human health (standards of EEC, WHO, EPA, of the USA, Russia) [5–7] to wholesome (Switzerland) [8], its composition corresponds more and more to that of Baikalian water [9]; therefore, a standard sample of Baikalian water will be indispensable for analysis of potable water quality in water supply systems and in production of bottled water.

When developing a standard sample, results of long-term hydrophysical, hydrochemical and hydrobiological studies carried out by the Limnological Institute (LIN), SB RAS, methods of creation of standard samples systematized in a monograph [3], documents on standards [14–17] and schemes proposed in publications [18–20] were used.

TABLE 1

Standards of potable water quality

No.	Component	EEC [5]	WHO [6]	EPA (USA) [6]	Russia [7]	Switzerland [8]	Baikalian water [9]
1	Ammonium	0.5	1.5		0.2	0.05	<0.03
2	Potassium	12				10	0.9–1.1
3	Calcium	270				40–125	15.6–16.4
4	Magnesium	50				5–30	3.0–3.3
5	Sodium	150	200		200	20	3.2–3.6
6	Nitrates	50	50	10	45	25	0.30–0.38
7	Nitrites	0.1	3	1	3	0.01	
8	Sulphates	250	250	250	250	10–50	5.0–5.4
9	Chlorides	200	250	250	250	20	0.45–0.60
10	Aluminium	0.2	0.2		0.2	0.05	<0.05
11	Barium		700	1000	100	–	
12	Boron		500		500	–	
13	Cadmium	5	3	5	1	0.5	<0.5
14	Manganese	50	500	50	100	20	<20
15	Copper	1500	2000	1000	1000	50	<50
16	Molybdenum		70		70		<50
17	Arsenic	50	10	50	10	2	<2
18	Nickel	50	20	100	100	–	<20
19	Mercury	1	1	1	0.5	0.1	<0.1
20	Lead	50	10	5	10	0	<2
21	Selenium	10	10	10	10	1	<1
22	Antimonium	10	5	6		–	
23	Chromium	50	50	50	50	1	<1
24	Zinc	–	3000	5000	3000	100	<100

Note. Measurement units are mg/l (No. 1–10) and μg/l (No. 11–24)

CHOICE OF WATER SAMPLING SITE

Investigations of the lake water composition both all over the aquatorium and at various depths [4, 10–13] have demonstrated that Baikal water has pH 7.6 and belongs to low mineralized soft carbonate-calcium kind. The total content of dissolved salts of Baikalian water does not exceed 100 mg/l, and therefore it obeys the law of ideal solutions [21]; consequently, in Baikalian water the solubility product for the majority of compounds is not attained. Compounds' secession from the dissolved stare takes place only due to adsorption, colloidal processes or injestion by living matter. Due to unsaturation of waters, their ionic composition depends on the life activity of hydrobionts. Baikalian water possesses, apart from low mineralization, high concentrations of soluble gases, first of all oxygen, which determines its chemical activity.

All the ingredients of chemical composition of Baikalian water may be divided into 2 groups. The first group includes the main ions: calcium, magnesium, sodium, potassium, hydrocarbonates, sulphates and chlorides. Their distribution is relatively uniform with respect to depth and does not depend on spatial or seasonal influences [10–12]. The second group of Baikalian water components consists of biogenic elements (nitrogen, phosphorus, silicon), organic substance and dissolved gases (oxygen, carbon dioxide). The depth distribution of these components is susceptible to the influence of biological processes. Systematic studies of trace element composition of Baikalian water and of the role of trace elements in biogeochemical processes began recently [4, 22–25].

