

Determination of the Oxidant Activity of Chlorinated Water by Chronoamperometry

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Abstract—A new version of the chronoamperometric method, adapted to the determination of the oxidative (oxidant) activity of a medium on an example of chlorinated water, was proposed. The supporting solution contained $K_4Fe(CN)_6$. By its oxidation with oxidants present in the sample, $K_3Fe(CN)_6$ formed; its reduction current served as an analytical signal. The current of $K_3Fe(CN)_6$ reduction was recorded at a potential of 0 V, selected from the cyclic voltammogram of the $K_3Fe(CN)_6/K_4Fe(CN)_6$ system in the range where the oxidized form of the reagent was reduced and the reduced form was stable. A gold electrode was the measuring electrode. The possibility of using a stable solution of $K_3Fe(CN)_6$ as a component of a standard addition and as a solution for plotting a calibration curve was demonstrated. The limit of detection of the amount of dissolved chlorine and products of its interaction with water is 8×10^{-6} M. The data obtained by the proposed procedure and by the iodometric methods correlate well with each other ($r = 0.93–0.95$). The proposed version of the chronoamperometric method can be used to monitor the amount of dissolved chlorine and products of its interaction with water in water supply systems, pools, and disinfecting solutions and to determine other water-soluble oxidants.

Keywords: chronoamperometry, oxidative (oxidant) activity, potassium hexacyanoferrate(III), potassium hexacyanoferrate(II), chlorine, potable water

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Monitoring of the integral oxidative (oxidant) activity (OA) of water, which is determined by the total content of molecular and radical oxidants, is very important, because drinking water is one of the main suppliers of oxidants to the human body. Excess of the latter leads to the development of oxidative stress and pathological conditions [1]. Monitoring of the oxidant activity of water and its decrease contribute to reducing the risks of harm to health. The main contribution to the integral oxidant activity of water is made by chlorine and ozone, used for disinfection in water treatment in the networks of centralized water supply and in pools. The maximum residual disinfectant level (MRDL) of chlorine (dissolved and products of its interaction with water—hypochlorous acid and hypochlorite ions) in the water of centralized water supply systems varies within 0.3–4.0 mg/L (4.2×10^{-6} – 5.6×10^{-5} M) [2, 3].

Monitoring of the integral oxidant activity is a sophisticated task that requires comprehensive consideration. The use of electron paramagnetic resonance [4, 5], chemiluminescence [6], spectrophotometry [7–9], chromatography [10], and fluorescence [11] for determination of free radicals is described. However, the information obtained by these methods

does not have much practical significance for the characterization of the oxidant activity of water, because the most common radicals, for example, oxygen, are short-lived.

Chlorine and ozone dissolved in water are determined by iodometric titration [12, 13] or potentiometry [14]. Taking into account that all oxidants are electron acceptors, it is necessary to recognize electrochemical methods as useful for determining the integral oxidant activity of a medium, as the result of the electrochemical reaction gives information on the total number of compounds taking part in it.

This study is devoted to the application of the chronoamperometric method for the determination of oxidant activity by the example of monitoring the amount of dissolved chlorine and the products of its interaction with water.

EXPERIMENTAL

Reagents. We used $K_3Fe(CN)_6$ and $K_4Fe(CN)_6 \cdot 3H_2O$ (both analytical grade), H_2SO_4 (cp grade), soluble starch (analytical grade), Al_2O_3 (cp grade, Reakhim), $Na_2S_2O_3 \cdot 5H_2O$ (analytical grade), KI

(cp grade, Reaktiv), and KCl (cp grade, UralEKOS) and working standards of pH (2nd and 3rd category, GOST 8.135, Ural'skii zavod khimicheskikh reaktivov) as buffer solutions.

Apparatus. For chronoamperometric and voltammetric measurements, an IVA-5 inversion voltammetric analyzer was used (IVA, Russia). A TA-ION pH/ions meter (Tomanalyt, Russia) was used to assess the stability of the potential of EVL-1M3.1 silver-silver chloride electrode and measure the pH of the solutions.

