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THE USE OF COPPER INDICATOR ELECTRODES IN VOLTAMMETRIC ANALYSIS (A REVIEW)*

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The review describes the application of solid electrodes based on copper for voltammetric analysis of major classes of organic and inorganic substances over the last fifty years. Despite the fact that there are many reviews of individual solid electrodes this review offers the first comprehensive report on all forms of copper electrodes. The advantages and disadvantages of copper electrodes in comparison with electrodes made of other metals are discussed. Varieties of copper electrodes, their basic physico-chemical properties and some specific characteristics of their surface are described. The electrochemical behavior of copper in aqueous solutions and electrocatalytic mechanisms of transformations of matter on its surface are reported. Examples of the use of electrochemical copper sensors for flow-injection analysis and liquid chromatography are given. Recent trends of the use of copper micro- and nanostructured electrodes in electrochemical analysis are reviewed. The prospects of using copper as a material for the creation of new electrochemical sensors are shown.

Keywords: *voltammetry, electrochemical analysis, copper indicator electrode, microelectrodes, nanostructured electrode.*

Introduction

Analytical voltammetry (VA) includes a group of methods based on obtaining and interpreting current-voltage dependences (that is, dependences of current via a sensor on tension on the sensor) of the interphase boundary between a polarized electrode and an electrolyte solution, which can contain determined electroactive agents [1]. The performance capabilities of voltammetric methods (sensitivity, selectivity and accuracy) considerably depend on the chemical and physical properties of the working electrode material, on the processing class of the electrodes surface, on the used variation range of electrode potential, on the composition of the used working solution (background electrolyte), and also on the hydrodynamic conditions of the experiment [2]. The geometrical form of the working electrode can affect not only the process of diffusion of the determined substance to the sensor. In some cases it can also have significant effect on the number of parameters including the process chemistry. Because voltammetry finds application in modern analytical practice, searching for new materials for electrodes and enhancing the abilities of the existing electrodes consistently draw the attention of researchers.

Voltammetry uses various indicator electrodes. As a rule, electrode materials are metals, among which platinum and gold are most often used, as well as various carbon materials, various forms of graphite, glass carbon and carbositalls. Silver, nickel and bismuth are used less often. Polarographic methods using electrodes based on mercury as indicator electrodes comprise a special

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VA section. A detailed consideration of electrodes and electrode materials used in voltammetric analysis is presented in a number of monographs [3, 4] and reviews [5−7].

Solid electrodes comprise the most quickly growing class of electrodes. Solid-state electrodes have important advantages (mechanical durability and hardness, considerable anode range of potentials and the possibility of application in a stream) despite the complexity of controlling the reproducibility of the state of their surface as compared to mercury electrodes. The small sizes of the former and the freedom from toxicity enable applying solid electrodes under natural conditions for studying biochemical processes.

In the present review we will consider the use of copper as a material for producing electrodes and electrochemical sensors and their application in the modern voltammetric analysis, as well as the use of these electrodes as highly sensitive sensors for chromatography and flowing and injection analysis.

The use of copper as an electrode material is of interest due to its relative low cost, mechanical durability, high conductivity, as well as the possibility of regenerating and modifying its surface. Copper electrodes are capable of keeping their sensitivity for a long time (more than 3 months). In contrast, in case of electrodes of noble metals, passivation of the surface due to adsorption of electrochemical reaction products is typical. Metallic copper is readily available in rather pure state in the form of wire of various diameters.

Copper is a rather low-active electropositive element. The standard electrode potential of copper is equal +0.34 V. Thus, its place in the standard electrode potentials series is to the right of hydrogen. Copper electrodes are characterized by a rather wide working area of potentials, at which they are still stable.

Characteristic oxidation levels of copper are +1 and +2, and their relative stability can be regulated by the solution composition. Copper oxides have pronounced basic properties, and the amphoteric nature of copper is shown extremely weakly. This allows using copper electrodes in strongly alkaline solutions, and oxides formed on the electrode surface remain insoluble. Owing to the formation of compounds with various oxidation levels and low solubility of oxides copper and copper compounds are capable of showing electrocatalytic activity. These properties are successfully applied when determining a wide range of inorganic and organic substances [8]. Thus, due to selective electrocatalytic oxidation of carbohydrates on copper electrodes used as detectors in chromatography and capillary electrophoresis it has been possible to reach one of the lowest limits of detection of glucose and its derivatives [9].

Copper is characterized by high affinity to mercury. However, the solubility of copper in mercury is much lower than the solubility of silver. Being dissolved in a mercury drop, metallic copper plays an important role in increasing peak current due to changing the electrode material composition. Copper is capable of forming intermetallic compositions with As, Se, Te, Cd and Zn. Therefore, it is successfully used for voltammetric determination of As, Se and Te, although it is a serious problem when determining Cd and Zn.

Copper electrodes and combined electrochemical sensors based on them have broad prospects of use for the analysis of various substances.

This review generalizes modern studies devoted to the application of copper electrodes in the voltammetric analysis. Besides, when writing the review, informative and/or classical data on physical and inorganic chemistry, chemical thermodynamics and electrochemistry were used.

Electrochemical behavior of unmodified copper electrodes in solutions

The electrochemical behavior of copper in solutions depends on such factors as polarity and pH of the medium, the structure and concentration of the electrolyte, the presence of complexing agents, temperature, the presence of ligands capable of forming coordination compounds with copper.

The dependence of thermodynamically stable forms of copper in a water solution at various pH and oxidation-reduction potential E values can be traced on Pourbaix diagram shown in figure 1 [10].

