

Using Ion-selective Electrodes in Environmental Monitoring

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Abstract. Environmental monitoring is an integral part of environmental protection. Control of hazardous substances wastewater occurs both in the laboratory and on-site sampling. The paper provides a method of injection analysis, which is used in data-measuring systems control the parameters of chemical and technological processes using flow-injection method. The method involves sequential injection analysis of the liquid sample supply for the hydraulic lines in the flow measuring channel slot detector. The detector is equipped with two solid-state heterogeneous ion-selective electrodes. Before measuring the detector further comprising sample preparation and filtration of samples. The estimation of the uncertainty of the measuring system with the use of ion-selective electrodes one of which performs the function of the measuring electrode, while the second an auxiliary. The ultrasonic sample preparation technique, which reduces the impact of uncertainty on the stage of sampling and preparation of samples for analysis is designed. The use of ultrasonic sample preparation directly into the stream allowed expanding the use of flow-injection analysis and reducing the time to control the quality of the process water.

Keywords: ion-selective electrode injection analysis, sample preparation, the uncertainty of the measurement systems, environmental monitoring.

Conference topic: Environmental protection.

Introduction

In general, the environmental monitoring scheme (Švancara, Kalcher 2014; Bard, Zoski 2013) is as follows: the environment (specific environmental objects or technological process) → measurement parameters → collection and transmission of information → processing and presentation of data (formation of generalized evaluations) → forecasting. The most promising way to automate the determination of the methods and the continuous monitoring of contaminants in ecologically important sites are flow techniques (Moskvin *et al.* 2008; Bylatov *et al.* 2015; Trojanowicz, Kolacinska 2016). The general scheme of performing chemical analysis involves four stages: sampling; sample preparation; measurement of an analytical signal; processing and presentation of the analysis results. The most important stages of almost any chemical analysis techniques that determine its metrological characteristics are the stage of sampling and sample preparation.

Sensitivity and selectivity in the flow conditions are electrochemical detectors with their numerous advantages (relatively simple and reliable design, low cost, wide range determined by the content, speed). The most common method of detection is ionometry using ion-selective electrodes (Camman 2012; Zuliani, Diamond 2012; Malan 1998).

Fluoride compounds are natural elements of the Earth's crust. It is therefore natural that a small dose of fluoride found in natural water. Drinking water typically contains less than 0.3 mg of fluoride per liter. Plants also absorb fluorine from ground water, which is a small amount of fluoride is always present in our food and water. Fluoride also accumulates in plant and animal tissues. Despite the fact that the fluoride is a natural substance, it is toxic to humans. Fluorine is often used in the industry for producing uranium hexafluoride (nuclear industry), for the manufacture Teflon and insecticides (chemicals to kill insects), the synthesis, in metallurgy, in the manufacture of complex fertilizer, medicine and in the manufacture of fluoridation water and toothpastes. Indeed, fluorine is not so useful, how much harmful. It is highly toxic, causing poisoning. Even small regular doses of fluoride cause stress on the body, reproach aging, reduce the health, lead to the development of chronic diseases. In (Sunitha, Reddy 2014; Yahyavi *et al.* 2016) are presented the current analytical methods, tools and techniques used in the analysis of the content of fluoride in various environmental objects. The potentiometric analysis of fluoride content in solutions using a fluoride-selective electrode is simple, reliable and cheap. Fluoride-selective electrode may be used to determine the concentration of fluoride in the drinking water due to its high selectivity, low detection limits, short response time and the possibility of its use in indirect determinations elements entering into complex compounds with fluorine by subtracting the standard additives.

The aim of this work is to developed injection analysis method and device implemented on the basis with ultrasonic sample preparation for the determination of fluoride ion with estimation of the uncertainty type B.

Experimental

Research materials and methods for injection analysis method

The aim of this research is to provide a method of injection analysis to improve the accuracy and reliability of the analysis of fluoride ions in different environmental objects and processes of chemical fertilizer production.

Known flow analysis method (Ruzicka, Hansen 1975), which is the use of a controlled process zone dispersion of one liquid in another moving fluid stream, which main disadvantages is the high consumption of reagents and solutions specificity individual hydraulic circuits, corresponding to the conditions determined by the definition of each element.

