GUIDELINE

MASS CONCENTRATION OF FLUORIDES IN WATERS. PROCEDURE FOR MEASUREMENT USING POTENTIOMETRIC METHOD WITH ION-SELECTIVE ELECTRODE

Enactment date 2008-05-20

Foreword

1 DEVELOPED by State Enterprise Hydrochemical Institute (SE HCI)

2 AUTHORS: L.V.Boeva, candidate of chemical science, N.S.Tambieva

3 REVIEWED by UMZA and NPO "Taifun" of Rosgidromet

4 APPROVED AND IMPLEMENTED by Deputy Manager of Rosgidromet on 1 February 2008.

5 CERTIFIED by SE HCI, certification No. 6.24-2007 dated 16.05.2007.

6 REGISTERED by SE NPO "Taifun", No. RD 52.24.360-2008 dated 28.03.2008.

7 SUBSTITUTES RD 52.24.360-95 "Methodological guideline. Procedure for measurement of fluoride mass concentration in waters using potentiometric method with ion-selective electrode"

Introduction

Fluorine in nature is most frequently found in the form of calcium fluoride CaF2, sellaite MgF2, cryolite $A1F_3$-3NaF. Significant amounts of it are contained in phosphoric minerals phosphorite and apatite.

The main natural sources of fluorine coming to water bodies are leaching of fluorine-containing minerals, as well as volcanic emissions. Man-made pollution of water bodies with fluorine is caused by its carry-over with waste water of a number of industrial (chemical, metallurgical, glass, ceramic, etc.) and agricultural facilities. Another source of fluorine coming to natural waters is also atmospheric precipitation, where it gets as a result of fuel burn, in the form of industrial releases, with soil dust.

Fluorine may be present in waters both in the form of free fluoride-ions, and in the form of complex ions $[FeF_4]^-$, $[FeF_5]^{2-}$, $[FeF_6]^{3-}$, $[AIF_6]^{3-}$, etc.

Fluoride-ion is related to stable components of natural waters. Its migration capability is notably affected only by calcium ions, forming poorly soluble compounds with fluorine ions. Of great importance is the condition of carbon dioxide that dissolves calcium carbonate. Alkaline nature of waters contributes to mobility of fluoride-ions. Leaching of fluorides from rock is contributed by sulfates, therefore the waters with high sulfates concentration are characterized by higher concentrations of fluorides. Normally their concentration in surface land waters is below 1 mg/dm^3, while in underground waters it may be as high as 10 mg/dm^3. Within-year variations of fluoride concentrations in natural waters are normally not large. In absence of sources of significant pollution fluorides come to rivers mainly with ground waters. During flood period the share of supply due to ground waters is reduced, therefore during flood periods the concentration of fluorides is always lower than during low-water seasons.

Fluorides have significant importance for normal physiological process in human and animal organisms; both lack and excess of fluorine in water have a negative effect on many organism systems, primarily skeletal system.

Fluorides content in natural waters is normalized. The maximum permissible concentration for fishing water bodies is 0.75 mg/dm^3, for water facilities of household-drinking and cultural-social purpose it is from 0.75 to 1.5 mg/dm^3 depending on the region.

1 Scope

1.1 This Guideline establishes a procedure for measurement (hereinafter procedure) of fluorides mass concentration in natural and purified waste waters in the range of 0.19 to 190 mg/dm^3 using potentiometric method with ion-selective electrode.

During analysis of water samples with mass concentration of fluorides exceeding 190 mg/dm^3, the measurement is allowed to be performed after the sample dilution with distilled water in such a way that the mass concentration of fluorides in the diluted sample is within the above indicated range of measured concentrations.

1.2 This Guideline document is intended for use at laboratories involved in analyses of natural and purified waste waters.

2 Regulatory references

This Guideline document contains references to the following regulatory documents:

GOST 12.1.005-88 SSBT. General sanitary-hygienic requirements to air in working areas

GOST 12.1.007-76 SSBT. Harmful substances. Classification and general safety requirements

GOST 17.1.5.04-81 Nature preservation. Hydrosphere. Instruments and devices for sampling, initial processing and storage of natural water samples. General technical specifications

GOST 17.1.5.05-85 Nature preservation. Hydrosphere. General requirements to sampling of surface and sea waters, ice and atmospheric precipitation

GOST R ISO 5725-6-2002 Accuracy (correctness and precision) of methods and measurement results. Part 6. Practical use of accuracy values

GOST P 51592-2000 Water. General requirements to sampling

MI 2881-2004 Recommendation. GSI. Procedures for quantitative chemical analysis. Checking procedures for acceptability of analysis results.

Note: References to other regulatory documents are provided in sections 4, A.4.

3 Assigned characteristics of measurement error

3.1 When all measurement conditions regulated by the procedure are met, the measurement result error characteristics shall not exceed with the probability of 0.95 the values provided in Table 1.