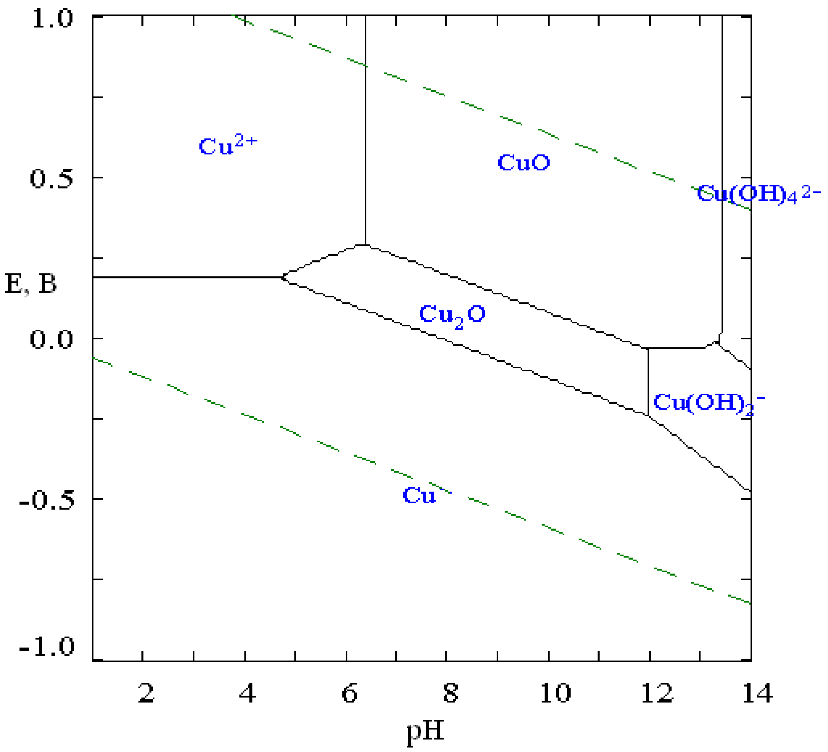


Figure 1. Potential − pH diagram (Pourbaix diagram) forCu−H_2O system (C_{Cu} = 10^{-6} mol/kg, T = 298.15 K)

[В means V]

According to the diagram, there is no region at pH 4.6 for Cu(I) compounds, because this oxidation state of copper is unstable, and Cu(I) disproportionates forming Cu^{2+} and Cu^0, if no precipitate or complex is formed. In strongly alkaline solutions copper electrodes have the typical voltammogram shown in Figure 2.

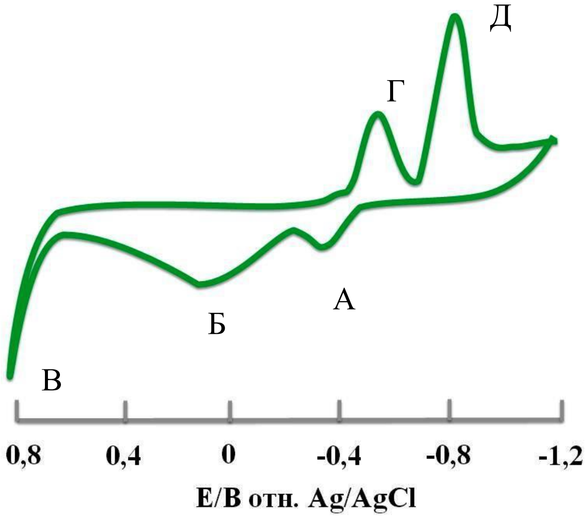


Figure 2. Cyclic voltammogram on a copper macroscopic electrode
in 0.1 M NaOH solution.

[E/В отн. means E/V rat.; А means A; Б means B; В means C; Г means D; Д means E]

This dependence was registered for the first time by Miller in 1969 [11] in the course of experiments on a round disk-shaped copper electrode. In the region of potentials from –0.4 to +0.4 V there are anode waves corresponding to oxidation-reduction processes of Cu(0)/Cu(I) and Cu(I)/Cu(II) (peaks A and B). At potentials above +0.4 V a signal characteristic of oxidation-reduction couple Cu(II)/Cu(III) is formed (peak C). As Miller [11] showed, this signal is formed at a potential of +0.6 V, but it is not always possible to record it on a voltammogram, because the potential of Cu(II)/Cu(III) transition is close to the potential of anode evolution of oxygen (+0.8 V) caused by water oxidation. Halem and collaborators [12] showed that the anode peak of Cu(III) can be found only in a strongly alkaline medium, i.e., at OH^- concentration not less than 0.1 M. The same authors found out that the ratio of anodic and cathodic charges in alkaline solutions with $[OH^-] > 0.1$ M is more than 1, that is, the integrals of the anode peaks are greater than the integrals of the cathodic peaks corresponding to them. The authors of [12] explain this stoichiometry irregularity by the formation of soluble compounds on the surface of copper in the course of anode curve measurement. These compounds are transferred into the solution and are not present on the cathodic branch.

In the cathodic region of potentials, copper reduction to Cu(I) and Cu(0) occurs. It is represented by sharp peaks (that is, the integrals of the anodic peaks are greater than the integrals of the cathodic peaks corresponding to them) at –0.5 and –0.8 V (peaks D and E). Besides, ellipsometric studies show that insoluble associates Cu_{ads}, $Cu_{ads}OH$, Cu_2O and $Cu_{2ads}O$ can be formed on the surface of copper before the oxide formation due to electrosorption type reactions.

$$Cu + H_2O \rightarrow Cu(OH)_{ads} + H^+ + \bar{e} \tag{1}$$

Therefore, a detailed study of processes of copper electrooxidation and electroreduction in alkaline solutions is a complex problem.

