

Final report – Harmonized water quality monitoring

Tender: RFQ_EMO_2013-038

“Intercalibration of analytical procedures for analytes, included into harmonized program of hydro chemical monitoring for Selenga river basin”

Executor: Central Laboratory of Environment and Metrology /CLEM/, Mongolia

The purpose of the work is inter-laboratory comparable testing of surface water quality analysis methods which are used in Russia and Mongolia on water objects of the Selenga river basin with the purpose of their compatibility.

The service will accomplish the following tasks:

- to carry out an intercalibration of developed harmonized program of hydrochemical monitoring under supervision of the leading Russian organization;
- to determine necessary elements which require intercalibration after consulting with Russian side, and determine Mongolian laboratories which will take part in this work;
- to conduct an analysis of control samples received from approved laboratory and hold a discussion of intercalibration results;
- to send Mongolian specialists to Russia for training study of methodological issues of surface water analysis and measure quality control with the purpose of further adoption of more selective and sensitive identification methods by Mongolian laboratories;
- Develop recommendations and cost enhancements to existing monitoring regime based on intercalibration.

In order to supply service described in the quotation we propose following staff as required according to the Terms of Reference: director Badarch Lkhagvasuren /Central Laboratory of Environment and Metrology/ Engineer Yadamsuren Erdenebayar, Bold Altantuya, Suren Otgonjargal, Gerelbadrah Oyunsuren.

The transboundary water bodies’ quality monitoring in the Mongolian territory is carried out in 13 sites agreed upon earlier. Additionally there are 6 stations in the Selenga river basin. Chemical analysis of the transboundary waters is conducted in cooperation with the Central Laboratory on Environment and Metrology (CLEM) in 5 more regional laboratories.

Quality control of analytical measurements

1. The inter-laboratory comparative tests (ILCT) of the Harmonized Water Quality Monitoring Program in the Selenga river basin

In order to provide the system of quality control of the analytical measurements and increase the reliability of results in the water pollution monitoring laboratories of Russia and Mongolia the approaches towards creation and implementation of quality control systems should be similar.

The proposed system of information quality guarantees and control is provided due to:

- correct selection of priority indicators of water composition entitled to testing;
- selection of a representative water sample;
- adherence to specifications of sample preparation and analysis specified by measurement methodologies, executed according to GOST (national standard) 8.563 or in accordance with other regulatory documents;
- use of **certified** measurement procedure (MP) of the composition of water;
- **internal measurement quality control**, including sampling selection quality, operative control of the analysis procedure and analysis results stability control (assessment of the total aggregate of the analysis results during a controlled period);
- participation in the inter-laboratory comparative testing of measurement procedure (external measurement quality control).

The control of compatibility of analysis results obtained by the Russian and Mongolian laboratories should be carried out by:

- organizing of joint water sampling and their analysis by methods used by each side followed by a comparison of obtained results with due regard to measurement errors;
- carrying out of a special experiment – dissemination of control samples prepared in Russia by the Hydrochemical Institute for the external control of measurements.

Carrying out of inter-laboratory comparative tests (ILCT) initiated by the coordinator Federal State Budgetary Institution “State Hydrochemical Institute” and coordinated with the Mongolian side: - preparation and distribution among the laboratories of control samples containing copper, lead and zinc ions due to periodical excess of the MPC for these chemical elements in the transboundary monitoring cross section.

In August, 2013, behalf of the Baikal Lake project which was entitled the “ Water quality monitoring plan of Selenge River Basin”, Water Chemistry Institute of Rostov-on Don, RUSSIA sent international quality control water samples for trace metals determination to CLEM. In September, 18, 2013, data results sent to CLEM.

Carrying out of control samples analysis and submission of the results to the coordinator Federal State Budgetary Institution “State Hydrochemical Institute” for the processing of data was obtained.