Table 1 - Measurement range, characteristic values of error and its components with confidence probability P =0,95

Measurement range of fluoride mass concentration X, mg/dm^3	Repeatability indicator (root-mean-square deviation of repeatability) σ_r, mg/dm^3	Reproducibility indicator (root-mean-square deviation of reproducibility) σ_R, mg/dm^3	Correctness indicator (systematic error boundaries) $\pm\Delta_c$, mg/dm^3	Accuracy indicator (error boundaries) $\pm\Delta$, mg/dm^3
From 0,19 to 19,0 incl.	0,01+0,05· X	0,01+0,10· X	0,052· X	0,02+0,20-X
Over 19,0 to 190,0 incl.	0,2+0,041· X	0,4+0,082· X	0,2+0,044 X	0,7+0,17· X

During measurements in samples with mass concentration of fluorides exceeding 190 mg/dm^3, after appropriate dilution, the error of fluoride mass concentration measurement in the initial sample is determined using the formula:

$$\pm\Delta = (\pm\Delta_1)\cdot\eta,$$

where - $\pm\Delta_1$ is the accuracy indicator of fluoride mass concentration measurement in the diluted sample, calculated using the equation from Table 1;

η is the rate of dilution.

The limit of fluoride identification using the potentiometric method is 0.1 mg/dm^3.

3.2 The values of the method accuracy indicator are used for:

- documenting the measurement results issued by the laboratory;
- assessment of laboratory activities for measurement quality;
- assessment of possibility to use the measurement results for implementation of the procedure at a specific laboratory.

4 Measurement means, auxiliary devices, agents, materials, solutions

4.1 Measurement means, auxiliary devices

4.1.1 Ion meter of any type or pH-meter, operating in the mode of millivoltmeter, provided with a magnetic stirrer (for example, I-500, TS 4215-002-18294344-02; "Ecotest-2000", TS 4215-005-41541647-99, etc.).

4.1.2 Measuring electrode ELIS-13Sch TS 4214-015-35918409-2002, or other type with similar characteristics.

4.1.3 Auxiliary electrode – chlorinated silver electrode EVL-1M3, TS 25.05.2181-77, or other type with similar characteristics.

4.1.4 Laboratory balance of high (II) accuracy class to GOST 24104-2001*.

---

* The document is not acting in the Russian Federation. The acting document is GOST R 53228-2008, here and further on in the text. – Comment of the data base creator.

4.1.5 Laboratory balance of middle (III) accuracy class to GOST 24104-2001, with the highest weighing limit 500 g.

4.1.6 State standard sample of fluoride-ion solution, SSS 7261-96 (hereinafter - SSS).

4.1.7 Thermometer to GOST 29224-91 with temperature measuring range from 0 °C to 150 °C and graduation mark not more than 1 °C.

4.1.8 Measuring flasks of accuracy class 2, models 2, 2a to GOST 1770-74, capacity 100 cm^3 - 7 pcs., 200 cm^3 - 21 pc., 1000 cm^3 - 1 pc.

4.1.9 Measuring pipettes of accuracy class 2, models 1, 2, GOST 29227-91, capacity 2 cm^3 - 2 pcs., 25 cm^3 - 5 pcs.

4.1.10 Pipettes with one mark of accuracy class 2, model 2 to GOST 29169-91, capacity 5 cm^3 - 1 pc., 10 cm^3 - 4 pcs., 20 cm^3 - 1 pc.

4.1.11 Measuring cylinders of models 1, 3 to GOST 1770-74, capacity 25 cm^3 - 3 pcs., 250

cm^3 - 1 pc.

4.1.12 Glasses V-1, THS, to GOST 25336-82, capacity 50 cm^3 - 30 pcs., 100cm^3 - 1 pc., 1000 cm^3 - 1 pc.

4.1.13 Weighing cups (bottles) SV-24/10, SV-34/12 to GOST 25336-82 - 2 pcs.

4.1.14 Laboratory funnel type B to GOST 25336-82, diameter 56 mm - 1 pc., 75mm - 1 pc.

4.1.15 Evaporation bowl N 2 to GOST 9147-80.

4.1.16 Desiccator model 2 with the housing diameter 140 mm or 190 mm to GOST25336-82.

4.1.17 Polyethylene (polypropylene) vessels for storage of samples and solutions capacity 0.1; 0.25; 1 dm^3 .

4.1.18 Common laboratory drying cabinet.

4.1.19 Closed spiral electric stove, GOST 14919-83.

It is allowed to use other types of measuring means, auxiliary devices, including imported ones, with characteristics not worse than those indicated in it. 4.1.

4.2 **Agents and materials**

The following agents and materials are used for measurement performance:

4.2.1 Sodium fluoride to GOST 4463-76, p.f.a. (pure for analysis) 99%

4.2.2 Sodium chloride to GOST 4233-77, c.p. (chemically pure)

4.2.3 Sodium acetate hydrate 3-water to GOST 199-78, c.p.

4.2.4 Sodium citrate hydrate 5,5-water, GOST 22280-76, p.f.a.

4.2.5 Potassium chloride to GOST 4234-77, c.p.

4.2.6 Acetic acid to GOST 61-75, c.p.

4.2.7 Distilled water to GOST 6709-72.

4.2.8 Ash-free paper filters “white strip”, TS 6-09-1678-86.

4.2.9 Filtering paper to GOST 7584-89.

Note - It is allowed to use agents made to other regulatory technical documents, including imported ones, with qualification not lower than that indicated in it.4.2.