According to literature data [13] the described oxidation states of copper Cu(I), Cu(II) and Cu(III) have the following standard potentials in an alkaline medium:

	E^0_{298}, B
$Cu_2O + H_2O + 2\bar{e} = 2Cu^0 + 2OH^-$	–0.58
$Cu(OH)_2 + 2\bar{e} = Cu^0 + 2OH^-$	–0.44
$2Cu(OH)_2 + 2\bar{e} = Cu_2O + 2OH^- + H_2O$	–0.30
$CuO_2^- + 2H_2O + \bar{e} = Cu(OH)_2 + 2OH^-$ or $Cu_2O_3 + H_2O + 2\bar{e} = 2CuO + 2OH^-$	+0.52

$$Cu^0 - 1\bar{e} \rightarrow Cu^+ \text{ (fast stage)} \tag{2}$$

$$Cu^+ - 1\bar{e} \rightarrow Cu^{2+} \text{ (slow stage)} \tag{3}$$

The behavior of copper in solutions also significantly depends on the presence of ligands in them. In the presence of such ligands as $CN^–$, $Cl^–$ and $S_2O_3^{2–}$ that form stable complexes with Cu(I) (pH of $[Cu(CN)_4]^{3–}$ complex is equal to 30.3, of $[Cu(Cl)_3]^{2–}$ 5.63, of $[Cu(S_2O_3)_3]^{5–}$ 13.84), the metal is transferred into the solution only in the single-charged state in a wide range of electrolyte concentrations. On the contrary, in electrolytes with $NO_3^–$, $SO_4^{2–}$ and $ClO_4^–$ copper is oxidized at 25 °C to oxidation level +2 [14].

The mechanism of copper ionization in electrolytes, the anions of which practically do not form complexes with copper ions, consists of the following stages [15]:

The introduction of compounds forming stable complexes with copper(II) ions into solutions reduces the region of copper(I) potentials on the current-potential curve. At high concentrations of ligands, the area of copper(II) disappears as well. This is due to the formation of a strong film of a complex copper salt.

The behavior of copper in KCl and $NaClO_4$ solutions containing ammonia is unusual. When ammonia concentration is from $1\cdot10^{–3}$ to $1\cdot10^{–2}$ M, the core role in copper activation is played by chlorides. As NH_3 concentration grows, the Cu(I) region increases. Without ammonia, anode dissolution of copper in the presence of 1 M $NaClO_4$ occurs only with the formation of Cu(II) [16].

The major factors affecting the formation of Cu(III) are the concentration of hydroxide ions and the state of the electrode surface. It was established [17] that preliminary polarization of an electrode at a potential of –0.1 V with respect to the silver chloride electrode (Ag/AgCl) for 10 s increases the signal of Cu(III)/Cu(II) by a factor of 10. According to XPS spectroscopy, a porous layer of Cu_2O starts to form at potentials more negative than –0.08 V. Apparently, this promotes the formation of Cu(III).

Thus, using copper as an electrode material provides a wide range of working potentials suitable for carrying out anodic and cathodic reactions. Operating conditions for carrying out a particular reaction on the surface of this electrode can be chosen precisely depending on pH and the medium composition.

Types of copper electrodes

Electrodes based on copper started to be used in electrochemistry more than fifty years ago. In the course of solid-state electrodes development it has been possible to develop and create a lot of various designs of copper electrodes. By now electrodes based on copper can be divided into several types depending on:

- the size: macro-, micro and ultramicroelectrodes;
- the shape: disk, ring, spherical, tubular, linear, etc.;
- the surface state: unmodified, modified, mercury-and-film, solid amalgam;
- the design: stationary, rotating, "3 in 1", planar, copper-and-film.
- Besides, electrodes of new type made with the use of copper oxides nanoparticles applied on a conducting substrate or dispersed in an appropriate carrier can be considered a separate type.

Originally, rods of high-pure copper 0.1–0.5 cm in diameter placed in a case of glass or teflon were used as copper electrode. Before measurements the copper surface was polished with the use of fine diamond and corundum pastes. Depending on the experimental task the electrode could be previously activated by imposing negative potential in an acidic medium for 10−15 min.

When polarizing platinum, gold or glass-carbon electrodes in the cathodic area of potentials in an acidic electrolyte containing Cu(II) ions, a copper film [18−21] can be obtained on their surface. Copper-film electrodes made by this method became common use in voltammetric flowcells.

The next stage of developing solid-state electrodes based on copper were micro and ultramicroelectrodes (UME). As compared to the usual electrodes, the dimensions of UME surface

($<10^{-1}$ mm) are comparable to the diffusion layer thickness. Thus, mass transfer of the substance occurs due to spherical diffusion. Due to this, carrying out electrochemical analysis on UME's provides a number of essential advantages. The most important advantages are high sensitivity, quickness of measurements and insignificant influence of ohmic potential drop [22]. From the viewpoint of manufacture, UME's based on copper microfibres with a diameter of 12−50 microns are the simplest ones. As a rule, these fibers unite in ensembles that are soldered or shrinked in glass or in an epoxide resin. There are also more manufacturable approaches for creating arrays. For example, [23] describes a method of producing a copper microdisk electrode with a ring including consecutive application of chemical sedimentation from a gas phase (CVD), electroetching and galvanization. Review [24] provides more detail about methods for creating microelectrodes.

In the last several years, copper "nanoelectrodes" and "nanosensors" appeared according to the current trend of miniaturization in electroanalytical chemistry. The large specific surface, extra surface energy and high catalytic activity of nanoparticles are the cause of unusual phenomena and reactions. Nanoparticles applied for the production of nanostructured copper electrodes are, generally particles of Cu_2O and CuO oxides of various shapes (nanowires, nanoflowers, nanocylinders) and various sizes. The preparation of such particles is based on such standard approaches as thermal oxidation, dehydration or vacuum deposition (PVD). Substrates for applying nanoparticles can be pyrographite, glass carbon, carbon nanotubes (CNT), graphene, noble metals, indium tin oxide or pastes. In order to stabilize copper nanoparticles, Nafion can be added to them. Various strategies of immobilizing metallic and metal-oxidic nanomaterials on solid substrates for analytical purposes are generalized in [25].

The ability of copper to form an amalgam with mercury is used for creating various copper mercury-film and solid amalgam electrodes. The main characteristics and methods of producing such electrodes are described by Donten and Kublik. Unlike other substrates, for example, platinum or carbon, copper provides the stability of a mercury film for a long time. In addition to the advantages of mercury electrodes, amalgam electrodes are less toxic and require much smaller consumption of mercury for their production and use. Nevertheless, these electrodes have a number of restrictions. The main of them are insufficient stability and reproducibility of mercury film thickness, which confines their analytical application.