The water mass of Lake Baikal is subdivided, taking into account the data of [26], into 3 zones. Especially stable is water of the "core" of Baikal – a zone at the depth of 300 m under the water surface to 100 m above the bottom [27]. The surface water reaches the bottom of Baikal on the average in 7–8 years. However, waters of the "core" are exchanged still more slowly: surface waters penetrate into the "core" on the average in 10–14 years [26, 28]. This means that water in the "core" zone is the best and longest purified by aquatic microorganisms. The zone of the "core" also escapes the turbid flows arising near the shores. In the "core" zone there are almost no diatomic algae which are abundant near the surface and pressed to the border of the hollow [29]. Here, the temperature keeps at the level of 3.5 °C throughout the year [26, 28]. A comparative characterization of distribution of the components with respect to the depth, according to various authors [12, 23, 24, 26] has shown (Fig. 2) that despite a considerable change of the chemical composition of water (especially anions), in surface and benthal zones, the water in the "core" zone remains stable with respect to most elements. In this way, sampling from the deep zone not only ensures a stable composition of the standard sample of Baikalian water, but also permits obtaining a representative water sample that reflects the composition of the bulk of water volume of the lake (over 17 000 km^3).

Regime observations on the stability of Baikalian water have proved the necessity of fixation of the sampling site of the deep zone. A site in the Listvennichny bay situated at the depth of 500 m and at the distance of 1.7 km from the shore was chosen as such. The bottom at this point is at about 200 m from the sampling point (Fig. 3).

In order to avoid saturation of water with foreign elements during its supply to the shore, experimental studies of water conduit material choice were carried out. They demonstrated that even a short-term interaction of water with steel or zinc-plated tubes gives a perceptible increase of iron, zinc, nickel, vanadium, chromium, manganese and other metals in it. The water conduit was paved with polyethylene tubes. The deep sampling, polyethylene water conduit, pumps of special corrosion-resistant steel guaranteed sampling of deep water from one constant site with unchanged initial composition of water. The water composition in this site was studied for 7 years. Water for analysis was supplied without any preparation, sterilization or filtration. The change of trace element concentration did not exceed 3–5 %.

Creation of a fixed water sampling point was the first important step to obtaining SS