5 Measuring method

The measurement is based on variation of ion-selective electrode potential, based on activity of fluoride-ions in solution. The measurement is performed in presence of a buffer solution – indifferent electrolyte supporting specified value of pH and ionic strength in the analyzed solution, which allows calibrating the instrument in concentration units, and not in fluoride-ion activity units. The fluorides concentration in the sample is determined based on the calibrating dependence of the value of electrode potential on the value of inverse logarithm of fluoride-ion activity (concentration) (pF). The ion-selective electrode potential depends only on concentration of free fluoride-ions. Fluorides that are present in suspended substances, or are fixed in stable complexes, do not affect the value of the electrode potential.

6 Requirements to safety, environment protection

6.1 During measurement of fluoride mass concentration in samples of natural and purified waste waters safety requirements shall be followed, established by national standards and applicable regulatory documents.

6.2 By their effect on organism the harmful substances used during measurements are referred to hazard class 3 according to GOST 12.1.007.

6.3 The content of the used harmful substances in the air of the working area shall not exceed the maximal permissible concentrations in accordance with GOST 12.1.005.

6.4 No special environmental safety requirements are imposed.

7 Requirements to qualification of operators

Measurements are allowed to be performed by persons having high professional training or having no professional training, but having at least one year of laboratory work experience and having mastered the analysis method.

8 Conditions for measurement performance

During measurement the following conditions shall be met at the laboratory:

- ambient air temperature (22±5) °C;
- atmospheric pressure from 84.0 to 106.7 kPa (from 630 to 800 mm mercury column);
- air humidity not more than 80% at 25 °C;
- grid voltage (220±10) V;
- alternating current frequency in the power grid (50±1) Hz.

9 Sampling and sample storage

Sampling for fluorides identification shall be performed according to GOST 17.1.5.05 and GOST R 51592. The sampling equipment shall meet GOST 17.1.5.04 and GOST R 51592. Samples are placed in polyethylene or polypropylene vessels. Samples are allowed to be stored in hermetically sealed vessels for up to one month. The sample volume shall be not less than 50 cm^3.

10 Preparation for measurement performance

10.1 Preparation of solutions and agents

10.1.1 Buffer solution (pH 5.4-5.5)

58.5 g of sodium chloride, 0.36 g of sodium citrate ($Na_3\ C_6\ H_5\ O_7$ * 5.5 H_2O) and 102 g of sodium acetate (CH_3 COONa * 3H_2O) are placed in a glass of 1000 cm^3 capacity, dissolve them in distilled water and add 14.4 cm^3 of glacial acetic acid. The resulting solution is transferred to a measuring flask of 1000 cm^3 capacity, and the glass is rinsed twice with distilled water. Add distilled water to the solution up to the mark on the flask and stir it. Store it in polyethylene vessel for not longer than 1 month.

10.1.2 Saturated potassium chloride solution

Dissolve 60 g of potassium chloride in 140 cm^3 of distilled water at the temperature of 50-60°C. After cooling use the solution above the sediment for filling the auxiliary electrode.

10.2 Preparation of calibration solutions

10.2.1 Calibration solutions are prepared from SSS (State Standard Solution) with mass fluoride concentration 1.00 mg/cm^3 (molar concentration 5.26·* 10^{-2} mole/dm^3) or certified solution with fluoride mass concentration 1.900 g/dm^3 (molar concentration 1.00·* 10^{-1} mole/dm^3). The method of certified solution preparation is provided in Annex A.

10.2.2. For preparation of calibration solution N 1 with fluoride molar concentration 1.00·* 10^{-2} mole/dm^3 from SSS, take 19.0 cm^3 of SSS solution using a clean, dry measuring pipette of 25 cm^3 capacity, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir.

For preparation of calibration solution N 1 from certified solution, using a pipette with one mark, take 10.0 cm^3 of certified solution with molar concentration 1.00·* 10^{-1} mole/dm^3, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir.

The resulting solution is assigned the pF value equal to 2.00.

10.2.3 For preparation of calibration solution N 2 with fluoride molar concentration 1.00 * 10^{-3} mole/dm^3, using a pipette with one mark, take 10.0 cm^3 of calibration solution N 1 with fluoride molar concentration 1.00·* 10^{-2} mole/dm^3, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir. The resulting solution is assigned the value of pF equal to 3.00.

10.2.4 For preparation of calibration solution N 3 with fluoride molar concentration 2.00·* 10^{-4} mole/dm^3 take 2.0 cm^3 of calibration solution N 1 with fluoride molar concentration 1.00·* 10^{-2} mole/dm^3 using a measuring pipette of 2 cm^3 capacity, place it in a measuring flask of 100 см^3 capacity, add distilled water up to the mark and stir. The resulting solution is assigned the value of pF equal to 3.70.

10.2.5 For preparation of calibration solution N 4 with fluoride molar concentration 1.00*10^{-4} mole/dm^3 using a pipette with one mark, take 10.0 см^3 of calibration solution N 2 with fluoride molar concentration 1,00·* 10^{-3} mole/dm^3, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir. The resulting solution is assigned the value of pF equal to 4.00.

10.2.6 For preparation of calibration solution N 5 with fluoride molar concentration 5.00*10^{-5} mole/dm^3 using a pipette with one mark, take 5.0 cm^3 of calibration solution N 2 with fluoride molar concentration 1.00·* 10^{-3} mole/dm^3, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir. The resulting solution is assigned the value of pF equal to 4.30.