Analytical application of copper electrodes in voltammetry

Voltammetric determination of inorganic substances. Mechanism of electrocatalytic oxidation of inorganic substances. Copper oxides can catalyze oxidation-reduction transformations of inorganic substances. For each of these processes a mechanism is suggested. However, H_2O_2 reduction is studied in most detail.

Hydrogen peroxide. The catalytic activity of a number of metals in H_2O_2 reduction is discussed in [26], and copper is of special interest as an electrode material. Copper peroxide reduction was studied for the first time by Delahay [27]. Further studies by Smyrl [28] and Moldov [29] with the use of a rotating disk electrode explained the catalytic mechanism by the formation of electrochemically generated Cu(I).

The reaction in a borate buffer in the absence of oxygen (pH 9.2) was studied in detail by Vazquez et al. [30]. They suggested a mechanism, according to which electron transfer from the 3d level of Cu(I) to the peroxide occurs followed by internal reduction of the formed Cu(II) by electrons from the Fermi level of the metal.

The oxidation-reduction cycle of the catalytic reduction of the peroxide in the borate buffer on a copper electrode with a preliminarily deposited thin Cu_2O film can be described as follows:

$$Cu_2O + H_2O_2 \rightarrow 2CuO + H_2O \qquad (4)$$

$$2CuO + H_2O + 2\bar{e} \rightarrow Cu_2O + 2OH^- \qquad (5)$$

Peroxide oxidation of Cu_2O is thermodynamically favorable: $\Delta G^0 = -227.2\ kJ\ mol^{-1}$. When chloride ions are present in the solution, Cu_2O film dissolution occurs due to the formation of $[CuCl_2]^-$ and $[CuCl_3]^-$ complexes:

$$Cu_2O + 4Cl^- + H_2O \leftrightarrow 2[CuC1_2]^- + 2OH^-,\ pK\ 18.6 \qquad (6)$$

Reaction (6) results in the decrease of currents on Tafel curves, which indicates peroxide reduction inhibition. This proves that it is Cu(I)/Cu(II) couple that is the main oxidation-reduction carrier in the electrocatalytic reduction of H_2O_2.

When carrying out the reaction in a phosphate buffer (pH 6.7) [31], H_2O_2 reduction occurs directly on Cu(0), because the Cu(I) form in this buffer is unstable, and its reduction occurs before it can be oxidized by H_2O_2. Therefore, the main catalytic mechanism of peroxide reduction in a phosphate buffer solution is controlled by means of Cu(I) generation on the electrode, i.e.

$$2Cu + H_2O_2 \rightarrow Cu_2O + H_2O \qquad (7)$$

The described process is characterized by a second order rate constant equal to 25±10 $M^{-1} \cdot s^{-1}$. The large spread of the constant values is caused by the copper surface heterogeneity after each act of polishing.

An important problem solved with the use of a copper electrode is hydrogen peroxide determination in food and pharmaceutical industry. From the viewpoint of electrochemical sensors H_2O_2 can be also determined by oxidation on a platinum electrode at $E = +0.7$ B (with respect to the silver chloride electrode). However, so high potentials often result in the oxidation of electroactive impurities, which complicates selective detection of the analyte. Thus, the state of copper surface plays a key role in hydrogen peroxide reduction providing the catalytic oxidation-reduction mechanism of this process.

As a rule, the voltammetric determination of hydrogen peroxide on a copper electrode is carried out in the amperometric mode at a preset potential. In works [31, 32] the use of a copper microelectrode for quantitative determination of hydrogen peroxide in acetic acid, chloroform and antiseptics for oral cavity is discussed. In the region of potentials from –0.8 to 0.3 V a reversible oxidation-reduction reaction of Cu(0) with Cu(II) occurs on the copper electrode. This reaction catalyzes the cathodic reduction of the peroxide. The limits of peroxide detection are at the level of $1.5–3.0 \cdot 10^{-6}$ mol/l, and the reproducibility is at the level of 8–13% (depending on the determined concentration). Removal of dissolved oxygen from the electrochemical cell lowers the basic line, because copper can react with it. As a result, an additional amount of peroxide is formed:

$$O_2 + 2Cu + H_2O \rightarrow Cu_2O + H_2O_2 \qquad (8)$$

Besides, the removal of oxygen leaves more Cu(0) sites available to the reaction with H_2O_2 added from outside, and sensitivity increases by a factor of 1.5 (0.211 and 0.303 $мA \cdot mmol^{-1} \cdot cm^{-2}$ in the presence of O_2 and without it, respectively). Besides, peroxide determination is impeded by the presence of anions forming complexes with copper. If H_2O_2 concentration is 460 μmol/L, gradual addition of OH^- and Cl^- to the level of 20 μmol/l decreases the detector response to 60 and 40%, respectively, as compared to the initial value. Further increase in concentration of the interfering ions does not exert impact on the value of the analytical signal.

The use of various nanosized compounds was a logical development of metal electrodes for electrochemical H_2O_2 reduction. In particular, sensors based on CuO nanowires introduced into a layer of graphite [31], glass carbon [33] and Nafion [34] allowed increasing the determination sensitivity and stability. As compared to "classical" copper macroelectrodes, the described sensors have a larger surface area, minimal resistance to mass transfer, a high energy of the surface and improved transfer of electrons. This provides electrocatalytic oxidation and reduction of H_2O_2 at lower overvoltage. Another approach to the increase of operational characteristics of copper sensors is the creation of micro- and ultramicroelectrodes consisting of ensembles of copper fibers soldered in glass, PVC or an epoxy resin. Work [32] reports about the use of a microelectrode consisting of copper fibers with a diameter of 12 μm. The determination of peroxide in the amperometric mode in a phosphate buffer (pH 7.0) at –0.2 V allowed reaching the limit of detection $2.7 \cdot 10^{-6}$ mol/l.

Other examples of reactions of inorganic substances on a copper electrode are the oxidation of cyanide, sulfite and nitrite ions, and, on the contrary, the reduction of nitrates and sulfates [35–40].