Chlorination of water under laboratory conditions was carried out in a glass unit [15] using reaction $2\text{KMnO}_4 + 16\text{HCl} = 2\text{KCl} + 2\text{MnCl}_2 + 5\text{Cl}_2\uparrow + 8\text{H}_2\text{O}$.

Electrodes. *Indicator electrodes* were a gold volumetric electrode ($\varnothing 2$ mm) (Metrohm, Switzerland) and screen-printed gold, platinum, and graphite-containing electrodes (IVA, Russia).

Before starting the work, the gold volumetric electrode was polished with a fine alumina powder (0.05 μm) applied to a cloth moistened with deionized water; the screen-printed electrodes were wiped with a filter paper moistened with deionized water. Then, the gold indicator electrodes were subjected to cyclic polarization in the potential range from 0 to 1.5 V in 0.5 M H_2SO_4 at a potential sweep rate of 0.1 V/s [16]. The platinum screen-printed electrode was subjected to cyclic polarization in the potential range from 0.04 to 1.5 V in 0.5 M H_2SO_4 at a potential sweep rate of 0.05 V/s [17].

The criterion for the quality of preparation of the indicator electrodes was the potential difference at that the anodic and cathodic current peaks were observed on a cyclic voltammogram recorded at a scan rate of 0.1 V/s in a solution containing 1 M of KCl, 5×10^{-4} M of $\text{K}_3\text{Fe}(\text{CN})_6$, and 5×10^{-4} M of $\text{K}_4\text{Fe}(\text{CN})_6$. The quality of preparation of the indicator electrodes was considered satisfactory if the potential difference of the peaks in the cyclic voltammogram did not exceed 0.1 V. This conclusion is based on the results of using electrodes in real studies.

An EVL-1M3.1 Ag/AgCl/3.5 M KCl electrode (Gomel plant of measuring equipment, Belarus) was *the reference electrode*. The potential of this electrode was evaluated relative to the potential of a control reference electrode, that is, a silver-silver chloride electrode (Metrohm, Switzerland), by measuring the EMF in a 3.5 M KCl solution using a TA-ION instrument. A value of ± 5 mV was considered permissible. Prior to each series of measurements, a 3.5 M KCl solution in the EVL-1M3.1 electrode was replaced with a fresh one. The potential of the EVL-1M3.1 electrode at 25°C is 0.222 ± 0.005 V relative to a standard hydrogen electrode. All the potentials are given below with respect to the EVL-1M3.1 electrode.

A rod made of SU-2000 glass carbon was *the auxiliary electrode*.

Object of investigation. Molecular chlorine, reacting with water, forms hypochlorous acid by reaction $\text{Cl}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HClO} + \text{HCl}$. In turn, hypochlorous acid is unstable and decomposes in aqueous solutions as $4\text{HClO} \rightleftharpoons 2\text{Cl}_2 + \text{O}_2 + 2\text{H}_2\text{O}$ (in acidic medium) or $2\text{HClO} \rightleftharpoons 2\text{HCl} + \text{O}_2$ (in weakly acidic and neutral media).

The object of investigation was water that contained dissolved chlorine and products of its interaction with water, namely, hypochlorous acid and hypochlorite ions, which are the oxidants that determine the oxidant activity of the system under study. The chlorine solutions were analyzed by a standard iodometric method [12, 13].

Characteristics of the procedure. The analytical signal is generated by the following chemical reaction: $\text{K}_4\text{Fe}(\text{CN})_6 + \text{Ox} = \text{K}_3\text{Fe}(\text{CN})_6 + \text{Ox}_{\text{red}}$, where Ox is the oxidant, and Ox_{red} is the reduced form of the oxidant. The reagent, $\text{K}_4\text{Fe}(\text{CN})_6$, was previously introduced into the electrochemical cell (ECC) in excess with respect to the sum of the oxidants under determination. The concentration of $\text{K}_3\text{Fe}(\text{CN})_6$, formed as a result of the above reaction between the reagent and the oxidants contained in the analyzed sample, is equivalent to the concentration of oxidants and is determined by the current of $\text{K}_3\text{Fe}(\text{CN})_6$ reduction. The current was recorded at a potential selected from the cyclic voltammogram for the $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$ system in the region where the oxidized form of the reagent is reduced and its reduced form is stable.

