

Results of testing the chemical parameters of artificial standard samples of rains and surface fresh waters

T.V. Khodzher, L.P. Golobokova, O.G. Netsvetaeva, V.M. Domysheva,
T.V. Pogodaeva, and I.V. Korovyakova-Tomberg

*Limnological Institute,
Siberian Branch of the Russian Academy of Sciences, Irkutsk*

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The results of international intercalibration made against standard samples of artificial acid rains by the Laboratory for Hydrochemistry and Atmospheric Chemistry of the Limnological Institute (Irkutsk) are presented. The results were obtained within the framework of two programs: EANET and WMO. The results were discussed at the session of experts in Bangkok (Thailand), Geneva (Switzerland) and included into the WMO and EANET reports. The methods of analysis of the objects studied were recognized acceptable and the results obtained were recognized authentic.

Very important requirements to observations of the chemical composition of various environmental objects at different places on the globe are the uniformity of the methods used and correctness of the results. This is necessary for representation of the actual features in the chemical composition of some environmental objects. Until the mid-1980s, the Quality Assurance/Quality Control (QA/QC) was not considered at the global level. Nowadays standardization of the methods for measurement of different parameters, exchange of the available information, unification of the forms of information and prediction service, and quality control are the requisites for investigation of the environmental objects.

The Laboratory for Hydrochemistry and Atmospheric Chemistry of the Limnological Institute SB RAS (Irkutsk) deals with the examination of drinking, natural, interstitial, and sewage waters, atmospheric precipitations and atmospheric aerosol and has many-year series of data of observations of these objects. The data compiled are arranged in the following databases: Current Hydrochemical State of Baikal Pelagic Region, Siberian Atmospheric Aerosols, and Yenisei Hydrochemistry. Since 1998 the Laboratory has continuously tested the artificial rain and surface water samples within the framework of two international projects of inter-laboratory comparison of analyses. One project is a part of the Global Atmospheric Watch (GAW) and the Quality Assurance/Science Activity Centres (QA/SAC) under the aegis of the World Meteorological Organization (WMO) [<http://qasac-americas.org/>]. The artificial samples are granted twice a year by the Atmospheric Sciences Research Center (ASRC, New York, USA). The Project involves more than 70 laboratories from different countries. Another program of inter-laboratory comparison has been carried out since 1998 within the framework of the International Acid Deposition Monitoring Network

in East Asia (EANET) – The Project on the Quality Assurance/Quality Control (QA/QC). The artificial samples of rain and fresh surface water are presented by the Acid Deposition and Oxidant Research Center (ADORC, Niigata, Japan) once a year. This Program incorporates more than 20 laboratories from 10 countries of the Southeastern Asia.^{1–4}

Objects and methods of analysis

The ions: NH_4^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , NO_3^- , Cl^- , as well as pH and electrical conductivity (EC) are recommended for the determination in the artificial samples to be tested. In addition, the alkalinity has been recommended to be determined in the samples of fresh surface water.

According to the EANET Program, the participants receive two samples of artificial rainwater with the high and low ion concentration and one sample of artificial fresh surface water. According to the recommended technique, before analysis three samples are prepared in parallel through diluting 10 ml of the initial sample by deionized water to 1000 ml. The electrical conductivity of the deionized water should be no higher than 1.5 $\mu\text{S}/\text{cm}$. The resulting solutions are similar to the natural rainwater in mineralization and ion composition. The sample of the fresh surface water is analyzed without dilution. Each of the samples is analyzed in three repetitions, and the results obtained are sent to ADORC. Table 1 presents the true concentrations of some analyzed samples, which were received within the EANET Program.

The total content of ions in the artificial rain samples varies from 2.28 to 24.51 mg/l, which corresponds to 0.04–0.48 mg-equ/l, and in the artificial samples of fresh surface water it varies from 35.4 to 46.2 mg/l or 1.07–1.29 mg-equ/l.

The participants of testing within the WMO Project receive three samples of artificial rainwater, whose composition corresponds to natural acid rains.