Nitrate-nitrite system. The application of a freshly polished copper electrode for direct reduction of nitrate ions [35, 36] was studied. Da Silva et al. used a copper microelectrode to determine nitrate ions in mineral waters within a concentration range 1−1070 μmol/l with a limit of detection $1.8\cdot10^{-6}$ mol/l. The use of copper cathodes for direct reduction of NO_3^- was studied also by Pletcher and Carpenter [37]. They found that the reduction is sensitive to halide ions that shift the wave of nitrate reduction to more negative potentials. Quite recently, a highly sensitive sensor based on copper nanostructures applied on a graphite electrode was suggested to determine nitrate ions. The developed sensor allowed determining the analyte in food and waters at the level of $1–35\cdot10^{-6}$ mol/l. Besides, the creation of a nitrate sensor consisting of ensembles of copper nanowires with a diameter of 400 nanometers and 10 microns long is known [38]. The detection limit for NO_3^- was $1.7–3.0\cdot10^{-6}$ mol/l depending on the method of preparing the described detector.

Cyanide and sulfite ions. Sulfite and cyanide ions can be determined due to electrocatalytic oxidation of CN^- into CNO^- and SO_3^{2-} into SO_4^{2-} in an alkaline medium on a copper electrode [39, 40]. It is expedient to combine this approach with chromatography.

Heavy metals. The copper electrode can be used for detecting heavy metals in objects of the environment due to the ability of copper to form amalgams and intermetallic compounds with mercury and a number of elements (see above) [41, 42].

Squarewave voltammetry on a film copper/mercury electrode was used to analyze trace amounts of lead and mercury in fresh and sea water [20]. There is a number of examples of using intermetallic compounds Hg−Cu, Co(II)–Cu, Pb−Cu and Sb−Cu for the quantitative determination of Se (IV) and Hg(II), respectively [20]. A disposable express microsensor based on copper was developed for the determination of Zn(II) in blood serum with a limit of detection 140 nmol and sensitivity 1 μA/μm [43].

Selenium, arsenic, tellurium. Note a number of works by Zaytsev et al. on Se(IV) determination by cathodic inversion voltammetry with the use of a mercury-film electrode modified by copper [44]. The method allows determining selenium in natural waters of various composition with a limit of detection 0.22 mkg/l. Work [45] describes a Cu_2Se-based microelectrode used for the voltammetric determination of Se(IV) due to its reduction in an acidic medium. The suggested method yields satisfactory results and can be recommended for the range of concentrations of Se(IV) ions from 5 to 50 μm in 0.1 M $HClO_4$. The relative standard deviation is less than 4% ($n = 10$) for Se(IV) concentration $5\cdot10^{-6}$ mol/l.

There are publications on the determination of trace amounts (at the level of nmol/l) of arsenic and tellurium on a hanging copper-mercury amalgam electrode [46] with good reproducibility ($S_r = 2.5\%$) at accumulation during 240 s.

Carbon dioxide reduction. The sphere of inorganic substances analyzed on modified copper electrodes continues to extend. The recent publication [47] devoted to the selective electrocatalytic reduction of CO_2 into formic acid on a composite copper electrode notes the potential applicability of this sensor for the determination of carbon dioxide. As compared to metallic and oxidic (Cu_2O) electrodes the developed detector has high selectivity and work stability.

Determination of organic substances

Voltammetric determination of alcohols. An important direction of using copper electrodes is the creation of sensors for the determination of alcohols in food, drinks and biofuels [48]. An amperometric copper sensor for the determination of ethanol in wine and whisky is described [17, 49]. The analysis was carried out in the flowing and injection modes. The analytical frequency of the method was 120 samples per hour. The linearity of the calibration curve remained in the range of alcohol content from 2 to 10% vol. A hydrophobic PETF-membrane acting as a barrier for impurities was placed in the analyzer block. This enabled minimizing the matrix influence due to its separation. The developed sensor was used as "an electronic nose" for identifying false samples.

To estimate the efficiency of the copper electrode when determining the content of ethanol in drinks, current signals were measured by means of a copper microelectrode [17]. When measuring in the amperometric detection mode, the electrode showed short response time proportional to concentration. Attempts of determining the content of ethanol directly in some drinks produced by distillation were unsuccessful because of the matrix effect of other organic compounds electroactive at the working potential.

A method of glycerin determination in biodiesel fuel with the use of a copper electrode is described [50−52]. When the experimental conditions are optimal, peak current increases linearly within the concentration range 3–160 mg/dm^3. The sensor sensitivity was 5.3 $\mu A \cdot cm^{-2} \cdot mg^{-1} \cdot dm^3$, the reached limit of detection was 0.25 mg/dm^3. The developed method allowed determining glycerin in real samples of biofuel with high precision.

Voltammetric determination of amino acids and amines. Amines comprise one more class of organic compounds perspective for the determination by means of copper electrodes. As a rule, the analysis of these substances is carried out by liquid chromatography with amperometric detection on metal detectors [53]. In this case copper as an electrode material has two advantages. First, it can participate in the reaction of oxygen transfer from water to oxidized particles. Second, Cu(II) ions form very stable complex compounds with amino groups. It is concluded in [54] that the increase in the current of the copper detector when determining amines is caused, first of all, by the kinetics of complex formation and, to a lesser extent, by the stability of the formed complex. The use of copper and silver electrodes modified by copper(I) oxide for studying the voltammetric behavior of aliphatic amines is reported [55]. The obtained results demonstrate that modified copper electrodes are preferable for the amperometric detection of aliphatic amines in liquid chromatography, because the behavior of amines on silver electrodes is more complex and is affected by a considerably larger number of factors as compared to modified copper electrodes.

Kok et al. [56] reported for the first time the use of a copper oxidized electrode for the voltammetric determination of amino acids. The best results of analytes detection were obtained in phosphate and carbonate buffers. The buffer concentration should be as low as possible, and pH should approach 8–10. A copper electrode was used further [57] as a detector for the separation and determination of L-amino acids by liquid reversed-phase chromatography in the concentration range 10^{-6}–10^{-3} mol/l.