In August, 2013, behalf of the Baikal Lake project which was entitled the “Water quality monitoring plan of Selenge River Basin”, Water Chemistry Institute of Rostov-on-Don, RUSSIA sent international quality control water samples for trace metals determination to CLEM. In September, 18, 2013, to end analysis and in October, 2013, data results sent to Water Chemistry Institute of Rostov-on-Don, RUSSIA.

Processing of the analysis results of the control samples for the inter-laboratory comparative tests obtained in the laboratories of Russia and Mongolia and their submission to the provider

The analysis results of the control samples for the inter-laboratory comparative tests copper, lead and zinc ions for the inter-laboratory comparative tests are shown in **Table 1 and 2**.

Table.1 **Determination of Copper, Lead and Zinc**

Take 5 ml of sample using a volumetric pipette and transfer to the volumetric flask from pure water. Add pure water up to the marked line of the flask to 500 ml.

Metal	Number of sample		Data, mcg/dm ³							
			\tilde{O}_1	\tilde{O}_2	$\tilde{O} \pm \Delta$	$\tilde{O}_{\tilde{E}1}$	$\tilde{O}_{\tilde{E}2}$	$\tilde{O}_{\tilde{E}}$	$\tilde{O}_{\tilde{E}} \pm \Delta$	$\tilde{N}\tilde{a} = \tilde{O}_{\tilde{E}} - \tilde{O}$
Copper	1		nd			nd				nd
	2					nd				nd
	3					nd				nd
Lead	1		nd			1.0	-		1.0±0.2	1.0
	2					1.2	-		1.2±0.2	1.2
	3					4.5	-		4.5±0.9	4.5
Zinc	1		0.2			2.8	-		2.6±0.5	2.6
	2					1.5	-		1.3±0.3	1.3
	3					1.2	-		1.0±0.2	1.0

Chemist engineer

Bold ALTANTUYA
Gerelbadrakh OYUNSUREN

Director

Badarch LKHAGVASUREN

Table.2 Determination of Copper, Lead and Zinc

Take 5 ml of sample using a volumetric pipette and transfer to the volumetric flask from pure water. Add pure water up to the marked line of the flask to 500 ml.

Metal	Number of sample	Data, mcg/dm ³								
		\tilde{O}_1	\tilde{O}_2	$\tilde{O} \pm \Delta$	$\tilde{O}_{\hat{E}1}$	$\tilde{O}_{\hat{E}2}$	$\tilde{O}_{\hat{E}}$	$\tilde{O}_{\hat{E}} \pm \Delta$	$\tilde{N}\tilde{a} = \tilde{O}_{\hat{E}} - \tilde{O}$	
Copper	4				nd					nd
	5				nd					nd
	6				nd					nd
Lead	4				3.0	-		3±0.6		3.0
	5				5.0	-		5±0.1		5.0
	6				nd	-		nd		nd
Zinc	4				5.8	-		5.8±1.2		5.6
	5				9.8	-		9.8±2.0		9.6
	6				4.8	-		4.8±1.0		4.6

Chemist engineer

Bold ALTANTUYA
Gerelbadrakh OYUNSUREN

Director

Badarch LKHAGVASUREN

2. Internship of the specialists to the Federal State Budgetary Institution “State Hydrochemical Institute” in Rostov-on-Don

Organization and carrying out of an internship of the specialists from the Central Laboratory of Environment and Metrology (CLEM) of Mongolia (2 persons) on the methodology issues of the surface water analysis and measurement quality control in order to introduce more selective and sensitive methods of the detection of ammonium, iron, chloride, nitrate, COD, petrochemicals and anionic synthetic surface active agents developed by the Federal State Budgetary Institution “State Hydrochemical Institute” and compliant to the international standards for the harmonization of methodological support.