The oxidant activity (the total concentration of oxidants) was determined from the previously plotted calibration curve or by the standard addition method and calculated by equation

$$\text{OA} = c_{\text{ad}} \frac{\Delta I_{\text{sample}}}{\Delta I_{\text{ad}}} f, \quad (1)$$

where OA is the oxidant activity of the sample, mol-eq/L; c_{ad} is the concentration of $\text{K}_3\text{Fe}(\text{CN})_6$ in the ECC, mol-eq/L; $\Delta I_{\text{sample}} = I_2 - I_1$ is the current increment after introduction of the analyzed sample into the ECC (I_1 is the reduction current after introduction of the first addition of $\text{K}_3\text{Fe}(\text{CN})_6$ into the ECC; I_2 is the current of $\text{K}_3\text{Fe}(\text{CN})_6$ reduction after injection of the sample into the ECC, μA ; $\Delta I_{\text{ad}} = I_3 - I_2$ is the current increment after introduction a standard additive of $\text{K}_3\text{Fe}(\text{CN})_6$ into the ECC (I_2 is the current of $\text{K}_3\text{Fe}(\text{CN})_6$ reduction after injection of the sample into the ECC; I_3 is the reduction current after the introduction of the second addition of $\text{K}_3\text{Fe}(\text{CN})_6$, μA ; and f is the dilution factor of an aliquot of the sample in the ECC.