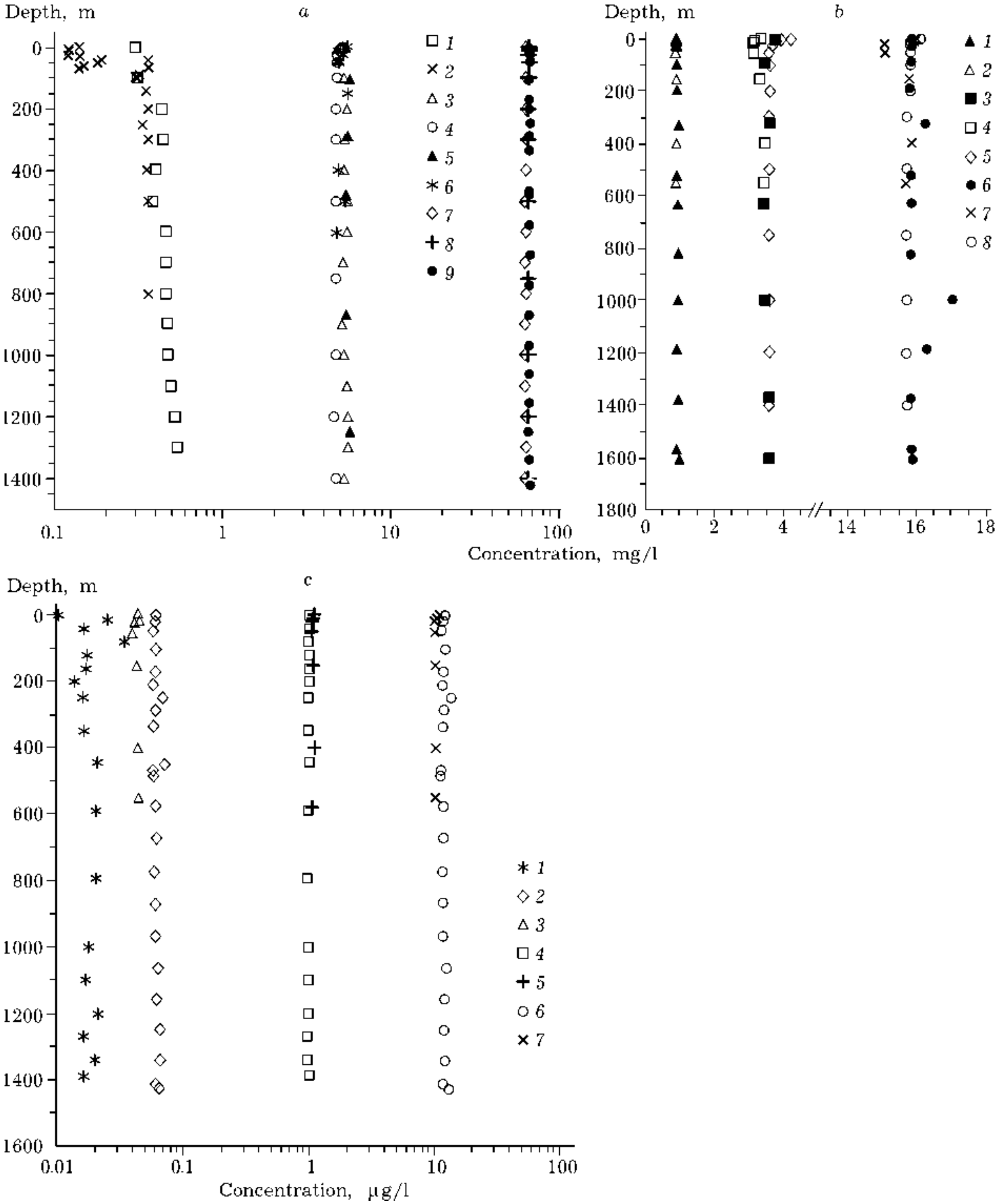


Fig. 2. Distribution of components across the depth of Lake Baikal according to the data of various authors: *a* – anions: NO_3^- (*1* – [12], *2* – LIN), SO_4^{2-} (*3* – [12], *4* – [10], *5* – [23], *6* – LIN), HCO_3^- (*7* – [12], *8* – [10], *9* – [23]); *b* – cations: K^+ (*1* – LIN, *2* – [23], Na^+ (*3* – LIN, *4* – [23]), $Na^+ + Ka^+$ [10] (*5*), Ca^{2+} (*6* – [10], *7* – [23], *8* – LIN); *c* – trace elements: Cu [24] (*1*), Rb (*2* – [23], *3* – LIN), Ba (*4* – [24], *5* – LIN), Sr (*6* – [23], *7* – LIN).