Participants:

Ms.Otgonjargal, Engineer, Central Laboratory of Environment and Metrology (Ulaanbaatar, Mongolia)

Ms.Altantuya, Engineer, Central Laboratory of Environment and Metrology (Ulaanbaatar, Mongolia)

Duration and Place: from 15 through 26 October 2013, Federal State Budgetary Institution “State Hydrochemical Institute”, Rostov on- Don, Russia

Main objectives of the training program are as follows:

- to improve the analytical methods and methodologies for monitoring surface water
- to conduct more advanced and certified methodologies in evaluating measurement errors and sensitiveness
- to improve measurement quality
- to conduct more selective and sensitive methods for detecting ammonium, iron, chloride, nitrate, COD, petrochemicals and anionic synthetic surface active agents in CLEM
- to improve the quality of analysis in order to detect the above mentioned elements.

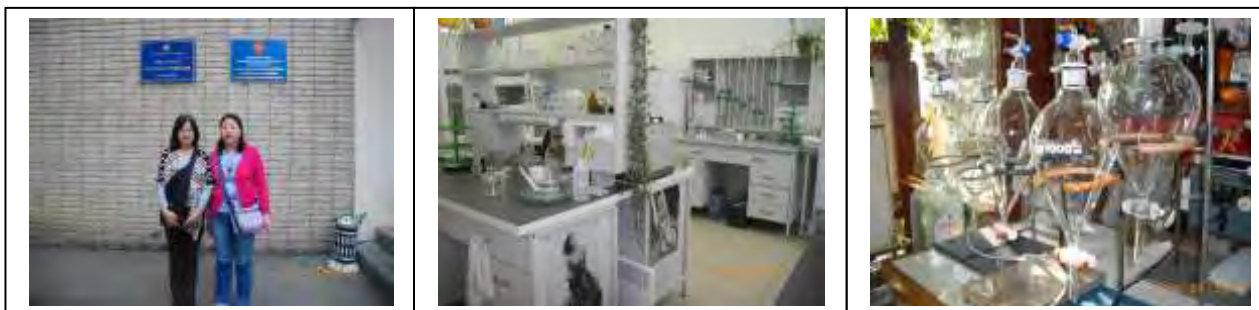
During the study programs, we were introduced to the State Hydrochemical Institute of Russia and had some lectures and labs (see Table 1).

Table 1. The training program on the “Methodology issues of the surface water analysis and the measurement quality control”

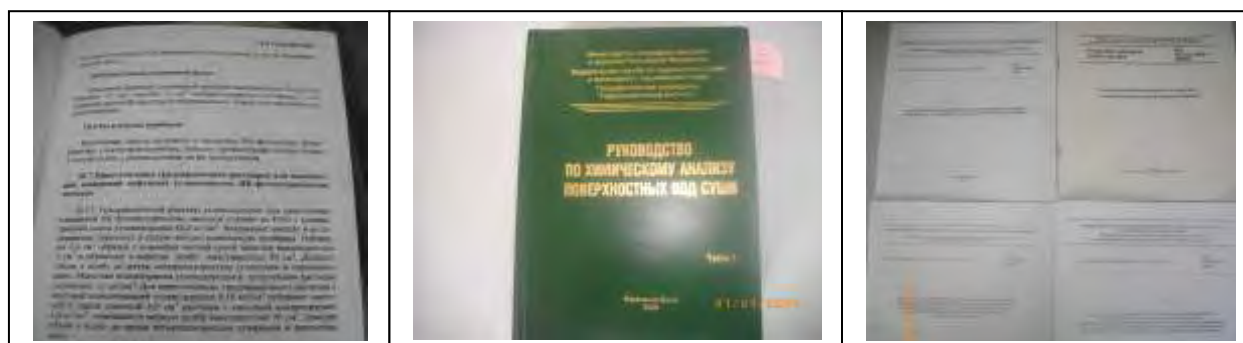
No	Title	Person in charge	Date
1	Opening speech, Introduction of the laboratory methods and techniques for water analysis	Nikanorov A.M Minina L.I Boeva L.V	15.10.13
2	Introduction of the current and future situation analytical methods of surface water and sediment, Use of certified, sensitive and selective measurement methodologies	Boeva L.V	16.10.13
3	Introduction of the system metrology validation	Nazarova A.A	17.10.13
4	Evaluation of laboratory error	Nazarova A.A	17.10.13
5	Quality control of the analytical measurements, Control of measurement error	Goncharova T.O	18.10.13
6	Graphical control of error	Goncharova T.O	18.10.13
7	Excursion	Michailenko O.A	19.10.13
8	Determination of Nitrogen and Nitrate	Boeva L.V Kileinova E.S	21.10.13
9	Determination of Ammonium and ammonium ions	Boeva L.V Tambieva N.S	22.10.13
10	Determination of Chloride	Boeva L.V Michailenko O.A	22.10.13
11	Determination of Chemical Oxygen Demand (COD)	Boeva L.V Evdokimova T.S	23.10.13
12	Determination of Total Iron	Boeva L.V Evdokimova T.S	23.10.13
13	Determination of Petroleum	Boeva L.V Ryazantseva I.A	24.10.13
14	Introduction of the methodologies for the detection of Anionic sintetic surface active agents, phenol and pesticides	Boeva L.V Andreev Yu.A	25.10.13
15	Discussion of inter-laboratory comparative test's data results (Determination of Copper, Lead and	Minina L.I Nazarova A.A	25.10.13