10.2.7 For preparation of calibration solution N 6 with fluoride molar concentration 2.00·* 10^{-5} mole/dm^3 take 2.0 cm^3 of calibration solution N 2 with fluoride molar concentration 1.00·* 10^{-3} mole/dm^3 using a measuring pipette of 2 cm^3 capacity, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir. The resulting solution is assigned the value of pF equal to 4.70.

10.2.8 For preparation of calibration solution N 7 with fluoride molar concentration 1.00*10^{-5} mole/dm^3 using a pipette with one mark, take 10.0 cm^3 of calibration solution N 4 with fluoride molar concentration 1.00·* 10^{-4} mole/dm^3, place it in a measuring flask of 100 cm^3 capacity, add distilled water up to the mark and stir. The resulting solution is assigned the value of pF equal to 5.00.

10.2.9 Calibration fluoride solutions shall be stored in polyethylene or polypropylene vessel with a tightly fitting stopper. Calibration solution N1 shall be stored not longer than for 3 months, solutions N 2, 3 – not longer than for 1 month, solutions N 4, 5 – not longer than for 2 weeks, solutions N 6, 7 – not longer than for 5 days.

10.3 Preparation of ion meter, measuring and auxiliary electrodes for work

Preparation of the instrument, measuring and auxiliary electrodes for work shall be performed according to the guideline for their operation or technical specification.

10.4 Identification of calibration dependence

10.4.1 Take clean dry glasses of 50 cm^3 capacity, place 15 cm^3 of each of the calibration solutions N 1-7 and add to them 15 cm^3 of the buffer solution, using measuring pipettes or measuring cylinders of 25 cm^3 capacity. Place the glasses on magnetic stirrer, immerse the stirring element, the measuring electrode and the auxiliary electrode in the solution. Turn on the stirrer and perform the potential measurement in the calibration solutions from the lower fluoride concentration ($1.00*10^{-5}$ mole/dm^3) to higher one ($1.00*10^{-2}$ mole/dm^3). The depth of the electrodes immersion and stirring rate shall be the same for all measurements. The ion meter readings shall be recorded after the constant potential value is established. The time of its identification depends on fluoride concentration in the calibration solutions, and is from several seconds to minutes. The temperature of calibration solutions is measured simultaneously. The temperature difference for different calibration solutions shall not exceed 1 °C.

Three parallel measurements of potential shall be performed for each calibration solution, and the arithmetic mean is taken as the result. The calibration dependence is calculated by least squares method in coordinates: values of pF of the calibration solutions ($pF = {}^{-}lg[F^{-}]$) – values of potential in millivolts corresponding to them.

The calibration dependence shall be established every time when fluoride mass concentration is measured in water samples.

If the fluoride mass concentration in the analyzed samples does not exceed 10 mg/dm^3, the calibration dependence is allowed to be established using calibration solutions N 2-7.

10.4.2 If the ion meter operating manual provides for another method of calibration dependence (calibration) establishment, it is allowed to establish it in accordance with the manual for the given ion meter. In the cases when the calibration dependence for a specific instrument is established using a smaller number of calibration solutions, than indicated in it. 10.4.1, after it is established, the check of calibration characteristic stability shall be performed in accordance with it. 10.5.

10.5 Check of calibration characteristic stability

The check is performed using calibration solutions N 1-7 according to it. 10.2 (not less than 3). The calibration characteristic is considered stable when the following condition is met

$$| X - C_m | \leq \sigma_R \qquad (2)$$

where X is the result of control measurement of the fluoride mass concentration in the calibration solution, mg/dm^3 ;

C_m is the assigned value of fluoride mass concentration in calibration solution, mg/dm^3;

σ_R is the reproducibility indicator for concentration C_m, mg/dm^3 (Table 1).

If the stability condition is not met for one calibration solution, the measurement of this solution shall be repeated to exclude a result containing a gross error. If the condition is not met again, the causes for lack of stability shall be identified, eliminated, and the measurement shall be repeated. If the calibration characteristic will not meet the condition (1) again, a new calibration dependence shall be established, or the measurement shall be performed in the mode of millivoltmeter, and the calibration dependence shall be established according to it. 10.4.1.

11 Measurement performance

11.1 Measurement performance when there are no interferences

15 cm^3 of analyzed sample and 15 cm^3 of buffer solution are poured into each of three glasses of 50 cm^3 capacity using graduated pipets or cylinders of 25 cm^3 capacity, mixed and hold for 15 min. The glasses are installed at the magnetic stirrer, the intermixing element and measuring and auxiliary electrodes are dipped into the sample to be analyzed. The stirrer is switched on, and potential of the measuring electrode is measured. Readings of the ion meter are recorded after the potential constant value is established. Upon completion of measurement, electrodes are washed with distilled water. Electrodes are washed rather rapidly with its threefold change. Water residues are removed from electrode surface with filter paper. Three parallel potential measurements are conducted in the analyzed water sample.

The temperature of analyzed samples shall not differ from the temperature of calibration solutions by more than ±1 °C.

11.2 Substances interferences and their elimination

11.2.1 Measurement of fluoride mass concentration with ion-selective electrode can be impeded by substances that form a film on the working surface of the electrode. In such cases, another method is expedient to be used to perform measurements. Very turbid samples should be filtered through ‘white strap’ filter.

The first portion of the filtrate is rejected.