Table 1. Chemical composition of artificial samples obtained within the EANET Program

Artificial samples of rainwater										
pH	EC	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	
	μS/cm	mg/l								
1998										
4.05	7.94	8.02	5.79	4.57	2.20	0.43	1.65	0.32	1.53	
4.51	2.82	2.80	2.24	1.60	0.77	0.29	0.57	0.11	0.53	
1999										
4.14	6.38	6.44	4.65	3.69	1.77	0.35	1.32	0.27	1.22	
4.59	2.30	2.31	1.67	1.35	0.64	0.13	0.48	0.09	0.45	
2000										
4.10	6.23	5.73	3.93	3.59	1.18	0.39	1.18	0.28	1.09	
4.85	1.55	1.93	1.71	0.55	0.20	0.19	0.44	0.19	0.33	
2001										
4.10	7.45	8.17	5.79	3.84	1.57	0.62	1.65	0.45	1.58	
4.82	1.76	2.07	1.20	1.22	0.63	0.16	0.53	0.09	0.30	
2002										
4.30	3.75	3.86	3.16	1.19	0.31	0.27	0.77	0.17	0.72	
5.15	0.69	0.85	0.53	0.32	0.12	0.08	0.26	0.04	0.08	
Artificial samples of fresh surface water										
pH	EC	Alkalinity	SO ₄ ²⁻	NO ₃ ⁻	Cl ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺
	μS/cm	mg-equ/l	mg/l							
2001										
6.10	7.45	–	15.74	3.19	5.47	3.54	0.77	3.53	0.38	2.73
2002										
6.69	7.76	0.21	10.61	4.13	4.87	8.07	0.77	4.12	0.57	0.27

Table 2. Chemical composition of artificial samples received within the WMO Project

Calibration	Sample	pH	EC	Cl ⁻	Ca ²⁺	K ⁺	Mg ²⁺	Na ⁺	SO ₄ ²⁻	NH ₄ ⁺	NO ₃ ⁻
			μS/cm	mg/l							
22	1	3.49	161.6	2.84	0.50	0.40	0.78	0.12	1.85	12.04	1.08
	2	3.53	136.5	0.94	0.27	0.01	0.10	0.09	0.49	11.41	1.02
	3	3.89	69.0	1.13	0.20	0.15	0.53	0.10	1.35	6.85	0.44
24	1	4.61	21.8	0.78	0.04	0.34	0.13	0.10	0.42	5.30	0.61
	2	5.12	8.4	0.30	0.03	0.15	0.09	0.05	0.15	1.94	0.29
	3	4.45	42.6	2.08	0.06	0.79	0.29	0.25	1.32	1.34	1.32
26	1	4.68	22.0	1.62	0.02	0.24	0.18	0.12	1.04	2.44	0.45
	2	4.96	11.9	0.80	0.01	0.17	0.11	0.08	0.48	1.47	0.25
	3	4.59	38.1	3.59	0.10	0.62	0.39	0.25	2.30	4.26	0.77
28	1	4.6	22.0	1.15	0.04	0.34	0.13	0.10	0.41	2.02	0.61
	2	4.74	11.5	0.34	0.02	0.11	0.03	0.04	0.08	0.73	0.21
	3	4.60	37.8	4.52	0.10	0.61	0.38	0.24	2.27	3.06	0.77

The samples differ considerably in the ion concentration. For the period of participation of our laboratory in the WMO Project, the ion sums in the samples varied from 2.67 to 29.17 mg/l or from 0.07 to 0.68 mg-equ/l (Table 2).

The correctness of the determination of the ion composition of a sample (R_1) is checked by comparing the equivalent sums of cations (ΣC) and anions (ΣA) [Ref. 5]:

$$R_1 = 100 \cdot (\Sigma C - \Sigma A) / (\Sigma C + \Sigma A).$$

The acceptable discrepancies between the cation and anion sums⁶ depend on the concentration of the components determined (Table 3).

The tested parameters are measured in the rainwater and fresh water samples by the methods, we used for analysis of the objects studied in our laboratory. It should be noted that we employ modern, highly efficient methods of hydrochemical analysis, which do not require, whenever possible, specialized preparation of a sample. The standard

solutions of some ions used are purchased from EANET (Niigata, Japan).

Table 3. Acceptable discrepancies for cation and anion sums

($\Sigma C + \Sigma A$), mg-equ/l	R_1 , %
<0.05	± 30
0.05–0.10	± 15
>0.10	± 8

A Horiba pH-meter (Japan) with a combined 6366-10C electrode was used to measure water pH accurate to 0.02. The electrical conductivity was measured by a Horiba conductometer with a 1 cm⁻¹ electrolytic cell accurate to 0.05 % in the range of 1 to 100 μS/cm (Ref. 7).

The concentration of HCO₃⁻ (alkalinity), NO₃⁻, Cl⁻, and SO₄²⁻ anions was determined with a Milikhrom A-02 microbore column chromatograph manufactured by EkoNova (Russia). This chromatograph is in operation since 1997, and it was

successfully used in more than 10000 measurements. The technique is based on the indirect UV detection of anions after their separation on a dynamically modified reversed-phase Nucleosil 5-C18 column (Macherey Nagel, Germany). Potassium biphthalate in 10% acetonitrile solution was used as eluent. The detection limit of chromatographic analysis is 0.05 mg-eq/l with a 4–7% error.⁸

Ammonia ions were determined by the colorimetric method with Nessler's reagent on a KFK-2 photocolometer. The error of determination was 10% at the NH_4^+ concentration higher than 0.03 mg-eq/l, 25% at 0.006–0.03 mg-eq/l NH_4^+ , and 50% at 0.001–0.006 mg-eq/l (Refs. 9, 10).