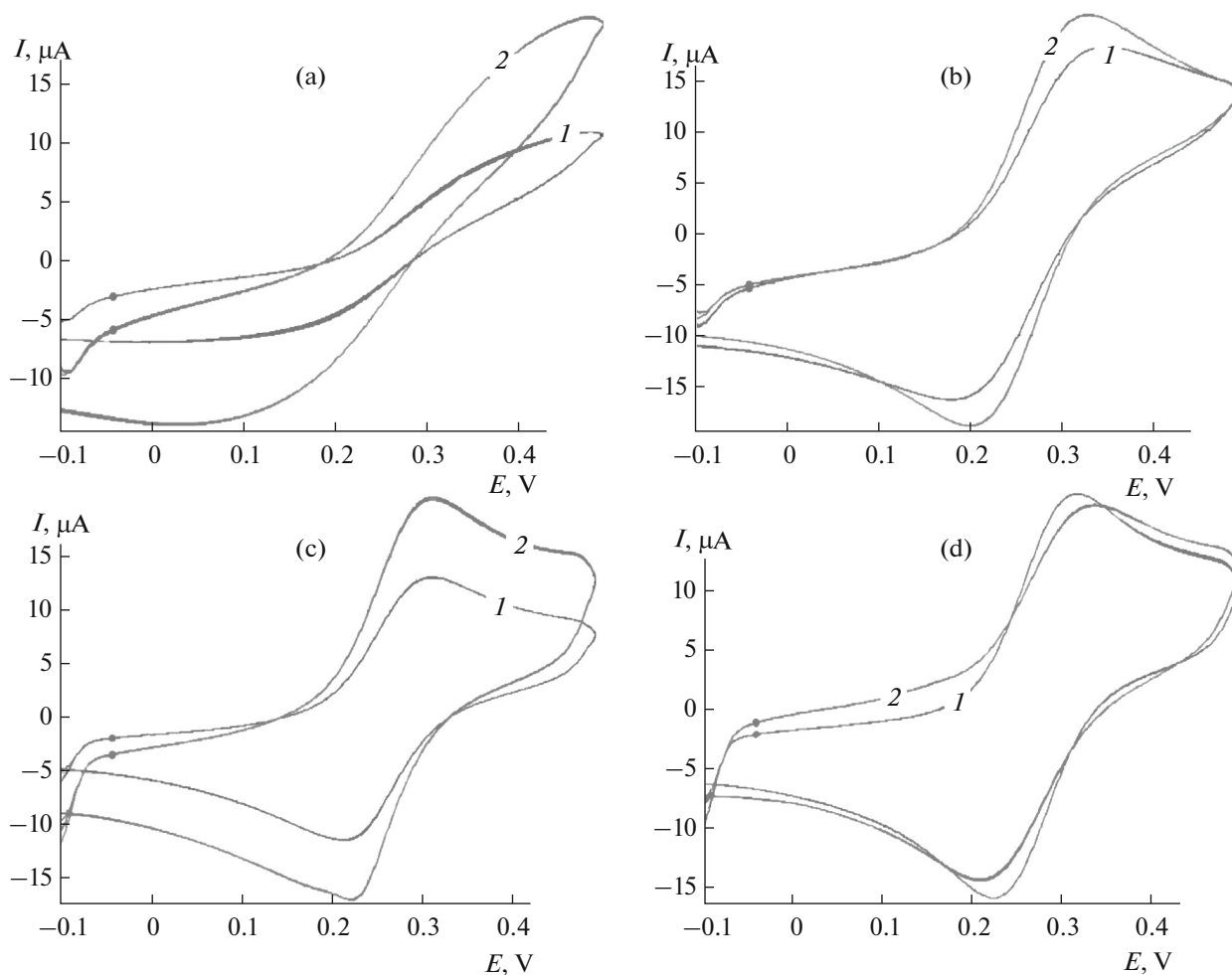


Fig. 1. Cyclic voltammograms recorded for a 1 M KCl solution containing 5×10^{-4} M of $\text{K}_3\text{Fe}(\text{CN})_6$ + 5×10^{-4} M of $\text{K}_4\text{Fe}(\text{CN})_6$, using screen-printed (a) carbon-containing, (b) platinum, and (c) gold electrodes and (d) volumetric gold electrode (1) before and (2) after their single contact with a 5×10^{-4} M chlorine solution for 5 min; potential sweep rate, 0.1 V/s.

The results of a single analysis of the sample are given below, which is caused by the instability of the object of investigation [12, 13]. The second problem arising from the analysis of such samples is the impossibility of preparing a standard analyte solution because of its instability. The solution to this problem is the use of potassium hexacyanoferrate(III) as a reference substance.

RESULTS AND DISCUSSION

Selection of indicator electrode. Figure 1 demonstrates cyclic voltammograms recorded for a 1 M solution of KCl containing 5×10^{-4} M of $\text{K}_3\text{Fe}(\text{CN})_6$ + 5×10^{-4} M of $\text{K}_4\text{Fe}(\text{CN})_6$ with various indicator electrodes before and after a single contact of the electrodes with a 5×10^{-4} M chlorine solution for 5 min. This time is comparable with the duration of the analysis of the sample. It is seen that cyclic curves with well-defined anodic and cathodic peaks are observed

for the platinum and gold indicator electrodes, which should ensure the possibility of obtaining an analytical signal. Preference should be given to the latter as more stable in an oxidizing environment. This paradoxical fact seems to be a consequence of a greater stability of the gold electrode with respect to the platinum electrode to the formation of oxide adsorption layers. There is no significant difference between the volumetric and screen-printed gold electrodes.

A volumetric gold electrode was used as the measuring instrument in further experiments.