Injection analysis method (Moskvin *et al.* 2006) is to feed the liquid sample and reagent solutions to the reaction vessel via reverse pump connected to the multi-port valve, however, it has disadvantages small accuracy and complexity of the analysis. Feeding the liquid sample and reagent solutions to the reaction vessel is carried out by a hydraulic line created and tap channel changeover detector.

Injection analysis method (Tychkov 2015a; Tychkov, Trembovetskaya 2015a, 2015b etc.), it consists of successively feeding a liquid sample flow line for measuring channel in the flow detector slit through one of the channels of two-way plug, one of the solutions the ratio of channel assembly. Through second channel node ratio feed solution a supporting electrolyte occurs through a reaction mixer with a pump. With the help of a second channel of two-way plug is carried out with distilled water washing device. The second flow channel slot detector pumped standard solution with a fixed concentration of the element. Before the measurements of the detector and sample preparation further comprises filtering the sample in one of the channels through a node relation of solutions and two-way plug and accessories, after which the sample is fed with the reactants in the reaction mixer.

Fig. 1 shows the device for the injection analysis (marked with a bold line hydraulic connection).

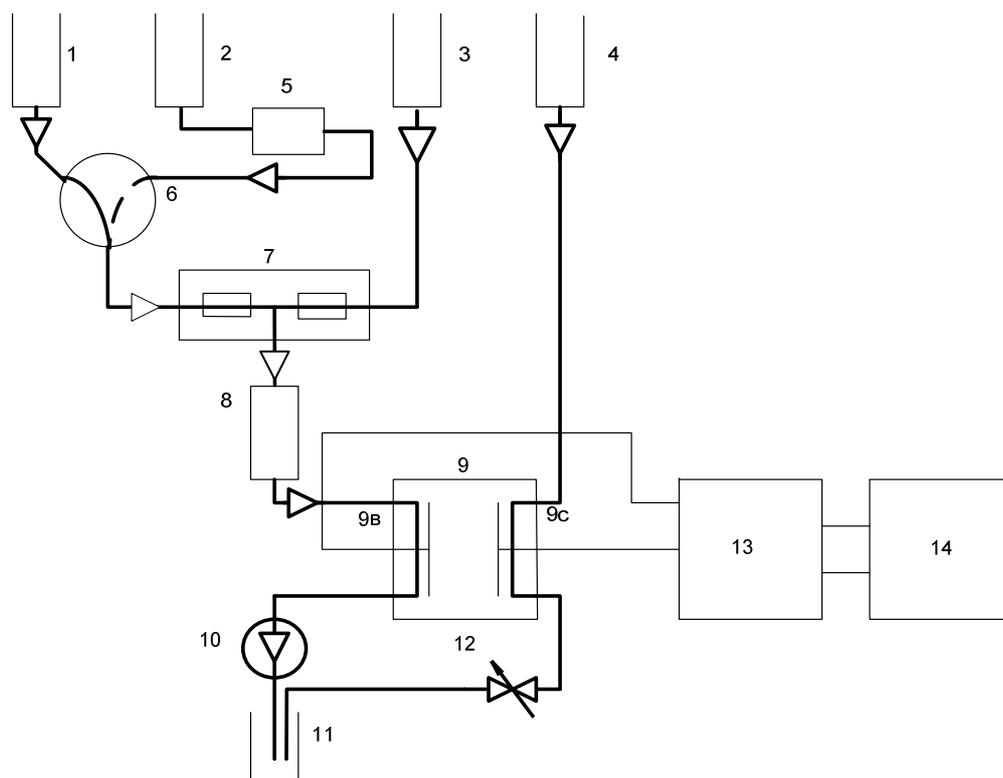


Fig. 1. Injection analysis device

In the injection analysis method can be used before measurements in a flow slit detector further perform filtering of the sample in the flow capacity between the sample 2 and sample preparation device 5. As a container with a standard solution of the element 4 can be used with a standard solution container with a maximum permissible concentration (MPC), or its multiple value of the element. As the two-way plug 6 can be used solenoid valve. As solutions ratio node 7 may be used slot flow device with a different ratio of the sample solution and the supporting electrolyte, which can be adjusted in length, height and width, or shape of the cross-sectional plane of the slot channel. The detector 9 can be used electrochemical converters flow slotted and combinations thereof. As the pump 10 may be used a peristaltic pump or electromagnetic dosing pump (Tychkov 2015b), or may be configured as a syringe pump. As the solenoid valve 12 can be used to reduce the costs of the standard solution.