The concentration of the magnesium and calcium ions was determined by the method of atomic absorption spectrometry with the air-acetylene flame on an AAS-30 atomic absorption spectrophotometer manufactured by Zeiss Jena, Germany (in operation since 1990). This method allows the determination of calcium ions to be done at $\lambda = 422.7$ nm within the range of 0.0025–1 mg-eq/l and magnesium ions at $\lambda = 285.2$ nm within the range of 0.0004–0.4 mg-eq/l accurate to 2–3% (Ref. 11). The content of sodium and potassium ions was determined by the method of flame emission spectrometry at $\lambda = 589$ nm (Na^+) and 766.5 nm (K^+). For the concentrations ranging from 0.003 to 0.3 mg-eq/l, the error of determination is 3% for sodium ions and 5% for the potassium ions.¹² To exclude interferences, lanthanum chloride additions were used in determination of calcium and magnesium ions and cesium chloride additions were used in determination of sodium and potassium ions.

Comparing the concentrations of the studied components in the samples (see Tables 1 and 2) with their detection limits in the methods used, we can conclude that the absolute concentrations of the determined ions in some cases were at the threshold of the method sensitivity.

Results

The measurement results on the artificial samples within the EANET Program are shown in Figs. 1 and 2. The smallest deviations from the true values are observed for pH and electrical conductivity, as well as for the concentration of Cl^- , NO_3^- , Mg^{2+} , and NH_4^+ . The most results on the concentration of these components have the deviation from the true values within 3%, and 20% of the results deviate from the true values by 5–10%. The determined concentrations of SO_4^{2-} in the artificial samples differ from the true ones by 0.4–5.2%, and only in one case the deviation exceeded 10%. The deviations of the obtained concentrations of Na^+ and Ca^{2+} ions from their true values are, on the average, within 10%. In the samples with a very low content of cations, the deviations achieve 15%. The largest deviations between the determined and the true concentrations were found for potassium ions.

Though in some cases the determined concentrations coincide with the true ones (deviation 0.0%), in other cases the deviation is as high as 19%. The balance discrepancy (R_1) is 0.3–2.9%, and only in the sample with the low concentration of the last series it achieves 4.3%.

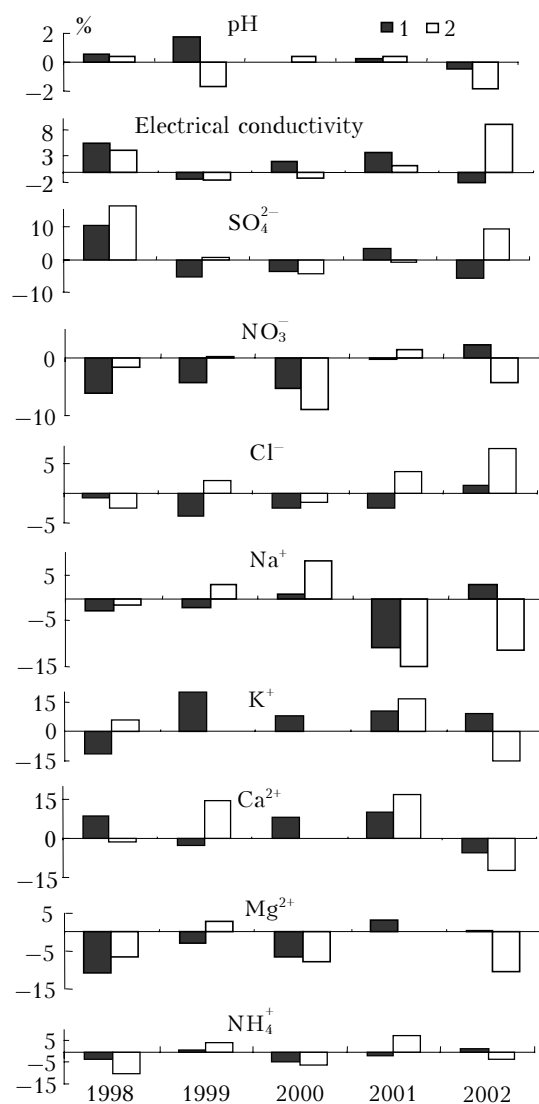


Fig. 1. Deviation of the obtained results of analysis of the artificial rainwater samples from the true values in the inter-laboratory testing within the EANET Program: sample with high concentration (1) and sample with low concentration (2).