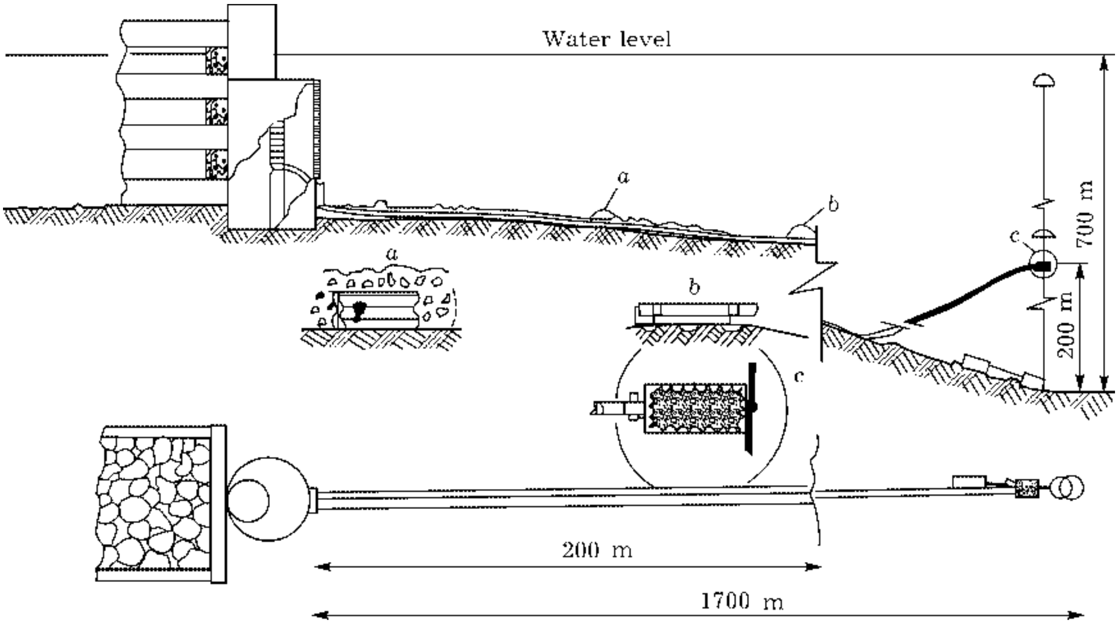


Fig. 3. Structure of the sampling site near the settlement Listvyanka (cross-section of the pipeline and view from above): *a* – a shallow site at the depth of 0–20 m; *b* – a deep site (over 20 m), water conduit in assembly with the fixing rope; *c* – water conduit head, filter for rough purification with mesh size of 0.35 mm.

of Baikalian water. Due to the existence of the stationary water sampling point, it became possible to obtain regularly SS with consistent certification characteristics.

WATER PREPARATION TECHNOLOGY

Deep water in the sampling site is not completely sterile. In Baikalian water there may be microorganisms, including sporulating bacteria and fungi, algae and their cysts. They all can reproduce in the Baikalian water, influencing its chemical composition. In deep water there are also suspended particles consisting of aleurite, clay, organic detritus, colloidal particles and aggregates. Redistribution of these particles may also influence the chemical composition of water. For a standard sample, water purified from biota and mechanical ultra-admixtures representing an ideal unsaturated true solution was necessary.

To solve this problem, a stepwise water filtration and sterilization system was used (Fig. 4). Deep water was run through 5, 1 and 0.45 μm filters, ozonized and treated with ultraviolet irradiation. The material of the ultra-fine filter influences considerably the filtrate composition. Studies have demonstrated that when a nickel filter was used, the nickel content of water increased to 95 μg/l (before filtration it was 0.17 μg/l), and iron content increased from 0.5 to 7.8 μg/l. That is why in the filtration system water was run through polypropylene filter cartridges which did not influence the water composition. For water accumulation, tanks made of special corrosion-resistant steel 12X18H10T (GOST 5632–72) approved for foodstuff industry were used. In the water coming from metal tanks, unlike metallic pipelines and filters, no increase of metal concentration was observed.