11.2.2 Fluorides form rather solid complexes with a number of metals. During the analysis of natural and purified waste waters, the greatest influence is exerted by high concentrations of iron and aluminium. Adding a buffer solution containing sodium citrate in its composition reduces their influence, to a considerable extent, due to destruction of complexes.

12 Calculation and measurement result recording

12.1 The pF values in analyzed water samples are found by calibration dependence. Mass concentration of fluorides X, mg/dm ^{3}, is calculated according to the following ratios:

$$pF = -lg[F^-];\ [F^-] = 10^{-pF}\ mole/dm^3\ ;\ X = 10^{“pF}\ 19{,}00\ 10^3\ mg/dm^3 \qquad (3$$

or found according to Table given in Appendix B for pF values in the range from 4,00 to 5,00. Concentration of fluorides in mg/dm^3 for pF values from 3,0 to 4,0 and from 2,0 to 3,0 is obtained by increasing table values in the range from 4,00 to 5,00, having the same values of the fractional part, by 10 and 100 times, respectively. For example, pF equal to 4,40 corresponds to 0,756 mg/dm^3 of fluorides, pF equal to 3,40 corresponds to 7,56 mg/dm^3, pF equal to 2,40 corresponds to 75,6 mg/dm^3 .

If an ion meter having a data processing program is used for measurements, the values of fluoride mass concentration are read directly from the display.

12.2 The measurement result in the documents where it is expected to be used is presented in the following form

$$X \pm \Delta,\ mg/dm^3 \quad (P = 0{,}95)\ , \qquad (4)$$

where X – arithmetic mean value of three results the difference among which does not exceed the repeatability limit r_η ($3{,}31 \cdot \sigma_r$). If the repeatability limit is exceeded, it is necessary to follow item 13.2.

$\pm\ \Delta$ – boundaries of measurement result error characteristics for a given fluoride mass concentration (Table 1).

Numerical values of the measurement result shall end with the figure of the same digit as error characteristics values which shall not contain more than two significant figures.

12.3 It is allowed to present the result in the following form:

$$X \pm \Delta_l\ P = 0{,}95, \text{ on the condition of } \Delta_l < \Delta$$

where - ± Δ_l – boundaries of measurement result error characteristics established during laboratory implementation of the method and supported by control of the stability of measurement results.

12.4 Measurement results are documented in a report or as a record in a logbook, according to the forms given in the Laboratory Quality Guideline.

13 Quality control of measurement results during laboratory implementation of the method

13.1 General

13.1.1 When the method is implemented at the laboratory, the quality control of measurement results provides for:

- operational control by the measurement procedure performer (based on assessment of repeatability and error during implementation of a separate control procedure);

- control of the measurement results stability (based on control of the stability of repeatability mean-square deviation, error).

13.1.2 The frequency of control by the measurement procedure performer as well as the implemented procedures for control of stability of the performed measurement results are regulated by the Laboratory Quality Guideline.

13.2 Algorithm of operational repeatability control

13.2.1 The repeatability control is carried out for each of the measurement results obtained in compliance with the method. To do this, the taken water sample is divided into three parts, and measurement is performed in accordance with Section 11.

13.2.2 The control procedure result $r_к$, mg/dm^{3}is calculated according to the formulae

$$r_К = |X_{\text{макс}} - X_{\text{мин}}|, \tag{6}$$

where Xmax, Xmin - maximum and minimum results of fluoride mass concentration measurement in a sample, mg/dm^3 .

The repeatability limit r_n, mg/dm^3, is calculated according to the formula

13.2.3

$$r_п = 3{,}31 \cdot \sigma_r, \tag{7}$$

13.2.4 The control procedure result shall satisfy the condition

$$r_К \leq r_п. \tag{8}$$

13.2.5 If the condition (8) is not met, three more measurement are performed, and the difference between maximum and minimum results is compared with the control standard equal to 4,03·σ_r. In case of repeated violation of the repeatability limit, it is necessary to act in compliance with Section 5 GOST R ISO 5725-6.

13.3 Algorithm of operational measurement error control using the additives method together with the method of sample dilution

13.3.1 Operational control of the measurement error using the additives method together with the sample dilution method is conducted if the fluoride mass concentration in the working sample amounts to 0,5 mg/dm^3 and more. Otherwise, operational control is conducted using the additives method, according to 13.4. To introduce additives, a state standard sample (GSO) or the certified fluoride solution is used (Appendix A).

13.3.2 Operational control of the measurement procedure performer is conducted by comparing the results of a separate control procedure K_{Kl} with the control standard Kι.

13.3.3 The control procedure result K_{Kl}, mg/dm^3, is calculated according to the formula

$$K_{K_1} = \overline{X''} + (\eta - 1) \cdot \overline{X'} - \overline{X} - C, \quad (9)$$

where X" – arithmetic mean of control measurement results of fluoride mass concentration in a sample diluted by ŋ times, with a known additive, mg/dm^3;

X' – arithmetic mean of control measurement results of fluoride mass concentration in a sample diluted by ŋ times, mg/dm^3 ;

X – arithmetic mean of control results of fluoride mass concentration measurement in a working sample, mg/dm^3;

C – additive concentration, mg/dm^3.

