Modified carbon-containing electrodes in stripping voltammetry of metals

Part I. Glassy carbon and carbon paste electrodes

Natalya Yu. Stozhko · Natalya A. Malakhova · Mikhail V. Fyodorov · Khiena Z. Brainina

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Abstract Papers dealing with modified electrodes made of carbon materials and composites for use in stripping voltammetry of metals have been reviewed. The review consists of two parts, of which the first considers applications of modified glassy carbon and carbon paste electrodes, while the second describes diverse modified carbon-containing composite and microscopic electrodes. Information about modifiers, electrode modification methods, conditions, and limits of detection of elements in different materials has been tabulated. The review covers 550 papers published in Russia and abroad between 1990 and the first half of 2007.

Keywords Modified electrodes · Glassy carbon · Carbon paste electrodes · Stripping Voltammetry · Metal ions determination

Introduction

Voltammetry is one of the most universal methods of electroanalytical chemistry, which is widely used as a technique for measurement of concentrations of substances and as a tool for analysis of their properties. The growing number of papers concerned with problems and urgent issues of voltammetry is indicative of the increasing interest among chemists to this method. The general status and future trends of voltammetry and electrochemical sensors are described in the reviews [1–7]. A priority line of its development that follows from the analysis of those papers is the creation, the study and the use of new electrodes, electrochemical sensors [8], transducers, and detectors for automated, flow-through, and “field” analysis. This is because the electrochemical signal is formed by processes taking place on the electrode surface. Therefore, the condition of the electrode surface, which depends on the origin, the defect content, and the mechanical inhomogeneity of the material, determines many significant quantitative characteristics of electrochemical measurement systems. Required electrochemical properties of the electrode can be obtained if its surface is modified purposefully. Therefore, the modification and the “molecular design” of the transducer surface and the formation of grafted layers on solid surfaces constitute an actively developing new area of investigation. Problems of the chemical modification of solid surfaces, specific and regular features of the modifier attachment to various solid matrices, and examples of practical applications of chemical sensors (modified electrodes) are overviewed in the papers [9–21].

Over a period of years, the development of the voltammetric method was connected with metal, primarily mercury, electrodes. But mercury is an extremely toxic material. This element presents the first-rate hazard leading to severe poisoning and heavy diseases. For this reason, some countries (USA, Japan, EC) have declared a moratorium on the use of mercury in storage batteries, lamps, thermometers, pesticides, etc. Electrodes made of nontoxic materials also tend to smoothly force out mercury electrodes in electroanalysis. As an alternative to toxic mercury electrodes, electrodes of a nontoxic “dental” amalgam (Ag2Hg3 with the surplus silver; [22, 23]) have been developed and used for measurements of heavy metals. Carbon materials (CMs) possessing some attractive features [24, 25] are widely used as mercury-free current-conducting...
electrode materials. Firstly, depending on the CM type, the character of the electrical conduction can change from the metal to the semiconductor conduction suggesting broad potentials for a wide range of capacitive, adsorption, catalytic, and kinetic properties. Secondly, the carbon surface can adsorb a variety of compounds by both the nonspecific physical sorption and the specific chemisorption with a functional coating, which can be formed either under the forced action of reagents or due to the presence of native functional groups resulting from a thermomechanical treatment of the material [25, 26]. Thirdly, the complexation capacity of carbon materials is higher than that of metals. Fourthly, CMs can form strong covalent bonds with some surface modifiers favoring the development of modified electrodes. Fifthly, the carbon surface is electrochemically inert over a wide interval of potentials. All these features predetermine the use of diverse carbon materials in electroanalysis. Glassy carbon, pyrolytic graphite, carbon glass-ceramics, impregnated graphite, carbon fibers, filaments, cloths, gauzes, and composite materials serve as the electrode material. The properties of CM electrodes, their specific features and drawbacks, and applications in voltammetric measurements of substances are described in the Russian reviews published in 1988 and 1990 [27, 28]. The present overview covers papers published in Russia and abroad since 1990. To narrow the borders of an extensive literature stream on modified carbon-containing electrodes for the 17-year period, the current review has been restricted on a method of analysis and analyte. So, the electrodes used for metal ion determination with SV have been described only. All the papers published over this period can be divided into six main groups depending on the type of the electrode used: glassy carbon (GCE), carbon paste (CPE), carbon-containing composite (CCE), impregnated graphite (IGE), thick-film graphite-containing (TFGE) electrodes, carbon microelectrodes (CME), and their arrays (ACME). As Fig. 1 suggests, GCE is the first with respect to the number of papers published over the 15 years. The minimum number of papers, most of which have appeared recently, are dedicated to TFGE and CME. This is due to the fact that these two groups of the electrodes represent recently emerging and vigorously developing lines of research into the use of carbon-containing electrodes.