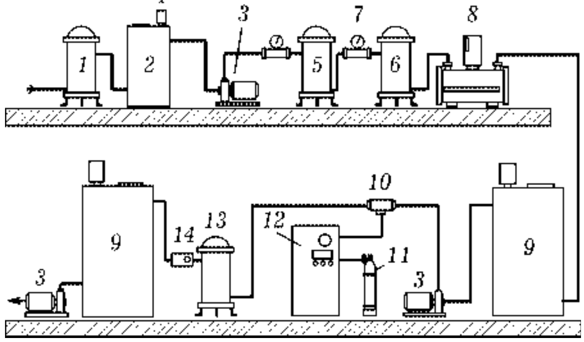
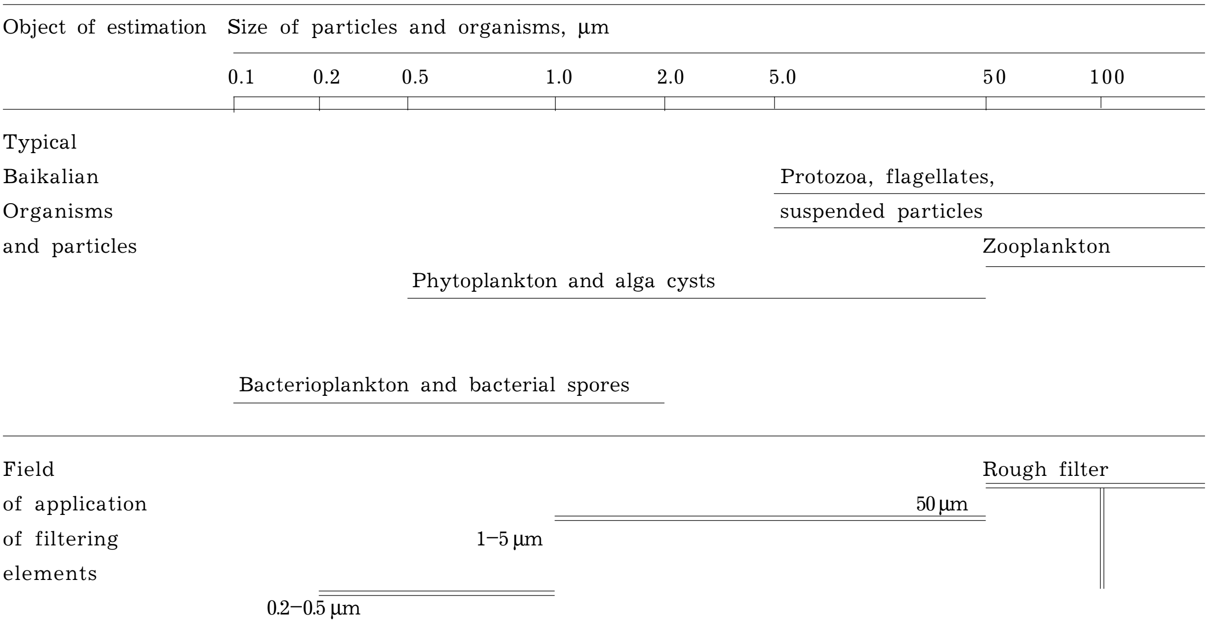


Fig. 4. Water preparation workshop: *1* – filter for rough purification (100 μm), *2* – accumulator tank (500 l), *3* – Wilo Jet 301 pump, *4* – filter for air purification, *5* – 5 μm filter, *6* – 1 μm filter, *7* – manometer, *8* – UV device with a DRT 1000 lamp, *9* – accumulator tank (1000 l), *10* – Venturi injector, *11* – oxygen balloon, *12* – ozonizer, *13* – 0.45 μm filter, *14* – ozone meter.

TABLE 2

Filtration effect of various systems of sterilization of Baikalian water



In Table 2, the filtration effect of various system of sterilization of Baikalian water is demonstrated. Rough filtration removes protozoa and zooplankton. Ozonization ensures water sterilization. Synergic effect of the UV device and ozonization removes alga cysts and bacterial spores. The 1–5 μm filter separates terrigenic suspended particles, and the fine 0.45 μm filter removes dead remains of bacterioplankton and picoplankton. All the junctions of the system are constructed so as not to let foreign elements penetrate into it. At the outlet of the water preparation system, deep Baikalian water fully sterile and not containing any terrigenic suspensions and microorganisms or their remains is obtained.

In this way, the proposed water preparation technology makes it possible to remove from water the microflora and microparticles larger than 0.45 μm and to ensure complete conservation of the unique chemical composition of Baikalian water.