The solid copper amalgam electrode [58] can be considered a perspective type of sensors for amino acids determination. This sensor combined with differential pulse voltammetry is used for cysteine determination. The reached limit of detection was $1 \cdot 10^{-8}$ mol/l, S_r was 7.2%. The developed sensor is durable and almost nontoxic, and its surface can be easily regenerated in the automatic mode [58].

There is a publication [59] devoted to the analysis of sympathomimetics in the flowing and injection mode with amperometric detection on a copper metal electrode. The working electrode has a stable response. The relative standard deviation was 4.6% for 30 consecutive injections of norephedrine at the level 0.15 mmol. The method is sensitive to such interfering substances as glucose, sucrose and ascorbic acid. Therefore, when analyzing complex mixtures, it should be combined with liquid chromatography.

Mechanism of electrocatalytic oxidation of alcohols and amines. The article by Fleischmann et al. [60] can be considered a pioneer work on the kinetics and mechanism of the electrooxidation of a number of aliphatic alcohols and amines in an alkaline media on metallic electrodes. The article shows that the electrooxidation of the studied substances on a copper electrode is a first-order reaction with respect to the concentration of the organic substrate and a zero-order reaction with respect to the concentration of hydroxide ions. The rate-limiting step of the reaction is the formation of an organic molecule adsorbed on the anode surface according to the scheme:

$$CuO + 2OH^- - \bar{e} \leftrightarrow CuO_2^- + H_2O \quad (9)$$

$$CuO_2^- + \text{organic substrate} \rightarrow CuO + \text{intermediate (rate-limiting step)}$$

$$\text{Intermediate} \rightarrow \text{product} + (n-1)\bar{e} \quad (10)$$

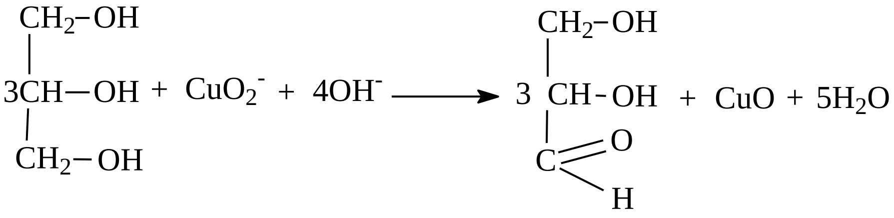
The main agent of electron transfer in case of electrochemical transformations of alcohols is Cu(III), as in case of electrocatalytic oxidation of carbohydrates. Thus, the participation of copper(III) in the catalytic oxidation of ethanol was confirmed by experiments on a copper rotating disk electrode. A signal observed on the voltammogram in a 0.1 M NaOH solution at 0.6 V after the addition of ethanol undergoes a considerable decrease. Studying the mechanism of the anode oxidation of ethanol the authors of [60] assumed that the first step of the mechanism is the substrate deprotonation followed by the molecule decomposition with the formation of radicals. Thus, the true catalyst is the radical CuOOH•. In order to explain the participation of Cu(III) in the anode oxidation of ethanol in an alkaline solution the following sequence of steps can be suggested:

$$CuO + OH^{-}_{(ads)} \leftrightarrow CuOOH\bullet + \bar{e} \qquad (11)$$

$$CuOOH\bullet + H_3CCH_2OH_{(ads)} \leftrightarrow CuO + [C_2H_4OH]\bullet + H_2O \qquad (12)$$

$$[C_2H_4OH]\bullet \leftrightarrow \text{ethanol molecule decomposition product} \qquad (13)$$

The mechanism of electrocatalytic oxidation of glycerin on a copper electrode was studied by scanning electron microscopy (SEM) [61]. According to the obtained results, the alcohol oxidation starts on the copper substrate at a potential of 0.3 V (with respect to the silver chloride electrode). This value of potential enables suggesting that Cu(III) ions originally do not take part in glycerin oxidation. As potential increases from 0.6 to 0.8 V, copper(III) starts to be formed on the electrode surface. Copper(III) catalyzes the oxidation process according to the following scheme:



$$3\,CH_2OH{-}CH(OH){-}CH_2OH + CuO_2^{-} + 4OH^{-} \longrightarrow 3\,CH_2OH{-}CH(OH){-}CHO + CuO + 5H_2O \qquad (14)$$

Thus, copper(III) makes the main contribution to the electrocatalytic oxidation of alcohols and amines.

Voltammetric determination of carbohydrates. A striking example of using a copper electrode is glucose determination by cyclic voltammetry in the stationary and flow-injection modes [62]. Alexander and Haddad [63] reported for the first time the use of a metal copper electrode for sugars determination. They performed measurements in the mode of flow-injection analysis, during which they recorded the system potential depending on the content of Cu(II) and Cu(I) ions in the solution. The mobile phase consisted of Cu(II) ions in a solution of tartaric acid or ammonia. Introducing various sugars resulted in a change of the copper electrode potential depending on the ratio Cu(II)/Cu(I). The latter is determined by the amount of oxidized carbohydrates. The authors of [63] studied in detail the influence of such factors as temperature, pH, the presence of ligands (tartrate and citrate ions, ammonia) and flow rate. It was found under the chosen optimal analysis conditions that the graduation linearity remains unchanged for glucose and fructose up to 10 and 2 mmol, respectively.

The creation of an amperometric sensor based on a modified copper chemical electrode for the determination of carbohydrates by HPLC was reported for the first time in [64, 65]. A glass carbon electrode was used as an indicator electrode, on which copper films were applied by interaction with a solution of $CuCl_2$. The authors of [65] assume that the main component of this film is the CuCl layer, along with which a layer of metallic copper and $Cu(OH)_2/CuO$ can be formed. The surface of the copper modified electrode was studied by scanning electronic microscopy and X-ray fluorescent analysis. This confirmed the formation of a layer of copper(I) chloride on glass carbon in the form of hexagonal crystal structures with a diameter of 1−2 microns.