As an auxiliary measuring device 13 can be used by a computer, data recorder. Computer (microcontroller, microprocessor) can be used as a control device for sample preparation device 5, the two-way plug 6, and the pump 10 and to make collection of information, data processing and optimization of the experiment with the flow slot detector 9, and display information on the screen or on the recorder with printing and documentation of the measurement. The method is as follows. A sample preparation device 5, a two-way plug 6, solutions unit ratio 7 in the reaction mixer 8 via a pump 10 is fed sequentially sample. For this two-way plug in series produces a hydraulic connection line formed channel tap changeover detector 6 and 9, with their inputs, one of which sample is applied. To ensure mixing of the sample and supporting electrolyte, and to provide one of the reaction solutions channel correlation node connected to the reservoir 3 with the background electrolyte, which is inert to the sample. Rinsing with distilled water two-way plug 6 is converted into a state where hydraulic line formed channel changeover plug 6 and the detector 9 connected to this channel, distilled water with a background electrolyte is pumped through the reactor mixer 8. After the reaction in a reaction mixer with 8 reaction products tank 1 and 3 through 9, the detector 11 provided to the drain, for this one channel changeover plug 6 is used as wash tank and connected to the drain 11. The detector 9 makes measurements (logs analytical signal) based on data which is the result of computation, e.g. by the information processing performed by a computer. If necessary, long-time measurements (for example, in the study of reaction kinetics) can stop the pump 10 at the time of measurement.

If necessary, the sample preparation prior to measurement in the detector 9 with a capacity between the sample 2 and the two-way valve is placed sample preparation device 5.

Device injection analysis is designed to control of environment parameters and supports methods of measuring the concentration of harmful impurities, such as a method of direct and indirect ionometry method, known additive and is operating in flow-injection, continuously, with a flow stop, time-injection, with injection various concentrations as upward and toward determining the dilution of samples and stores the calibration parameters several characteristics.

Research materials and methods for the ultrasonic sample preparation

The research aims to provide a method of sample ultrasound preparation, which is used in the injection to increase analysis accuracy and reliability analysis.

There is a method of ultrasonic sample preparation, which contains cavitations mechanisms that take into account the behavior of individual bubbles that characterize the phenomenon with a special acoustic power of 2...3 W/cm², which exceeds the threshold of cavitations. With increasing ultrasonic transducer displacement amplitude above 10...15 micrometers at 20 kHz relative acoustic power in the aqueous medium reaches 12...15 W/cm², and the nature of cavitations changes in volume substantially (Kardashov 1990). The disadvantage of this method is the relative complexity and length of the sample preparation, small precision and accuracy of the analysis.

Known sample preparation method for the ultrasonic flow liquid media in reactors with a radiator and an extended type flow chamber has an inner surface, creating the conditions for resonance amplification oscillations propagating and intended to enter into technological environment of ultrasonic vibrations at high power intensity of 10...30 W/cm² oscillation (Khmelev *et al.* 2013). The disadvantage of this method is the relative complexity and length of the sample preparation, small precision and accuracy of the analysis.

The formulation of the method of ultrasonic sample preparation tasked to simplify the method, reducing the length of the sample preparation, increases the accuracy and reliability of the analysis in the flow by performing an ultrasound emitter in the form of a hollow cylindrical piezoceramic element and housed in a cavity of the hydraulic cylinder injection analysis device line.

Sample preparation method (Tychkov 2015c) includes injection ultrasound in ultrasound technology environment. The ultrasonic sample preparation in order to simplify the process of reducing the length, increasing the accuracy and reliability of analysis performed in the ultrasonic flow sample preparation process solutions with a frequency of 20...22 kHz and an intensity of up to 2 W/cm².