PACKAGE AND STORAGE OF A STANDARD SAMPLE

Glass of quartz ampules are usually considered preferable for packing SS of aquatic objects. However, this material is not fit for Baikalian water. Our studies [30] have shown that during storage in glass packages sorption of cobalt on the recipient walls and desorption of manganese, copper, zinc, sodium, barium cations and sulphates from glass take place. That is why for packing a standard sample, recipients of polyethylene terephthalate (PETP) were chosen. This material, unlike other plastics, is gas-proof and does not release any perceptible amount of organic ingredients (acetaldehyde, phthalates *etc.*) into the water. No sorption of any macro- or trace elements on the walls of PETP recipients was noted (Table 3).

In order to determine the condition of storage and transportation of a standard sample, experiments on freezing and heating SS to a high temperature were carried out. Freezing and subsequent thawing a standard sample resulted in the fact that organic compounds dissolved in water were partially precipitated: their content in water decreased from 0.4 to 0.2–0.3 mg/l. The trace element composition of water also changed slightly. A study of dependence of pH on the temperature of heating a hermetically packed sample of Baikalian water gave the following results. Up to the tem-

TABLE 3

Comparison of results of element analysis of Baikalian water sampled in 1999 and of bottled Baikalian water sampled in 1993 (n = 3, P = 0.95)

No.	Element	Water sampled in 1999	Water bottled in 1993	
			Glass	PETP
1	Na	3.26±0.21 (0.05)	4.83±0.22	3.23±0.05
2	Mg	2.56±0.17 (0.05)	2.85±0.07	2.53±0.02
3	K	1.02±0.06 (0.04)	1.11±0.10	1.01±0.06
4	S	1.84±0.11 (0.03)	1.71±0.15	1.79±0.17
5	Ca	15.7±1.0 (0.04)	15.7±0.5	16.1±0.4
6	Sr	0.105±0.002 (0.01)	0.099±0.005	0.107±0.003
7	Al	3.07±0.57 (0.13)	3.64±0.01	2.87±0.75
8	Li	2.06±0.19 (0.07)	2.22±0.11	2.21±0.17
9	B	10.6±0.4 (0.03)	11.1±1.4	10.3±0.7
10	V	0.60±0.09 (0.11)	0.63±0.04	0.61±0.08
11	Cr	5.47±0.37 (0.04)	5.21±0.19	5.37±0.39
12	Mn	0.44±0.04 (0.07)	1.72±0.52	0.47±0.09
13	Ni	0.31±0.14 (0.19)	0.67±0.20	0.33±0.13
14	Co	0.11±0.01 (0.08)	0.088±0.015	0.10±0.01
15	Cu	0.87±0.11 (0.09)	1.11±0.04	0.86±0.07
16	Zn	1.94±0.20 (0.07)	6.77±0.79	2.13±0.21
17	Se	1.53±0.22 (0.11)	1.64±0.62	1.51±0.50
18	As	0.33±0.06 (0.08)	0.37±0.14	0.40±0.07
19	Rb	0.84±0.05 (0.04)	0.99±0.11	0.87±0.04
20	Mo	1.54±0.05 (0.02)	1.59±0.08	1.57±0.03
21	Cd	0.010±0.009 (0.22)	0.029±0.008	0.009±0.001
22	Ba	10.8±0.6 (0.04)	76.7±5.2	11.1±0.5
23	Pb	0.064±0.005 (0.06)	0.095±0.012	0.065±0.012
24	U	0.56±0.03 (0.04)	0.58±0.12	0.53±0.10

Note. Measurement units are mg/l (No. 1–6) and μg/l (No. 7–24). In brackets, relative standard deviation is indicated.

perature of 40 °C, the pH value remained constant. Within the range of 40–70 °C, removal of dissolved CO_2 with respective increase of pH to 7.8–7.9 took place. Boiling and heating to 137 °C at an increased pressure led to an increase of pH value to 8.0–8.2, which told on the proportion of ions in the solution. In this way, during storage and transportation of a standard sample a temperature of 1 to 40 °C must be maintained.