Zinc)	Boeva L.V
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State Hydrochemical Institute is the lead institution in the country on hydro-chemical research technologies. The institute conducts research to improve the methods and methodologies of monitoring of surface water, to determine the mass concentration of toxic and hazardous contaminants such as phenol, organochlorine compounds, pesticides using the following methods such as liquid and gas chromatographs, chromatomass-spectrometers, solid phase extraction, and other sophisticated and computerized techniques and technologies.



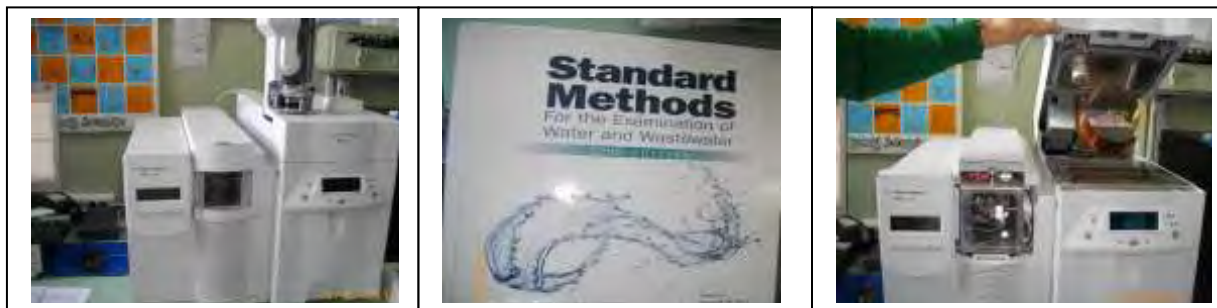
The State Hydrochemical Institute developed and approved the hundreds of regulatory documents for methods and methodologies of hydrochemical analysis.



Our training lectures focused on chemical analysis techniques to determine the composition of the main ions (sodium, potassium, calcium, magnesium, alkalinity, hydro carbonate, sulfate, and chloride), hardness, metals, nitrates, organic and petrochemical compounds indicators of water. Moreover, we studied the analytical method to determine mass concentration of synthetic anionic surfactants of water as well as gas chromatography method to measure mass concentration of hexachlorobenzene, alpha-, beta-and gamma-HCH, dicofol, digidrogeptahlora, 4,4 '-DDT, 4,4'-DDE, 4,4 '-DDD, trifluralin.



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There are several methods to determine mass concentration of sodium and potassium of water. The flame photometric method is traditional and more studied method. Potentiometric method with ion-selective electrode, ionic chromatography method, and capillary electrophoresis method are modern technological methods. These methods to mass concentration of sodium and potassium of water are similar measurement methods for water analysis in terms of accuracy or preciseness and selectiveness.