13.3.4 The control standard Kl, mg/dm^3 , is calculated according to the formula

$$K_1 = \sqrt{\Delta^2_{лX''} + (\eta - 1)^2 \Delta^2_{лX'} + \Delta^2_{лX}}, \quad (10)$$

where values of r $\Delta_{лX''}$, $\Delta_{лX'}$ и $\Delta_{лX}$ - or characteristics, established in laboratory implementation of the method, corresponding to fluoride mass concentration in diluted sample, in diluted sample with an additive, in working sample, mg/dm^3.

Note – When the method is implemented at the laboratory, it is allowed to establish the measurement result error characteristic based on the expression:
$\Delta л_{x''}$. = 0,84 ·Δx", $\Delta л_x$ = 0,84 Δx’, and $\Delta л_x = 0,84\ \Delta_\chi$ with subsequent refinement as the information

is being accumulated in the process of control of the measurement result stability.

13.3.5 If the control procedure result satisfies the condition:

$$(11)\ |K_{K_1}| \le K_1,$$

the analysis procedure is recognized as satisfactory.

If the condition (11) is not met, the control procedure is repeated. In case of repeated non-fulfillment of the condition (11), the causes leading to unsatisfactory results are identified, and measures for their elimination taken.

13.4 Algorithm of operational measurement error control using the additives method

13.4.1 The control by the measurement procedure performer is conducted by comparing the results of a separate control procedure $К_к$ with the control standard К.

13.4.2 The control procedure result $К_к$, mg/dm^3, is calculated according to the formula

$$K_{K_2} = |\overline{X}''' - \overline{X} - C|.$$

where X" – arithmetic mean of the control measurement results of fluoride mass concentration in a sample with a known additive, mg/dm^3 .

13.4.3 The error control standard К, mg/dm^3, is calculated according to the formula

$$K_2 = \sqrt{\Delta^2_{лx'''} + \Delta^2_{лx}} \qquad (13)$$

where $Δл_x$ - value of mea characteristic, established during laboratory implementation of the method, and corresponding to fluoride mass concentration in a sample with a known additive, mg/dm^3.

13.4.4 If the control procedure result satisfies the condition

$$(14) \qquad |K_{K_2}| \le K_2$$

the procedure is recognized as satisfactory.

If the condition (14) is not met, the control procedure is repeated. In case of repeated non-fulfillment of the condition (14), the causes leading to unsatisfactory results are identified, and measures for their elimination taken.

14 Check of acceptability of results obtained under reproducibility conditions

14.1 The difference between measurement results obtained at two laboratories shall not exceed the reproducibility limit R. If this condition is met, both measurement results are acceptable, and their common average value can be used as final result. The reproducibility limit value is calculated according to the formula

$$R = 2{,}77 \cdot \sigma_R \quad . \qquad (15)$$

12.4 If the reproducibility limit is exceeded, methods for assessment of the measurement result acceptability can be used, according to Section 5 GOS R ISO 5725-6 or MI 2881.

12.5 The acceptability is checked if it is necessary to compare the measurement results obtained by two laboratories.

Appendix A
(recommended)

Method for preparation of certified fluoride solutions CS1-F and CS2-F

A.1 Purpose and field of application

This method regulates the procedure for preparation of certified fluoride solutions, designed to establish calibration characteristics of the instruments and to control accuracy of the fluoride mass concentration measurement results in natural and purified waste waters with ion-selective electrode.

A.2 Metrological characteristics

Metrological characteristics of certified solutions are given in Table A.1.

Table A.1

Characteristic name	Characteristic value for certified solution	
	CS1-F	CS2-F
Certified value of fluoride molar concentration, mole/dm^3	1,000	0,1000
Error boundaries in establishing certified value of fluoride molar concentration (P=0,95), mole/dm^3	0,010	0,0011

Certified value of fluoride mass concentration, g/dm^3	19,00	1,900
Error boundaries in establishing certified value of fluoride mass concentration (P=0,95) g/dm^3	0,19	0,020

A.3 Measuring means, auxiliary devices

A.3.1 Laboratory balance of high (IInd) accuracy class according to GOST 24104-2001.

A.3.2 Measuring flasks of 2nd accuracy class according to GOST 1770-74, of 200 cm^3 capacity – 2 pcs.

A.3.3 Pipet with one mark according to GOST 29169-91, of 20 cm^3 capacity.

A.3.4 Weighing cup (weighing bottle), SV-34/12 according to GOST 25336-82.

A.3.5 Laboratory funnel according to GOST 25336-82, of 75 mm diameter.

A.3.5 Evaporation bowl N 2 according to GOST 9147-80.

A.3.6 Drying bottle, model 2, with vessel diameter of 190 mm according to GOST 25336-82.

A.3.7 Drying box of general laboratory purpose.

A.4 Initial components of certified solutions

A.4.1 Sodium fluoride according to GOST 4463-76, p.f.a. (pure for analysis). Base substance: NaF, its mass fraction is no less than 99%, molar mass: 41,99.

A.4.2 Distilled water according to GOST 6709-72.

A.5 Procedure for preparation of certified solutions

A.5.1 Preparation of certified fluoride solutions CS1-F

8,398 g of sodium fluoride, previously dried at a temperature of 110 °C for 2 hours is weighed in a weighing bottle at a high-class balance, with accuracy of up to the forth decimal digit. The added weight is transferred quantitatively in a measuring flask of 200 cm^3 capacity, dissolved in distilled water, brought up to the flask mark and mixed.