The results of testing within the WMO Project are shown in Fig. 3. As in the artificial samples received within the EANET Program, the smallest deviations of the determined values from the true ones took place in determination of pH, electrical conductivity, and the concentration of NH_4^+ , Cl^- , and NO_3^- . The satisfactory agreement of the results was obtained for the concentrations of SO_4^{2-} and Mg^{2+} ions. The large deviations (up to 20%) are observed between the true and determined concentrations of K^+ ions, as well as Na^+ and Ca^{2+} ions.

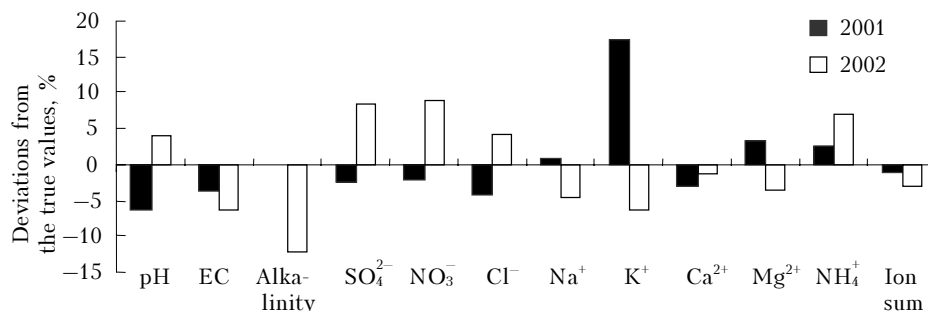


Fig. 2. Deviation of the obtained results of analysis of artificial fresh surface water samples from the true values in the inter-laboratory testing within the EANET Program.

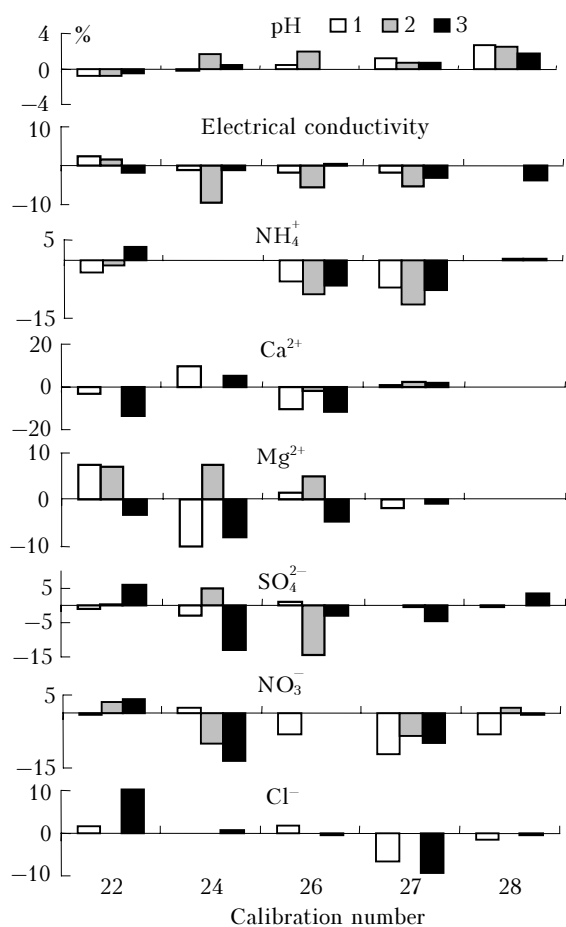


Fig. 3. Deviation of the obtained results of analysis of artificial rainwater samples from the true values in the inter-laboratory testing within the WMO Project (1 to 3 are the sample numbers).

In general, the deviations of the concentrations determined in the artificial samples of rainwater and fresh water from the true values do not exceed the acceptable values. Large deviations are characteristic mostly of the samples, in which the concentration of the analyzed component is close to its detection limit.

Conclusions

The results of international testing made using artificial samples of rainwater and fresh water were

discussed at the session of experts in Niigata (Japan), Bangkok and Pattaya (Thailand), Geneva (Switzerland) and included into the WMO and EANET reports. It was recognized that the methods of analysis of such objects employed in the Laboratory of Hydrochemistry and Atmospheric Chemistry are acceptable, the results obtained are authentic, and the quality of analysis carried out at the Laboratory satisfies all the requirements. Thanks to the results of this international testing, the Laboratory of Hydrochemistry and Atmospheric Chemistry has gained high rating.

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