The most common measurement procedure to determine water hardness and mass concentration of calcium is titrimetric method (Trilon B, complexion III). Based on this method water hardness is determined by the difference between magnesium and calcium ions of water. The titrimetric method is pretty accurate, sensitive, selective, and more suitable method for analyses for surface water and calcium hardness. The atomic absorption spectrometric method is more appropriate method to determine a negligible amount of magnesium and calcium ions of water. Ionic chromatography method, capillary electrophoresis method, and potentiometric method with ion-selective electrode are also possible to use for measurement of magnesium and calcium ions of water.

Titrimetric method is the most commonly used for mass concentration measurement of hydrocarbons and the amount of alkalinity surface water. Reverse titrimetric method gives more accurate measurements than titrimetric method. Potentiometric titration also can be used for measurement procedure of hydrocarbons and the amount of alkalinity of surface water.

There are several methods to determine mass concentration of sulfates in water. The most commonly used measurement procedure is the gravimetric method. Ionic chromatography and capillary electrophoresis methods are analytical techniques that separate cations and are used for measurement of small amount of sulfates in water (0.1-0.5mg/l). The turbidimetric method is used for determination of larger than 1mg/l sulfates concentration in water. The turbidimetric method has similar capability to ionic chromatography and capillary electrophoresis methods and

it does not require many complex technical instruments. However the result of this method significantly depends on the quality of reagents and experimental procedures.

The following methods are covered in laboratory period.

Determination of Nitrate

1. RD 52.24.523-2009 “Mass concentration of nitrates in waters. Methodology of measurement by the photometric method with sulfanilamide and N-(1-naphtyl) ethyldiamine dihydrochloride after reduction in the cadmium reduction gear



2. RD 52.24.528-2012 “Mass concentration of nitrates in waters. Methodology of measurement by the photometric method with sulfanilamide and N-(1-naphtyl)ethyldiamine dihydrochloride after reduction in the sulfate hydrazine.



Nitrate may be found in river water, lake water, and most importantly in ground water. Nitrates in drinking water are particularly dangerous to small children, infants, and fetuses. Nitrate nitrogen may be present in small amounts in fresh domestic wastewater. However, it is seldom found in influents to treatment plants because the nitrates serve as an oxygen source in the biologically unstable wastewater. On the other hand, nitrate is often found in the effluents of biological treatment plants because it represents the final form of nitrogen from the oxidation of organic nitrogen compounds.

Determination of Chloride

- RD 52.24.402-2011 Mass concentration of chlorides in waters. Methodology of measurement by the mercury metric method

In the form of chloride ions, chlorine is necessary to all known species of life. Other types of chlorine compounds are rare in living organisms, and artificially produced chlorinated organic range from inert to toxic. In the upper atmosphere, chlorine-containing organic molecules such as chlorofluorocarbons have been implicated in ozone depletion. Small quantities of elemental chlorine are generated by oxidation of chloride to hypochlorite in neutrophils, as part of the immune response against bacteria.



Determination of Iron

- RD 52.24.358-2006 Mass concentration of total iron in waters. Methodology of measurement by the photometric method with 1.10-phenanthroline



Any solution which is colored or can be made to be colored by adding a complexing agent can be analyzed using a spectrophotometer. Solutions containing iron ions are colorless but, with the addition of ortho-phenanthroline, the iron (II) ions in the sample are immediately complexed to produce a species which is orange in color. More iron (II) ions in a sample will

result in a deeper orange color. From data obtained from a series of iron (II) standards, it is possible to be able to determine the amount of iron in an unknown sample.

Determination of Chemical Oxygen Demand (COD)

5. RD 52.24.421-2007 Methodology of measurement of COD in waters

Chemical Oxygen Demand (COD) test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD determine the amount of organic pollutants found in surface water (e.g. lakes and rivers) or wastewater, making COD a useful measure of water quality. It is expressed in milligrams per liter (mg/L) also referred to as ppm (parts per million), which indicates the mass of oxygen consumed per liter of solution.