The obtained solution is assigned the fluoride molar concentration of 1,000 mole/dm^3 and mass concentration of 19,00 g/dm^3 .

A.5.2 Preparation of certified fluoride solution CS2-F

20,0 cm^3 of the solution CS1-F is introduced in a measuring flask of 200 cm^3 capacity using a pipet with one mark. The solution volume is brought to the flask mark with distilled water and mixed.

The obtained solution is assigned the fluoride molar concentration of 0,1000 mole/dm^3 and mass concentration of 1,900 g/dm^3 .

A.6 Calculation of metrological characteristics of certified solutions

A.6.1 Calculation of metrological characteristics of the certified solution CS1-F

The certified value of fluoride molar concentration, M_1, mole/dm3, and mass concentration C_1, g/dm^3, is calculated according to the formulas

$$M_1 = \frac{m \cdot 1000}{V \cdot 41{,}99}, \quad C_1 = \frac{m \cdot 19{,}00 \cdot 1000}{V \cdot 41{,}99}, \qquad \text{(A.1)}$$

where m – mass of sodium fluoride added weight, g;

V – measuring flask capacity, cm^3;

19,00 и 41,99 – mass of fluoride-ion mole and sodium fluoride mole, respectively, g/mole.

The limit of possible error values in establishing molar Δ_{1M}, mole/dm^3, and mass Δ_1, g/dm^3, fluoride concentration in the CS1-F solution is calculated according to formulas:

$$\Delta_{1M} = M_1 \cdot \sqrt{\left(\frac{\Delta_\mu}{\mu}\right)^2 + \left(\frac{\Delta_m}{m}\right)^2 + \left(\frac{\Delta_V}{V}\right)^2}, \quad \Delta_1 = C_1 \cdot \sqrt{\left(\frac{\Delta_\mu}{\mu}\right)^2 + \left(\frac{\Delta_m}{m}\right)^2 + \left(\frac{\Delta_V}{V}\right)^2}, \qquad \text{(A.2)}$$

where $\Delta\mu$ –limit value of possible deviation of base substance mass fraction in the reagent from the assigned value, %;

μ – mass fraction of base substance in the reagent, assigned to the agent of pure for analysis (p.f.a.) qualification, %;

Δ_m – limit possible weighing error, g;

Δ_V – limit value of possible deviation of measuring flask volume from the rated value, cm^3.

Errors in establishing molar and mass fluoride concentration in CS1-F solution are equal to

$$\Delta_{1M} = 1,000 \cdot \sqrt{\left(\frac{1,0}{100}\right)^2 + \left(\frac{0,0006}{8,398}\right)^2 + \left(\frac{0,3}{200}\right)^2} = 0,0101 \text{ mole/dm}^3,$$

$$\Delta_1 = 19,00 \cdot \sqrt{\left(\frac{0,2}{100}\right)^2 + \left(\frac{0,0006}{8,398}\right)^2 + \left(\frac{0,3}{200}\right)^2} = 0,192 \text{ g/dm}^3$$

A.6.2 Calculation of metrological characteristics of certified solution CS2-F

The certi fluoride concentration is calculated according to formulas

(A.3)

$$M_2 = \frac{M_1 \cdot V_1}{V} \qquad C_2 = \frac{C_1 \cdot V_1}{V}$$

where V_1 – volume of solution CS1-F, taken out with a pipet, cm^3.

The limit of possible error values in establishing molar Δ_{2M}, mole/dm^3, and mass Δ_2, g/dm^3, кfluoride concentration in solution CS2-F is calculated according to formulas

$$\Delta_{2M} = M_2 \cdot \sqrt{\left(\frac{\Delta_{1M}}{M_1}\right)^2 + \left(\frac{\Delta_{V_1}}{V_1}\right)^2 + \left(\frac{\Delta_V}{V}\right)^2},$$

$$\Delta_2 = C_2 \cdot \sqrt{\left(\frac{\Delta_1}{C_1}\right)^2 + \left(\frac{\Delta_{V_1}}{V_1}\right)^2 + \left(\frac{\Delta_V}{V}\right)^2},$$

(A.4)

where Δ_{V1} - limit value of possible deviation of V_1 volume from the rated value, cm^3.

The errors in establishing fluoride molar and mass concentration in the solution CS2-F are equal to

$$\Delta_{2M} = 0,1000 \cdot \sqrt{\left(\frac{0,0101}{1,000}\right)^2 + \left(\frac{0,06}{20}\right)^2 + \left(\frac{0,3}{200}\right)^2} = 0,00106 \text{ mole/dm}^3$$

g/dm3:

$$\Delta_2 = 1,900 \cdot \sqrt{\left(\frac{0,0106}{0,100}\right)^2 + \left(\frac{0,06}{20}\right)^2 + \left(\frac{0,3}{200}\right)^2} = 0,00202 \text{ g/dm}^3$$

A.7 S

It is necessary to comply with the general industrial safety requirements when working at chemical laboratories.

A.8 Requirements to performers qualification

Certified solutions are allowed to be prepared by an engineer or a laboratory assistant with secondary professional education, having received special training and whose experience of work at a chemical laboratory is no less than 6 months.