Selection of potential for recording chronoamperograms. Under the potentials less than 0.2 V, the reduction of $\text{K}_3\text{Fe}(\text{CN})_6$ mainly occurs, and $\text{K}_4\text{Fe}(\text{CN})_6$ is electrochemically stable (Figs. 1b–1d). Figure 2 shows the dependence of the current recorded in the introduction of 1.96×10^{-5} M of $\text{K}_3\text{Fe}(\text{CN})_6$ into the background solution (1 M of KCl + 2×10^{-2} M of $\text{K}_4\text{Fe}(\text{CN})_6$) on the magnitude of the applied potential. As a reference point, a current was used, fixed in

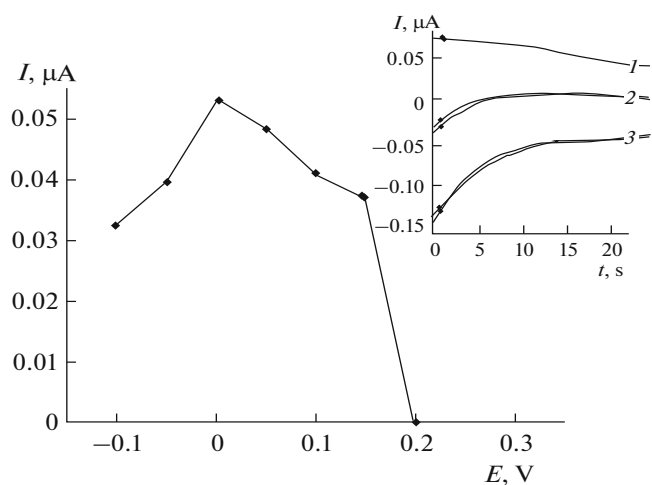


Fig. 2. Dependence of the current recorded at a given potential on the magnitude of this potential. Inset: chronoamperograms recorded at $E = 0$ V in solutions containing (1) 1 M of KCl + 2×10^{-2} M of $K_4Fe(CN)_6$ (background solution), (2) solution 1 + 1.98×10^{-5} M of $K_3Fe(CN)_6$; and (3) solution 2 + 1.96×10^{-5} M of $K_3Fe(CN)_6$.

the background curve 30 s after the measurement was started. This method of measurement was used in subsequent experiments. It follows from Fig. 2 that the current increment is well expressed and has a maximum value at the potential of the electrode of 0 V. Therefore, the current was then measured at this potential.

Selection of pH. It is known that the properties of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ used depend on the acidity of the medium. The compounds enter protonation reactions accompanied by the formation of $H_3Fe(CN)_6$, $H_4Fe(CN)_6$, and HCN. Hydrolysis occurs in weakly alkaline and alkaline media [18, 19], while the electrochemical properties of the system change. The region of its stability is pH 5–8.

The dependence of the current recorded in the injection of 1.96×10^{-5} M of $K_3Fe(CN)_6$ into the background solution (1 M of KCl + 2×10^{-2} M of $K_4Fe(CN)_6$) on the solution pH is given in Fig. 3. Indeed, the current is the highest in weakly acidic and neutral media (pH 4–7). All further measurements were performed at the natural pH of the deionized or analyzed water containing 1 M KCl (pH 5–6).

The current of $K_3Fe(CN)_6$ reduction as an analytical signal. Chronoamperograms of the reduction of $K_3Fe(CN)_6$ at a gold electrode in a solution containing 1 M of KCl + 2×10^{-2} M of $K_4Fe(CN)_6$ are presented in Fig. 4a. Figure 4b illustrates the current dependence on the $K_3Fe(CN)_6$ concentration, which can be described by the linear regression equation of $I = 0.0224 + 2.1168c$ with a correlation coefficient of 0.99.