Since then, other oxidizing agents such as ceric sulphate, potassium iodate and potassium dichromate have been used to determine COD. Of these, potassium dichromate ($K_2Cr_2O_7$) has been shown to be the most effective: it is relatively cheap, easy to purify, and is able to nearly completely oxidize almost all organic compounds.



In these methods, a fixed volume with a known excess amount of the oxidant is added to a sample of the solution being analyzed. After a refluxing digestion step, the initial concentration of organic substances in the sample is calculated from a titrimetric or spectrophotometric determination of the oxidant still remaining in the sample.

Hydro Chemical Institute, using Termion (Lumex, Russia) at 1500C for 2 hour. The concentrations in samples were determined using Fluorate (02-2M Lumex, Russia) Limit of measurement 4.0-80 mg/l.

In CLEM, the strong oxidizing agent potassium permanganate ($KMnO_4$) was used for measuring chemical oxygen demand. Measurements were called oxygen consumed from permanganate, rather than the oxygen demand of organic substances. Method specified is applicable to water with a value between 30 mg/l and 700 mg/l. Potassium permanganate's effectiveness at oxidizing organic compounds varied widely, and in many cases BOD measurements were often much greater than results from COD measurements. This indicated that potassium permanganate was not able to effectively oxidize all organic compounds in water.

Determination of petroleum components

- RD 52.24.476-2007 Mass concentration of petroleum components in waters. Methodology of measurement by the IR-photometric method. Detection limit of the method is from 0.04 to 2mg/l.

Petrochemical products are toxic, creditable for water pollution which is commonly distributed and their structures are complex because of the non- homogenized mixture of organic compound. In today's world, the weighting, the infra-red photometry, the luminescence, gas and open-column displacement chromatography or HPLC methods are using for determination of petrochemical products in natural water. Petrochemical products will extract by tetra chloromethane and separate from water when samples are passing through the column which was filled by aluminum hydroxide. Separated products will be detect and count at KH-2 Concentra meter.



Also, we known and introduced gas chromatographic method. When photo-illuminator disperse radiation through the compound, compound provides reflected colors(spectral) such as blue, brown, yellow etc.,



The CLEM is using the weighting method for petrochemical products. Disadvantages of the weighting method are availability of distillation funnels, it is time consuming and in accuracy of method. Also, the method requires chemical pure tetra chloromethane.

Determination of ammonium and ammonium ions

- RD 52.24.383-2005 Mass concentration of ammonia and ammonia ions in the surface waters of the land. Methodology of measurement by the photometric method in the form of indophenols blue

The nitrogen is important biogenic element and it has three types such as nitrate, nitrite and ammonium nitrogen in aquatic system. Ammonium nitrogen is mostly dissolved form in water and unstable at aquatic system. It will be transfer easily to nitrite and nitrate ions due to dissolved oxygen and photochemical reaction. During the analysis contamination will be occurring. Therefore, lab requires to avoid contamination and solution should be prepared by cationic water. This method uses the phenol, since we are extracting it more purely. Measurement would be 12 hours later. This method is very sensitive.