A.9 Marking requirements

Bottles containing certified solutions shall have glued label indicating reference designation of a certified solution, values of fluoride molar and mass concentrations in the solutions, error of its determination and preparation date.

A.10 Storage conditions

Certified solutions are stored in tightly closed polyethylene or polypropylene vessels, months, no longer than:

CS1-F – no longer than 6 months;

CS2-B – no longer than 3 months.

Appendix B
(for reference)

Conversion of pF values in the range from 4,00 to 5,00 into fluoride mass concentration

pF	X, mg/dm^3
4,00	1,900
4,01	1,856
4,02	1,814
4,03	1,773
4,04	1,733
4,05	1,693

4,06	1,655
4,07	1,617
4,08	1,580
4,09	1,544
4,10	1,509
4,11	1,475
4,12	1,441
4,13	1,408
4,14	1,376
4,15	1,345
4,16	1,314
4,17	1,284
4,18	1,255

4,19	1,227
4,20	1,199
4,21	1,172
4,22	1,145
4,23	1,119
4,24	1,093
4,25	1,068
4,26	1,044
4,27	1,020
4,28	0,997
4,29	0,974
4,30	0,952
4,31	0,931
4,32	0,909

4,33	0,889
4,34	0,868
4,35	0,849
4,36	0,829
4,37	0,810
4,38	0,792
4,39	0,774
4,40	0,756
4,41	0,739
4,42	0,722
4,43	0,706
4,44	0,690
4,45	0,674

4,46	0,659
4,47	0,644
4,48	0,629
4,49	0,615
4,50	0,601
4,51	0,587
4,52	0,574
4,53	0,561
4,54	0,548
4,55	0,535
4,56	0,523
4,57	0,511
4,58	0,500

4,59	0,488
4,60	0,477
4,61	0,466
4,62	0,456
4,63	0,445
4,64	0,435
4,65	0,425
4,66	0,416
4,67	0,406
4,68	0,397
4,69	0,388
4,70	0,379
4,71	0,370
4,72	0,362

4,73	0,354
4,74	0,346
4,75	0,338
4,76	0,330
4,77	0,323
4,78	0,315
4,79	0,308
4,80	0,301
4,81	0,294
4,82	0,288
4,83	0,281
4,84	0,275
4,85	0,268

4,86	0,262
4,87	0,256
4,88	0,250
4,89	0,245
4,90	0,239
4,91	0,234
4,92	0,228
4,93	0,223
4,94	0,218
4,95	0,213
4,96	0,208
4,97	0,204
4,98	0,199

4,99	0,194
5,00	0,190

Federal Service for hydrometeorology and environment monitoring

STATE INSTITUTION
HYDROCHEMICAL INSTITUTE

344090, Rostov-on-Don
av. Stachki, 198
Fax: (8632) 22-44-70
Telephone: (8632) 22-66-68
E-mail: ghi@aaanet.ru

CERTIFICATE of measurement procedure qualification
N 6.24-2007

Procedure for measurement of fluoride mass concentration in waters using potentiometric method with ion-selective electrode,

developed by State Institution ‘Hydrochemical Institute’

and regulated by RD 52.24.360-2008. Fluoride mass concentration in waters. Procedure for measurement using potentiometric method with ion-selective electrode,

qualified in compliance with GOST R 8.563-96.

The qualification is carried out based on the results of experimental investigations.

As a result of the qualification, it was established that the measurement procedure corresponds to the imposed metrological requirements and has metrological characteristics given in Tables 1 and 2.

Table 1 – Measurement range, values of measurement error characteristics and its components at accepted probability of P =0,95

Measurement range of fluoride mass concentration X, mg/dm^3	Repeatability indicator (repeatability mean-square deviation) σ_r, mg/dm^3	Reproducibility indicator (reproducibility mean-square deviation) CTR , mg/dm^3	Correctness indicator (systematic error boundaries) $\pm\Delta_c$ mg/dm^3	Accuracy indicator (error boundaries) $\pm\Delta$, mg/dm^3
From 0,19 to 19,0 incl.	0,01+0,05· X	0,01+0,10· X	0,052· X	0,02+0,20· X
over 19,0 to 190,0 incl.	0,2+0,041· X	0,4+0,082· X	0,2+0,044· X	0,7+0,17· X

Table 2 – Measurement range, values of repeatability and reproducibility limits at accepted probability of P =0,95

Measurement range of mass fluoride concentration X, mg/dm^3	Repeatability limit (for three results of parallel determinations) r, mg/dm^3	Reproducibility limit (for two measurement results) R , mg/dm^3
From 0,19 to 19,00 incl.	0,03+0,17· X	0,03+0,28· X
over 19,0 to 190,0 incl.	0,7+0,14· X	1,1+0,23· X

When the method is implemented at the laboratory, the following is provided for:

- operational control by the measurement procedure performer (based on assessment of repeatability and error during implementation of a separate control procedure);

- control of the measurement results stability (based on control of stability of the repeatability mean-square deviation, mean-square deviation of internal laboratory precision, error).

The algorithm of operational control by the measurement procedure performer is given in RD 52.24.360-2008.

The frequency of operational control by the measurement procedure performer as well as the implemented procedures for control of stability of the performed measurement results are regulated by the Laboratory Quality Guideline.

Delivery date: 16 May 2007

Director	A.M. Nikanorov
Chief Metrologist	A.A. Nazarova