As compared to such "classical" metal electrodes as Au, Pt, Ni, Cd and Co used for the electrocatalytic determination of carbohydrates, the developed sensor had a number of advantages: high stability and reproducibility of the signal for more than 2–3 days, a wide range of response linearity and low limits of detection at the level of 20–30 ng. In case of platinum and gold electrodes, which also have catalytic activity with respect to sugars in the course of electrochemical transformations on their surface, gradual adsorption of reaction products occurs. This results in passivation of the electrodes and fast decrease in the response with respect to the analyte. Therefore, when using Pt and Au electrodes, it is necessary to carry out desorption and conditioning operations in order to provide stable and high reproducibility of the reaction.

The developed electrode was used subsequently as an electrochemical detector for determining a wide range of carbohydrates, amines and alcohols by liquid chromatography [66]. When comparing the chromatograms of standard samples of tobacco leaves obtained with the use of the developed detectors and the refractometric one, it was shown that the suggested sensor provides the best reproducibility, stability and correctness of determination. For example, the limit of glucose detection under the optimal measurement conditions was 0.2 ng, and the signal reproducibility after 80–100 test injections was 1–5%.

A highly selective and highly sensitive detector based on copper/copper oxide particles dispersed in a Nafion film for the determination of carbohydrates by liquid chromatography is known [67]. The Nafion membranes made by Dupont since 1964 are cation-exchange polymers based on fluorocarbon vinyl esters containing sulfonate groups. This material is characterized by high inertness in the majority of electrolytes. The use of Nafion as a substrate increases the mechanical stability and selectivity of the copper electrode due to controlled three-dimensional electrodeposition of copper particles in a polymeric matrix. Besides, it prevents poisoning and passivation of the catalytic centers, if the analyzed solution contains catalytic poisons. In particular, adding 500 mkg/g of albumin and sodium dodecyl sulfate to a 10^{-3} M solution of glucose decreases its response to the Nafion-modified copper electrode by 6 and 8%, respectively. In contrast, when using an unmodified electrode, the signal falls by 75 and 18%. Applying the Nafion-modified copper electrode as a chromatographic detector provided effective separation of a mix of carbohydrates. The reached limit of detection varied in the range from 10 to 120 pmol. Standard deviation in 100 consecutive measurements of a $1 \cdot 10^{-4}$ M glucose solution for 18 h was 4.5%.

A method for producing copper electrodes with the use of coal paste [68, 69] was suggested. The electrode was modified either by introducing high-disperse Cu_2O, $Cu(OH)_2$ and CuO powders into the coal paste or by means of electrogeneration of a thin CuO film on the coal paste layer. It followed from the obtained cyclic voltammograms that the highest detector response was on an electrode that contained CuO. The mechanism of sugars electrooxidation was studied with the use of a round rotating disk CuO/carbon paste electrode. The kinetic parameters of the reaction were determined. The developed electrode was successfully used for separating a mixture of carbohydrates by anion-exchange chromatography. The reached detection limit according to the 3σ criterion was $3 \cdot 10^{-7}$ mol/l, the relative standard deviation was 1.79%. The detector stability remained unchanged within three months.

It is also worth noting works by Abdullin and Budnikov et al. on the voltammetric determination of glucose on a copper electrode in blood serum in the stationary and flow-injection modes [70]. The linear range of the copper detector response is $2.5\text{–}10 \cdot 10^{-4}$ mol/l. The suggested technique allows analyzing 50 samples per hour, and S_r does not exceed 4% [70].

A sensor based on a modified Cu/CuO electrode for the determination of glucose in alkaline media [9] is described. Selective catalytic oxidation of glucose occurred at 0.7 V on the electrode. The presence of such interfering substances as ascorbic acid, uric acid or dopamine had no significant effect on the determination of the target analyte. The developed sensor was used to determine the level of glucose in blood serum. The limit of detection by this technique was $1 \cdot 10^{-6}$ mol/l.

Comparative analysis of the values of relative oxidation of various carbohydrate groups was carried out on the basis of experimental data obtained by hydrodynamic voltammetry [71]. Samples of glucose and its derivatives with concentration $1 \cdot 10^{-4}$ M are characterized by oxidation currents in the range of 1.5–2.5 μA at rather low potential. The molecule linearity increases its activity to oxidation. As a result, higher current values are registered than in case of cyclic structures. Blocking of the C_1 hydroxyl group as, for example, in 1-*O* methylglucose resulted in sharp decrease in the currents. The authors assume [71] that a key factor of easy oxidation is the presence of a considerable number of hydroxyl groups. The presence of at least two hydroxyl groups is the minimal requirement. Sterical factors can also affect the values of the currents.

The creation of sensors based on nanosized Cu and CuO applied on various carriers was further development of the considered direction of studies. The high dispersion of copper nanoparticles increased their catalytic activity thus enabling to increase the sensitivity of carbohydrates determination. For example, the sensitivity of a copper electrode coated with CuO nanowires to glucose was 490 μA · mm^{-1}. The use of graphite films, modified glass carbon, carbon nanotubes and indium tin oxide (ITO) as substrates allows significantly expanding the performance characteristics of copper nanosensors. Quite recently a nanostructured electrode based on porous column films of copper applied by vacuum coating onto ITO [72] was developed. The working range of the new sensor was $5 \cdot 10^{-3}$–1 mol/l, the detection limit was 0.36 μmol/l. The operation stability remained for three months.

The available data enable concluding that modified copper electrodes have good analytical characteristics and provide excellent opportunities for the detection of carbohydrates from the viewpoint of working concentration range, detection limits, stability and selectivity [73].

Mechanism of electrocatalytic oxidation of carbohydrates. Materials based on copper and copper oxides have been of interest in the field of electrocatalytic oxidation of various organic substances for a long time. As a rule, these reactions occur in strongly alkaline solutions (0.01–0.5 M NaOH) in the anodic potential region. The practical value of these reactions was used for the first time by Barreswil as a test for sugar. A few years later Feling developed an analytical technique for the quantitative determination of glucose. It was established subsequently that copper(II) in an alkaline medium is an oxidizer for a wide range of organic substrates [74].