Fig. 2 shows a schematic diagram of the ultrasonic sample preparation.

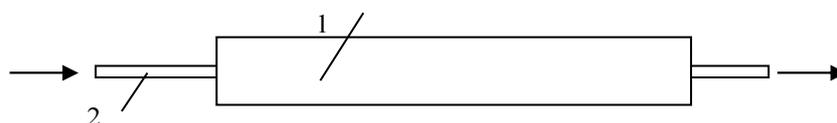


Fig. 2. Device for ultrasonic sample preparation

Device for sample preparation ultrasonic comprises: 1 a flow reactor with an extended type emitter, 2 cylinder injection flow line analysis device.

In order to simplify the construction of the flow reactor with an extended type emitter is formed by a hollow cylindrical ceramic member, and the flow chamber in the form of injection cylinder hydraulic line analysis device situated in the cavity of the hollow cylindrical ceramic member, the inner surface of which creates the conditions for resonant vibrations propagating gain.

Research materials and methods for estimating the uncertainty

The aim of the research is to assess the uncertainty analysis.

Designed metrological aspects of estimation uncertainty potentiometric measurement method (Ellison *et al.* 2011; Ramsey, Ellison 2007) using the injection method at each stage of the control parameters of environmentally hazardous facilities. Model equation of the measuring ion channel activity of the constituent elements of the process water with ion-selective detectors measuring flow type upgraded from the Nernst equation (Vasilevsky *et al.* 2008):

$$\Delta U = U_0 + \frac{2.3 \cdot R \cdot T}{n_A \cdot F} \cdot \lg \left(a_A + K_C \cdot (a_B)^{n_A/n_B} \right),$$

where: ΔU the potential difference at the output of the transmitter; U_0 Standard constant potential sensor (reference electrode); R Universal gas constant; T Absolute temperature; F Faraday number; n_A , n_B charges of the ions A and B , respectively; a_A ion activity A , which is necessary to determine; a_B ion activity B in which interferes with the determination of ions A ; K_C selectivity ratio (the maximum possible value).

Due to the fact that the detector is a thin-layer converter, the standard sensing element constant potential (reference electrode) is shown to 0.

The sensitivity of the flow detector lanthanum-fluoride crystal confirmed the passport to the electrode and is 59.16 mV. Both electrodes measuring and comparisons were made method (Tychkov, Stepanenko 2004) in the same conditions that reduced the contribution of manufacturing techniques uncertainty measurement conditions.

The calculations took standard uncertainty due to sources of uncertainty that are systematic and considered this distribution of values within the boundaries of the uniform. Components of a buffer solution of uncertainty have been evaluated with the possibility of influence of interfering ions and ionic strength influence the process water.

Injection analysis device determines the suitability of the electrodes to the measurements, stores the measurement results, and also supports the standard method of measurement, that reduce the measurement uncertainty of type B.

The scheme should have features that reduce the measurement uncertainty of type B, to determine the suitability of the electrodes to the measurements, remember measurements, and should support a standard measurement method.

The key in (Tychkov, Trembovetskaya 2016a) uncertainty components according to the type of measurement include:

1) Uncertainty of measurement of EMF, temperature, temperature compensation, and the uncertainty of the influencing variables (climatic and mechanical), the measuring system;

2) Calibration uncertainty, which includes the uncertainty buffer with uncertainty device.

The uncertainty of the measurement circuit is not limited to the uncertainty of the measuring device, you must also take into account the uncertainty of the transmitter with the characteristics of the measuring and reference electrode and temperature sensor.

Besides instrumental uncertainty there is uncertainty of measurement techniques, which usually do not appreciate, because of the variety of techniques the most, but it is necessary to explore all kinds of type B.