ESTIMATION OF UNIFORMITY, STABILITY AND COMPOSITION OF A STANDARD SAMPLE

The main requirements to the material of a standard sample are uniformity of chemical composition and stability during storage [14]. Methods of estimation of homogeneity and stability of water samples have not been considered in the standardization documents of this country. Only uniformity and stability of dispersed materials have been considered in detail [15, 16]. On the basis of these documents and of publications [18–20], a method for estimation of these characteristics in SS of Baikalian water has been proposed. As an experimental express method, mass-spectrometric technique with inductively bound plasma (IBP-MS) was chosen. Measurements were performed on the device VG PlasmaQuad2$^+$.

The uniformity of material of a standard sample is expressed quantitatively by the value for non-uniformity parameter. SS non-uni-

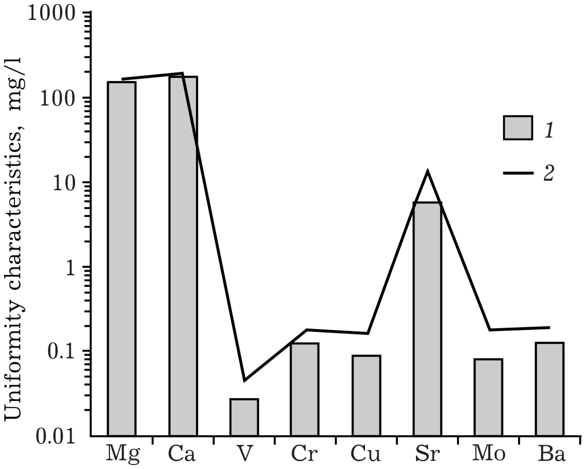


Fig. 5. Estimation of uniformity characteristics of a standard sample: *1* – absolute value for the non-uniformity parameter, *2* – $(1/3)\Delta_{tol}$.

formity parameter is the mean square deviation of the component content in separate samples from the mean content of the same component in the whole SS mass [15]. On the basis of experimental data, spot dispersions characterizing the convergence of the method, the total dispersion, and the non-uniformity of distribution of the material under study in the SS mass were calculated. The significance of difference between dispersions was estimated by the Fisher test. The value for tolerance (Δ_{tol}) was calculated from the standards of error for measurement of parameters of natural waters [31]. From Fig. 5 one can see that the absolute value for non-uniformity parameter of Mg, Ca, V, Cr, Cu, Sr, Mo and Ba is smaller than $(1/3)\Delta_{tol}$. Therefore, according to [15], the SS material may be considered as uniform with respect to these components.

The stability of a standard sample was estimated, according to [15], by comparing the content of the components to be certified in a sample stored for a few years in a hermetically closed packing and that in a sample stored under usual conditions. The analysis of the whole lot was carried out simultaneously by one analyst. The results of estimation of stability of the composition of deep Baikalian water packed in March 1992, September 1994, October 1997, and August and November 1999 into polyethylene terephthalate bottles are presented in Fig. 6. The composition of bottled water was compared with a sample of water taken in December 2000. From Fig. 6 one can see that for the majority of studied elements the condition $t_{exp} < t_{0.05f}$ is fulfilled, *i. e.* according to the Student test the value of the mean difference in all the estimations ($\bar{d}$) does not differ significantly from zero; therefore, the certified characteristics are stable. In the case $t_{exp} \geq t_{0.05f}$, the estimate of statistical significance of $\bar{d}$ was obtained by the negligible error test, *i. e.* the $\bar{d}$ value was compared with that of the tolerable mean root square error σ_{tol} calculated from [31]. In this case, too, the composition of the standard sample was stable with respect to these elements, because $\bar{d} \leq (1/3)\sigma_{tol}$.