The article by Vassilyev et al. [63] can be considered the first work devoted to studying the mechanism of glucose electrooxidation on a copper electrode. In this work it was established by comparing the catalytic properties of electrodes made of various metals that the greatest oxidation currents of glucose were registered on copper and gold electrodes. Nevertheless, the excess voltage of glucose electrooxidation was much greater than in case of gold and platinum electrodes, and the beginning of the oxidation process was shifted towards more positive potentials.

Until now the mechanism of glucose oxidation on copper or on modified copper electrodes in an alkaline medium is not known with certainty. The most acceptable explanation is the assumption made by Marioli and Kuwana [79]. According to their studies electrooxidation occurs due to glucose deprotonation and its isomerization into the enediol form followed by adsorption on the electrode surface and oxidation by superficial Cu(I), Cu(II) and Cu(III). This process takes place in the range of potentials from 0.40 to 0.80 V, which includes the oxidation potential of Cu(II)/Cu(III). Experiments on a rotating disk electrode provide strong evidence that Cu(III) plays an important role in carbohydrates oxidation. Cu(III) reacts in a strongly alkaline medium with hydroxide ions to form hydroxyl radicals that act as intermediates of electron transfer. This specified assumption is confirmed in works [76, 77], according to which electrode passivation with the formation of copper(II) oxide occurs in a strongly alkaline medium at potentials 0.2–0.5 B. This oxide, in turn, is at equilibrium with cuprite ions:

$$CuO + 2OH^- \leftrightarrow CuO_2^{2-} + H_2O \qquad (15)$$

The authors of [21] assume that this reaction results in the formation of Feling reagent on the electrode surface. It catalyzes glucose electrooxidation into gluconic acid. In contrast, in case of glucose oxidation on platinum and graphite electrodes against the background of NaOH peaks are not observed.

Ueda et al. [78] performed experiments with the use of glucose, xylose and sorbitol using a copper rotating disk electrode. They established that carbohydrates oxidation on copper electrodes is a multielectronic process: sorbitol in 0.15 M NaOH at 0.45 V (with respect to the silver chloride electrode) is oxidized into 6 formate molecules donating 14 electrons. Glucose and xylose are oxidized with the transfer of 12 and 10 electrons, respectively. The estimated mechanism of glucose electrooxidation can be shown as follows (Figure 3):

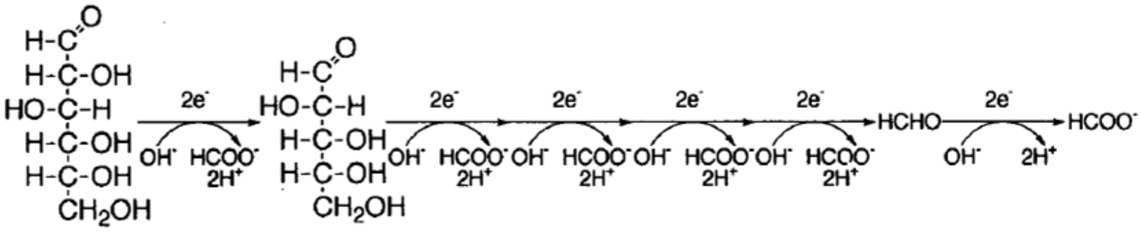


Figure 3. The mechanism of glucose electrooxidation of a copper electrode

Because the pK_a of most carbohydrates is in the range from 12 to 13, they will be in the dissociated form in a strongly alkaline solution. Due to this the oxygen of the C_1 alcohol group and the Cu(III) ions will form an alkoxide, which will probably play a key role in electron transfer and in the generation of radical intermediates and CuO. The radicals are subsequently oxidized directly with the formation of the formate, and Cu(II) (or CuO) will regenerate the catalytically active Cu(III) form due to the oxidation. The formation of the formate as a final product is confirmed by ^{13}C and ^{1}H NMR [74]. Thus, two electrons are transferred in each catalytic cycle.

The mechanism of catalytic carbohydrates oxidation was studied subsequently by Torto et al. [79] with disaccharides as an example. In case of glucose the amount of CuO catalyzing electrooxidation does not exert impact. In contrast, in case of disaccharides the number of donated electrons considerably changes depending on its quantity. In particular, the use of a nanostructured copper electrode modified by carbon nanotubes opens an opportunity of carrying out the quantitative determination of glucose and amino acids at the submicromolar level with good reproducibility (S_r = 3%) [80]. Works [81, 82] published in recent years describe a method of quantitative voltammetric determination of nitrites, nitrates and glucose with the use of two-layer platinum-copper (Pt-Cu) and nickel-copper (Ni-Cu) electrodes. These bimetallic electrodes are characterized by a large surface area in addition to very good catalytic activity, which makes them excellent sensors for quantitative voltammetric analysis.

Other organic and biologically active agents. The number of substances available to voltammetric determination on copper electrodes gradually extends. Recently, researchers concentrated their attention on biologically active compounds and pharmaceuticals. There are publications on the quantitative determination of ascorbic acid [83], melamine [84], dopamine [85], antiviral medication valacyclovir [86] and doxorubicine [87] on modified copper electrodes.

Conclusion

Developing and applying new copper-based electrochemical sensors, especially for application in strongly alkaline media remains a topical direction of modern electroanalytical chemistry development. In some cases, copper sensors allow determining substrates of practical importance, for example, of glucose in blood, practically without sample preparation.

Analyzing recent publications on the use of copper electrodes in voltammetry shows that miniaturization, modification and nanostructuring of the surfaces of electrode materials are the main tendencies in this field. This allows increasing the analysis selectivity and sensitivity, and also determining substances previously not available to massive copper electrodes. The gradual disuse of mercury electrodes promotes the spread of solid bimetallic copper electrodes.

As for substrates for the production of modified nanostructured copper electrodes, special attention is paid at the moment to carbon materials: glass carbon, graphite, carbon nanotubes and graphene [88]. These materials provide good distribution of copper nanoparticles and have high electrochemical reactivity, mechanical hardness and commercial availability. Using carbon materials as substrates for electrocatalytically active copper particles will remain the priority direction that keeps on developing.

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