By the uncertainty of type B using the buffer, graduate, calibration solutions following its components include (Tychkov, Trembovetskaya 2016b; Tychkov 2015c; Kardashov 1990):

- $u_B(rp)$ uncertainty of life, storage conditions and the presence of impurities in the reference powders of which will be prepared solutions;
- $u_B(\mu)$ uncertainty use measuring utensils;
- $u_B(md)$ uncertainty of using measurement scales and dosing of powders in a volumetric ware;
- $u_B(dw)$ uncertainty of the distilled water and the storage conditions for the preparation of solutions and dilution;
- $u_B(ps)$ uncertainty dosing, mixing distilled water and powder when preparing solutions of complex shape;
- $u_B(sm)$ uncertainty calculations for preparing solutions of complex shape in measuring utensils of different sizes;
- $u_B(s)$ uncertainty of life and storage solutions for the environment;
- $u_B(ds)$ uncertainty dosing system works and its impact on the measurement during the injection of various types of solutions with different concentrations;
- $u_B(d)$ uncertainty of the detector from the impact of solutions on the surface of the membrane potential-electrodes;
- $u_B(T)$ uncertainty of temperature conditions of calibration, graduation and measurement;
- $u_B(g)$ uncertainty of graduation frequency detector at low concentrations measurements or to the maximum allowable concentrations;
- $u_B(l)$ uncertainty of linearity of the graduation characteristics and making amendments to the memory;

- $u_B(ii)$ uncertainty of the effect of interfering ions which present in solution in the measurement and pollution and the dissolution process the surface of the membrane potential-electrodes;
- $u_B(ba)$ uncertainty of the action of the buffer additive in disguise interfering ions;
- $u_B(c)$ uncertainty compliance activity and concentration, and ionic strength influence the measurement.

Given the calculated uncertainty type B, to uncertainties of each measurement signal conversion stages, combined measurement uncertainty ion channel activity, and analyzing the results, it is seen that the maximum ion selective uncertainty is a primary transducer or a flow detector slit.

Uncertainty of measurement techniques is particularly important when measuring device injection analysis. Injection analysis device typically has features that allow you to transfer readings pX concentration values. But indications pX depends on the measurement method. As a rule, the uncertainty does not account for the fact pX depending on the measurement method and thus normalizes the characteristics of the conversion value in the pX concentration in a replacement of measuring and reference electrode imitators electrodes.

Components of uncertainty of type B using the buffer, graduation, calibration solutions can be eliminated or lead to 0 using standard measurement techniques, or the development of measurement techniques using flow analysis. When using freshly prepared solutions, distilled water, optical measuring scales can be reduced to 0 uncertainty $u_B(rp)$, $u_B(\mu)$, $u_B(md)$, $u_B(dw)$, $u_B(ps)$, $u_B(sm)$, $u_B(s)$, $u_B(ds)$.

Uncertainties $u_B(d)$, $u_B(T)$, $u_B(g)$, $u_B(l)$ can be reduced through the use of more sophisticated measuring techniques, matching amplifiers, ADC, the development of metrological provision of calibration conditions, graduation and measurement for flow techniques, as well as amending the measurement with the auxiliary measuring device.

Uncertainties $u_B(ii)$, $u_B(ba)$, $u_B(c)$ can be reduced by optimizing the use of buffer solutions is directly determined for each component and specific environmental object or process.

Results

To determine the fluoride ions in different environmental objects and technological solutions, the greatest interest represents a crystalline solid membrane electrode, the features of which are low inertia, long-term operation, chemical resistance to many acids and alkalis, Nernst dependence electrode function that it is kept in the range of several orders of magnitude change in the fluoride ion activity, and no effect of reducing oxidants which are present in solution.

The basis of the LaF_3 crystal is an idea of the mechanism of ion conduction that has already manifested at room temperature. Charge transfer occurs in the crystal due to fluoride ions in the crystal lattice defects. Jobs are engaged in free neighboring ions, which have a fixed size, shape and charge distribution. Other types of ions that are different sizes of charge or can not participate in the transfer of current through the crystal. Therefore LaF_3 crystal is sensitive and selective detector element fluoride ions.