Estimation of composition of the standard sample was carried out by the results of analysis of deep Baikalian water obtained in 1991–2000 at 10 laboratories in Russia and

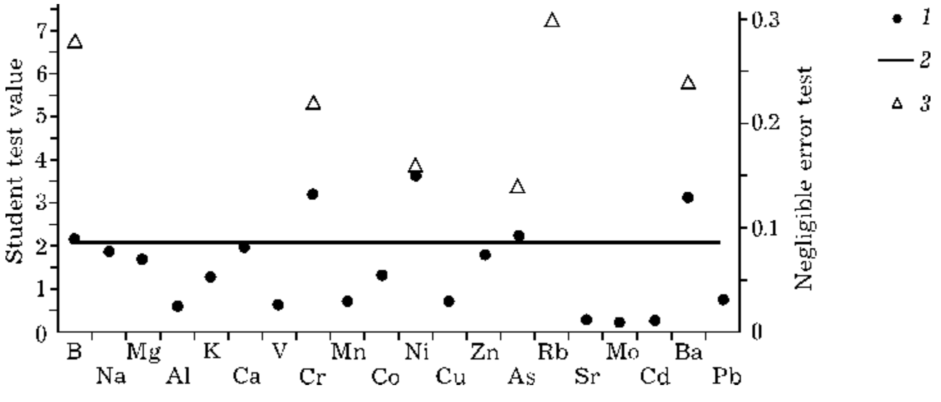


Fig. 6. Estimation of stability of a standard sample: *1*, *2* – experimental and table (n = 20, P = 0.95) values of t-test; *3* – $\bar{d}/\sigma_{tol}$.

abroad. The water submitted for analysis was treated by the above described technology. The components were assayed by the following methods: anions – by ion chromatography, direct titration, gravimetry, argentometry, photometry, spectrophotometry, turbidimetry, fluorimetry, colorimetry, potentiometry with ion-selective electrode; Na and K – by flame photometry, atomic absorption, atomic emission with inductively bound plasma (IBP AES), IBP MS; the rest of elements – by atomic absorption, IBP AES, IBP MS. Most results in an interlaboratory experiment were obtained with respect to trace elements, much less with respect to trace elements and anions. The considerable dispersion of concentrations of most trace elements was associated, first of all, with the problem of correctness and reliability of the results. In Table 4, the putative content of components is presented.

CONCLUSIONS

As a result of the works performed, the possibility of creating SS of natural water with conservation of the matrix composition has been substantiated, a standard sample has been developed and produced. When developing SS of deep Baikalian water, international requirements to standard samples of environment objects were met. The stationary system of water taking and preparation ensures obtaining any amount of water of uniform composition with respect to majority of elements. When taking samples from any part of the sample, results of analysis coincide within the limits of measuring technique error. The stability of certified elements in SS of Baikalian water has been confirmed by long-term analytical studies of water taken from the given site. In long-term storage of the sample in packing made of polyethylene terephthalate no changes of its composition or contamination have been observed. The estimated cost of SS is by an order lower than that of currently existing water SS.

The present work is a new type of water standards with conservation of the natural composition matrix which has serious analytical perspectives.

TABLE 4

Putative content of components of Lake Baikal water

Component	Concentration	Component	Concentration
HCO_3^-	66 (7)	Mn	0.10 (6)
NO_3^-	0.4 (7)	Co	0.03 (5)
SO_4^{2-}	5.4 (13)	Ni	0.5 (9)
PO_4^{3-}	0.03 (3)	Cu	0.8 (10)
F^-	0.2 (5)	Zn	1.0 (10)
Cl^-	0.5 (10)	As	0.5 (6)
Na	3.3 (18)	Rb	0.5 (5)
K	0.9 (12)	Sr	100 (11)
Mg	2.9 (16)	Mo	1.2 (5)
Ca	15.9 (17)	Cd	0.01 (5)
Si	0.90 (5)	Ba	0.0 (12)
Al	1.0 (6)	Pb	0.04 (5)
V	0.5 (5)	Li	2.0 (5)
Cr	0.5 (8)	B	10 (5)

Note. Measurement unit for anions and for Na, K, Mg, Ca, Si is mg/dm^3, for the rest of elements – mg/dm^3 In brackets, the sample is indicated.

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