Metrological support of ion-selective electrodes

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Abstract. In this paper the determination of calcium ions concentration in drinking water using ion-selective electrodes are presented.

Recently, due to the development of new types of ion-selective electrodes, the ionometric method of analysis is increasingly used. Compared to other methods of analysis, the ionometric method with ion-selective electrodes has several advantages. Ionometric measurements are carried out in a short time, and herewith the usage of sophisticated measuring equipment is not required. Therefore, these electrodes are widely used in research the rate of passage chemical reactions and in the regulation of technological processes at various enterprises of the chemical industry.

It is also important that measurements using ion-selective electrodes belong to the group of non-destructive testing.

If ion-selective microelectrodes are being used, it becomes possible to measure liquid samples with a volume of up to 1 milliliter. At the same time, it should be noted that preliminary sample preparation is not required. Measurements may be carried out in turbid solutions and even in gels; long-term operations of purification, distillation and extraction of the sample are excluded. Therefore, measuring systems based on measurements of electrode potentials are simple to put into operation. Ionometry is also widely used to determine various biologically active compounds and medical supplies.

Another area of applying ionometry is hydrochemical researches, where it is necessary to determine the concentration of cations (sodium, potassium, calcium and magnesium) and anions (chloride, fluoride, nitrate, sulfate and carbonate) in various types of waters: surface, sea and rain.

The expansion of the scope ionometric method has led to the need to create constant conditions for verification (calibration) of ion-selective electrodes. For metrological support of this measurement area in Russia, the State primary standard of indicators of pX activity of ions in aqueous solutions of GET 171-2011 is used, which today has the highest metrological characteristics in Russia.

The aim of our work is to develop a stable mono-element solution of a divalent calcium ion, which is necessary for determining ion-selective electrodes.

In this paper the results of determining the concentration of calcium ions in drinking water using ion-selective electrodes are presented.

During the development process, a pilot batch of calcium-based mono-cell solution samples was prepared, ion-selective electrodes were also calibrated, and the concentration of calcium ions in various samples of drinking water was measured.
Calcium chloride was used to make the monoelement solution. Calcium chloride was subjected to further purification and dehydration. After that, a chemical analysis was performed on content of the main component. A solution of divalent calcium ion was prepared in deionized water at a temperature of \( t = 20 \) with a specific conductivity of \( 5 \times 10^{-4} \) Ohm\(^{-1}\) \( \cdot \) m\(^{-1}\). The prepared solution was stored in a tightly closed plastic container in a dark place, to prevent photochemical destruction.

The Nernst equation is used in all analytical methods with ion-selective electrodes. In order to establish the accurate adequacy of work the electrochemical circuit of Nernst equation, ion-selective electrodes are checked. Calibration curves are used to determine the activities and concentrations of ions in the analyzed samples.

Measurements of the electromotive force in the electrochemical cell were carried out on the installation including the following elements: potentiometer (1), ion-selective electrode (2), reference electrode (3), measured sample of calcium solution (4), thermostat (5), thermometer (6), a mixing device (7). The installation is shown on Figure 1.

![Figure 1. Installation for measuring the electromotive force of an electrochemical cell.](image)

A high-precision pH meter was used as a potentiometer with a voltage measurement error of 0.1 mV. The ion-selective electrode (for calcium) (2) was subjected to conditioning before work. Conditioning the electrode involves soaking it in a solution of calcium chloride with a concentration corresponding approximately in the middle of linear portion on the calibration curve. A silver chloride electrode of the ESO-01 type was used as a reference electrode (3). All measurements were carried out at a temperature of \( t = 20 \) with using a thermostat (5). Analyzed solutions were mixed with using an electric stirrer to reduce response time of the electrode (7).

Standard solutions of calcium chloride with calcium ion concentrations of 0.001, 0.01, 0.1, 1, 10, 30, 100, 300, 1000, 4000, 10000, 40000, 92000, mg/dm\(^3\) were used for construct the calibration graph.

Auxiliary solution of 1 M potassium chloride was used for maintain a constant ionic strength.

The measurements were carried out in order of increasing concentration of calcium ions in solution. After each measurement, the electrodes were washed with distilled water and wiped with filter paper. An each standard solutions in volume 40 cm\(^3\) and an auxiliary solution in volume 10 cm\(^3\) were successively poured into 50 cm\(^3\) measuring cylinders and mixed. Then the cylinders were immersed in the thermostat and thermostated, after that equilibrium potentials were measured.

Measurement results are presented on Figure 2.

As can be seen on the Figure 2, the calibration curve has a linear section in the range of Ca\(^{2+}\) concentrations from \(10^0\) to \(10^4\) mg/dm\(^3\). Slope of the linear section corresponds to Nernst and equal 28.9 (2.3RT/zF = 58.1/z) mV/z. Detection limit of the Ca\(^{2+}\) ion was found at intersection of the asymptotes linear sections is 0.33 mg/dm\(^3\). Deviation from linearity at high concentrations is associated with an abnormally high coefficient activity of CaCl\(_2\) salt in this concentration area [5].
Attempts were made to use CaNO$_3$ salt as the standard titer for determination of Ca$^{2+}$ ion. On picture 2 of the dashed line, shows the calibration curve for calcium nitrate. The narrower linear section from $10^0$ to $10^1$ mg/dm$^3$ has a slope different from the Nernst 25.0 (2.3RT/zF = 29) mV/z. Such an electrode function of a calcium selective electrode is associated with the influence of the NO$_3^-$ anion on the operation electrode membrane. Calcium nitrate can partially dissolve in the organic phase of membrane. Thus, it was concluded that calcium nitrate cannot be used as a standard titer for calibration of a calcium selective electrode.

The paper also presents the results of determining concentration of calcium ions in drinking water with using ion-selective electrodes.

Measurement of the electromotive force of the analyzed samples was carried out on the installation, shown in picture 1.

The experimental procedure was as follows: in a measuring cylinder in volume 50 cm$^3$ were added to the analyzed sample in volume 40 cm$^3$ and of the auxiliary solution in volume 10 cm$^3$. It was mixed, thermostated and the value of the equilibrium potential was measured. After each measurement, the electrodes were washed with deionized water and wiped with filter paper. Two parallel measurements were carried out for each water sample. The logC value was found and the concentration of calcium ions was determined from the calibration graph. The accuracy of the determination corresponds to the error of slope the linear portion calibration curve was found. The inaccuracy is constant throughout the linearity range. The measurement results are shown in table 1.

**Table 1.** The content of calcium ions in various samples of drinking water, measured using ion-selective electrodes.

| Samples of drinking water        | Concentrations of Calcium ions, mg/dm$^3$ |
|---------------------------------|------------------------------------------|
| Mendeleev settlement:           |                                          |
| - tap water                     | 71,2±6,4                                 |
| - spring 1                      | 95,1±8,6                                 |
| - spring 2                      | 95,3±8,6                                 |
| Zelenograd city:                |                                          |
| - tap water 4 microdistrict     | 44,0±4,0                                 |
| - tap water 5 microdistrict     | 56,1±5,1                                 |

It should be noted that the measurements uncertainty by ion-selective electrodes was 9%, which is less than the permissible error for the measurement of drinking water hardness [6].

During the development process, an experimental batch of mono-element calcium solutions was produced. Ion-selective electrodes were calibrated, and the concentrations of calcium ions in various sources of drinking water was measured.

**References.**

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