Supporting electrolyte maintains a constant ionic strength and gives the best solution conductivity. To solve large complex problems in the quality of the supporting electrolyte choose buffer solution that, along with the same characteristics as the background electrolyte has other. The buffer solution maintains a constant ionic strength value irrespective of dilution, that is, for a number of repeated measurements of the ionic strength of the solution, which has a buffering agent, remains constant or changes insignificantly. A different prevalence buffer is masking interfering ions in determining the potential-ion. Buffer solution breaks down complex compounds ions and converts it to a free state. Besides the above mentioned, supporting electrolyte, and the buffer solution should not be potential-ion, or need to know with a high accuracy of its concentration.

In the fluoride ions determining in the reaction apparatus in one of the channels and the two-way tap node ratio supplied sample solution. According to another channel assembly ratio supplied supporting electrolyte solution, which is used as the acetate-chloride-citrate buffer solution supplemented with EDTA (Tychkov 2015d). The solutions ratios are 1:1. After stirring the reaction contents of the mixer using a pump mixer reactor contents is fed through a flow measuring channel detector slit to drain. In this case, the detector used as a flow detector slit with two solid silver chloride electrodes as a measuring electrode and a reference electrode and a membrane with a fluoride selective electrode. Based on the obtained values do EMF calculation result (the concentration of fluoride ions). Acetate-citrate-chloride buffer solution with the addition of EDTA is used to mask the action of cations, forming fluoride ion complexes that prevent its definition.

All solutions were prepared with reagent purity as chemically pure. The standard solution was 0.001 M NaF. Working solutions were prepared by serial dilutions of the standard solution with distilled water. For storage solutions used plastic utensils. For the measurement of the potential difference used ionomer. For the continuous pumping of media solutions and reagents used peristaltic pump NP-1M or newly developed electromagnetic dosing pump. The crystal membrane fluoride lanthanum used as a sensitive detector element with a fluoride electrode (manufacturer-enterprise M-5649). Silver-chloride electrodes fabricated laboratory method. Power analyzers – valve dispenser, analytical module, a reactor, a detector are made in the laboratory and have re-designed the structure.

The measurement results of fluoride ions and calibration using newly developed equipment and methods for measuring and sample preparation (Table 1) showed good results on these samples drinking water, rain, the well, wastewater, fluoridated dental paste and complex fertilizer.

Table 1. Results of the fluoride-selective electrode measurement and calibration

Concentration, pF	Signal, mV	Concentration, pF	Signal, mV
2	minus 100, minus 99	5.5	105,106
3	minus 40	5.6	107
4	22,20,19	5.7	108,109
5	75,74,79	5.8	110,111
5.1	86,87	5.9	112
5.2	93,94	6	113,114
5.3	99,100	Background electrolyte	126
5.4	103,104	Water	129

The limit of detection in the rapid analysis is 5.3 pF.

When used in a standard solution 3 pF (Table 2) we received the following results.

Table 2. Results of the fluoride-selective electrode measurement and calibration with a standard solution 3 pF

Concentration, pF	Signal, mV	Concentration, pF	Signal, mV
2	minus 59, minus 58, minus 60, minus 63	6	152
3	0,1,2	6.5	154,155
4	57,59,62,60	7	154,155,153
5	118,120,124,117	Background electrolyte	167,161
5.5	142,144	Water	134,135,136

When using solution 0 mV with a high concentration, we have reduced the system time response to 0.1 seconds, moved the limit of detection to 6.5 pF. The steepness of the characteristics of the system confirmed passport data to the electrode.

Developed ultrasonic sample preparation device as a hollow cylinder, which is placed inside a capillary diameter of 0.8...1.2 mm, in which the sample enters the measuring unit injection analysis device. The optimal parameters of ultrasonic influence on the flow of the process water were 20...22 kHz with an intensity of 2 W/cm². At low flow rates up to 10 μl/s. Measurement uncertainty decreased by 0.2% due to reduction of ultrasound influence quantities.

Conclusions

Developed injection analysis method and device implemented on the basis thereof. In the method of injection analysis can before measurements in a flow slit detector further perform filtering of the sample in the flow capacity between the sample and the sample preparation device. The above example is a particular application of the method for determination of fluoride ion. The use of ultrasonic sample preparation directly into the stream allowed expanding the use of flow-injection analysis and reducing the time to control the quality of the process water. The uncertainty type B is estimate.

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