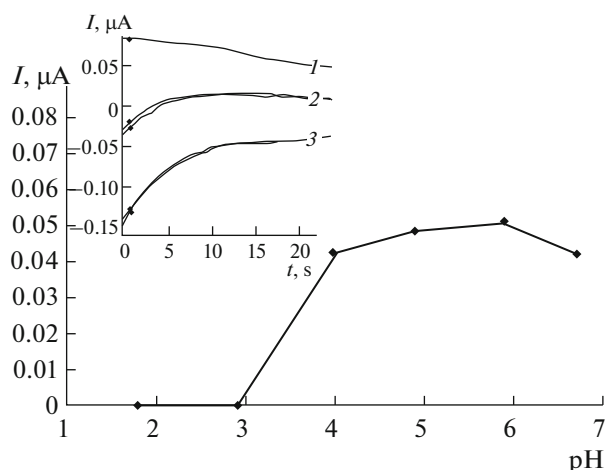


Fig. 3. Dependence of the current recorded at $E = 0$ V on the solution pH. Inset: chronoamperograms recorded at $E = 0$ V in solutions containing (1) 1 M of KCl + 2×10^{-2} M of $K_4Fe(CN)_6$ (background solution, pH 6.0), (2) solution 1 + 1.98×10^{-5} M of $K_3Fe(CN)_6$; and (3) solution 2 + 1.96×10^{-5} M of $K_3Fe(CN)_6$.

Chronoamperograms recorded in the concentration range of $K_3Fe(CN)_6$ of 2×10^{-6} – 1×10^{-2} M have a similar shape.

These data show that the cathode current can be used to determine the concentration of $K_3Fe(CN)_6$, and therefore, it can serve as an analytical signal for the determination of water-soluble oxidants oxidizing $K_4Fe(CN)_6$. This conclusion is supported by the results of analysis of chlorinated water, given below.

The procedure for the analysis of chlorinated water consists of the following stages: (1) the recording of the chronoamperogram of the background solution (1 M KCl + 2×10^{-2} M $K_4Fe(CN)_6$) yields current I_0 ; (2) the introduction of $K_3Fe(CN)_6$ into the ECC at a concentration corresponding to the assumed range of chlorine concentration in the sample; (3) the recording of the chronoamperogram of $K_3Fe(CN)_6$ additive gives current I_1 ; (4) the injection of the analyzed sample into the ECC; (5) the recording of the chronoamperogram of the sample yields current I_2 ; (6) the introduction of $K_3Fe(CN)_6$ additive into the ECC at a concentration corresponding to the assumed range of chlorine concentration in the sample; (7) the recording of the chronoamperogram of $K_3Fe(CN)_6$ additive gives current I_3 ; and (8) the calculation of the results using Eq. (1).

The Table 1 shows the results of determination of the amount of dissolved chlorine and products of its interaction with water, obtained by chronoamperometry and iodometry. The data presented indicate that with a decrease in the analyte concentration in the sample, the correlation coefficients decrease slightly, and the Student and Fisher criteria increase. The