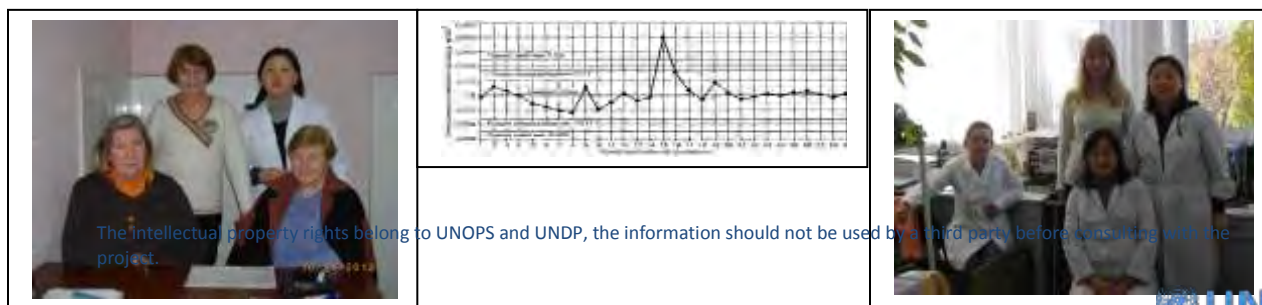


The CLEM is using the Nessler method for ammonium and ammonium ions which detection limits are from 0.04 to 4 mg/L. The laboratory is not using the special room. Sometimes, ammonium in air was higher than the ammonium in water; therefore it might be disturb measurement.

Result validation

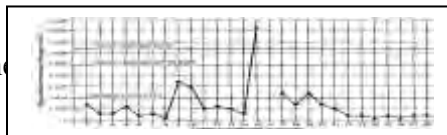
- RD 52.24.383-2005 Water chemistry information internal data control

Conclusions about measurement which was followed lab handout or standard method should conclude results of measurement based on the control number of variables. When we are confirming the results, we are focusing next following conditions: methods of chemical and quantitative, quality control and quality assurance results, number of samples, frequency of samples (RPD), lab equipment differences, technician's experiences, data errors and standard deviations, relative percent difference for samples etc.,



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Error would be calculated for the



Standard method of result calculation requires sample duplicates at least 5 and 6 times for quality control and average value and dispersion calculates every 15 measurements. Laboratory notes of every processes and measurements needed and it will be useful for systematic errors of equipment and laboratory with sample frequencies.

Summary

In CLEM, for water chemical analysis, laboratories are using spectrophotometers, pH meters, conductivity meters, AAS (flame atomization), X-Ray fluorescence and some field testing equipment. The laboratories are analyzing just basic parameters such as dissolved inorganic ions, nutrients and a few metals. Currently, chemical analyses of water are not good because analytical laboratories haven't had more sophisticated equipments for appropriate methods. Results necessitate a real, so, the selective and sensitive methods needed with included effects, calculated errors and validations. We need to analyze dissolved gases, organic components, petroleum oils, toxic elements, and chloro-organic compounds using liquid and gas chromatographs, AAS with electrothermal and flame atomization, chromatomass-spectrometers, solid phase extraction, systems of microwave treatment of samples, ICPOES and IR spectrophotometers, mercury analyzer based on the method of atomic absorption of cool vapor, and different types gas analyzers and other sophisticated and computerized techniques and technologies.

Methods and procedures of Hydrochemical Institute are useful because it was checked and used for many laboratories, detection limits are flexible, calibration curve and internal standard are clear, data analyses are clear and updates are commonly made.

Classic and more sensitive methodology should be selected for real results and initially we have to consider interferences and errors of those methodologies then to remove or reduce the interferences and errors. Method and methodology which are produced by chemical institute of water are sensitive and classical methods which should respond those requirements, and should check at various laboratories. The method includes not only consideration and removal of interferences but also uses of standard reagent, solution, devices, instruments, calibration curve. Also the method considers quality control activities (QA/QC), accuracy and errors of measurements. In addition, advantage of the method is always renewed.

One purpose of the monitoring, through the evaluation of analytical results, analytical equipment and its operating condition, to recognize the analytical precision and accuracy of the measurements, give to an opportunity to improve the quality of the analysis on water quality monitoring, improve reliability of analytical data through the assessment of suitable analytical methods and techniques.



UNDP-GEF project
"Integrated Natural Resource Management in the Baikal Basin Transboundary Ecosystem"



To get verified information: about if those laboratories have a laboratory certificate, what standards, methods and calibrations they use, and those methods are appropriate for today's conditions or not; on internal and external QA/QC is very difficult.