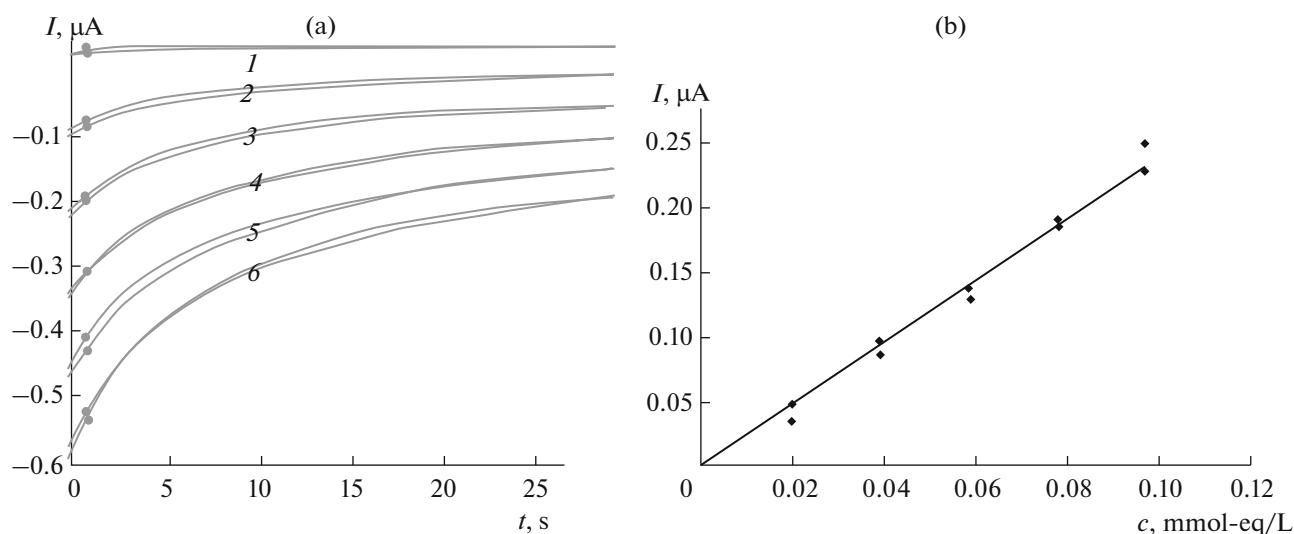


Fig. 4. (a) Chronoamperograms of the $K_3Fe(CN)_6$ reduction: (*I*) background solution (1 M of $KCl + 2 \times 10^{-2}\text{ M}$ of $K_3Fe(CN)_6$) and (2)–(6) background solution + $K_3Fe(CN)_6$ at a concentration of (2) 1.98×10^{-5} , (3) 3.94×10^{-5} , (4) 5.88×10^{-5} , (5) 7.8×10^{-5} , and (6) $9.7 \times 10^{-5}\text{ M}$. (b) Dependence of the current on the $K_3Fe(CN)_6$ concentration in solution at an electrode potential of 0 V .

obtained values of the Student and Fisher criteria do not exceed the critical values ($t_{crit} = 2.57$ and $F_{crit} = 5.05$ for the significance level of 0.05 and $n = 6$), which indicates an insignificant difference in the results. The limit of detection of the amount of dissolved chlorine and products of its interaction with water is $8 \times 10^{-6}\text{ M}$. It was not possible to record the lower concentrations of dissolved chlorine and products of its interaction with water [12, 13] using chronoamperometry.

The good agreement between the results of analysis of chlorinated water and the proposed and standard iodometric [12, 13] methods (Table 1) confirms the validity of using the current of $K_3Fe(CN)_6$ reduction as an analytical signal.

CONCLUSIONS

Thus, a possibility of using a stable solution of $K_3Fe(CN)_6$ as a standard addition and as a solution for plotting a calibration curve instead of an unstable analyte (chlorine) solution has been confirmed once again. This approach is of interest not only for the determination of chlorine, but can also be useful in the quantification of other unstable compounds. The proposed version of the chronoamperometric method can be used to monitor the amount of dissolved chlorine and products of its interaction with water in water supply systems; it can also be adapted to determine other water-soluble oxidants.

Table 1. Determination of the concentration (M) of dissolved chlorine and products of its interaction with water by chronoamperometry and iodometry

Iodometry [12, 13]	Chronoamperometry	<i>r</i>	<i>t</i>	<i>F</i>
3.0×10^{-3}	3.4×10^{-3}	0.95	0.12	1.30
2.6×10^{-3}	2.6×10^{-3}			
2.4×10^{-3}	2.1×10^{-3}			
2.1×10^{-3}	2.4×10^{-3}			
2.0×10^{-3}	2.0×10^{-3}			
1.0×10^{-3}	1.1×10^{-3}			
5.0×10^{-4}	4.6×10^{-4}	0.94	0.18	1.31
6.1×10^{-4}	6.9×10^{-4}			
2.4×10^{-4}	2.3×10^{-4}			
4.5×10^{-4}	4.5×10^{-4}			
1.2×10^{-4}	0.9×10^{-4}			
8.5×10^{-4}	6.7×10^{-4}			
5.3×10^{-5}	4.8×10^{-5}	0.93	0.26	1.83
4.8×10^{-5}	6.6×10^{-5}			
9.2×10^{-5}	8.2×10^{-5}			
2.1×10^{-5}	3.3×10^{-5}			
8.0×10^{-5}	8.4×10^{-5}			
3.3×10^{-5}	4.2×10^{-5}			

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