**Glassy-carbon electrodes**

Glassy carbon is isotropic, is almost gas-tight, has low porosity, is very hard, is a good current conductor, and is stable in many corrosive media [25]. The adsorptivity and the reactivity of glassy carbon are low compared to those of other structured graphite materials having a hexagonal or a rhombohedral lattice. These factors account for the low sensitivity of unmodified glassy-carbon electrodes in analysis [29–34]. The detection limit of elements is reduced by increasing the electrochemical accumulation time (up to 40 min) [35–42], using additional accumulation operations, e.g., the ultrasonic extraction [43] or modifying the GCE surface.

Table 1 shows some applications of modified GCE for voltammetric measurements of inorganic ions [44–190]. Methods of the preliminary modification of the surface (ex situ) and the in-analysis modification (in situ) are widely used for the purposeful transformation of the GCE surface properties. These methods are sometimes combined to enhance the selectivity. For example, a film of a metal or a current-conducting polymer is applied to GCE and a selective organic reagent or mercury, gold, or bismuth ions, which co-precipitate with the element to be determined, are added to the solution. GC is a preferable substrate for mercury film electrodes [191]. In this case, the two-layer modification of the surface is realized by the “ex situ/in situ” scheme. On occasion, up to three modified layers each, having its specific application and certain function, are built up on the surface. For example, the layer-by-layer modification by a clay mineral, a cation-exchange cross-linked polymer and mercury [156] results in that the GCE surface forms a layer, which possesses cation-exchange properties, can form an amalgam, and separates coarse molecules or cations.

The GCE modifiers in common use are metals (mercury [44–68], gold [81–85], cadmium [87], copper [88], lead [89], platinum [90], bismuth [91–96]) and facilitating the precipitation of amalgam-forming and electropositive elements. Organic substances (OS) [107–121], macrocyclic compounds [122–126], polymers [127–131, 157–159, 165–166, 169–175], bioactive compounds [186], and nanotubes [187–190] can also serve as GCE modifiers. Different combinations of the modifiers—a metal and OS [70–80, 97–105, 106], a polymer and a metal [86, 132–147, 160–180]—
Table 1 Modified glassy carbon electrodes

| Modifier a | Manner | Analyte | Detection limit (M) | Supporting electrolyte b | Sweep mode c | Purge d | Sample e | Reference |
|------------|--------|---------|---------------------|--------------------------|--------------|---------|----------|----------|
| Hg         | In situ Ni (II) | 2·10⁻⁶ | 30 gL⁻¹ H₃PO₄ + 70 gL⁻¹ Na₂SO₄ + 10 gL⁻¹ NaCl + Hg (II) (pH 4.5) | LS ASV | – | Nickel electrodeposits [44] |
| Hg         | In situ Pd (II) | 9·10⁻⁶ | 0.2 M KCl (pH 3) + Hg (II) (Hg:Pd ≤ 1:10) | LS ASV | – | BGD [45] |
| Hg         | In situ Fe (II, III), Mn (II) | 1·10⁻⁶ | 0.5 M NaCl + Hg (II) (pH 4.0–6.0) | LS ASV | + | Sea, drinking, service waters [46] |
| Hg         | In situ Pb, Cd (II), Bi (II, III) | 4·5·10⁻¹² (Cd); 1·10⁻⁹ (Pb); 1·10⁻⁴ (Bi) | 0.01 M amm. buf. (pH 5.6) + 5·10⁻³ M SCN⁻ + 3·10⁻⁵ M Hg (II) | SQW ASV | + | Lake water [47] |
| Hg         | In situ Cu, Pb (II), Cd (II) | 5·10⁻⁴% (Pb); 2·10⁻⁵% (Cd); 7·10⁻⁷% (Bi) | 0.35 M KCl + 0.01 M HCl + 5·10⁻⁶ M Hg (II) (pH 2.0) | LS ASV | – | Soils, cement, rocks [49] |
| Hg         | In situ Cu, Pb (II), Cd (II) | 1·10⁻⁸–10⁻¹¹ | 1 M HClO₄ + 5·10⁻⁴ M Hg (II) | DP ASV | + | Sea waters [50] |
| Hg         | In situ Cu, Pb (II), Cd (II) | 2·10⁻⁵ (Pb); 7·10⁻⁵ (Cd); 1·6·10⁻⁴ (Cu) | 2 M NaCl (0.5 M HCl) + 1·10⁻⁴ M Hg (II) | AC ASV | – | Surface, waste water [51] |
| Hg         | In situ Cu, Pb (II), Cd (II) | 1·10⁻⁹ (Pb); 1·10⁻¹⁰ (Cd); 1·10⁻⁸ (Cu); 1·10⁻⁸ (Zn) | 1 M LiCl (0.2 M HCl) + 1·10⁻⁴ M Hg(NO₃)₂ | SQW ASV | + | Surface, waste water [52–53] |
| Hg         | In situ Cu, Pb (II), Cd (II), Zn (II) | 2·10⁻¹⁰ (Cu); 1·10⁻¹⁰ (Pb); 7·10⁻¹¹ (Cd); 6·10⁻¹⁰ (Zn) | 0.1 M NaAc + 5·10⁻⁵ M Hg (II) (Cu, Cd, Pb); 0.1 M NaAc + 5·10⁻⁵ M Hg (II) + Ga (III) (Zn) | LS ASV | – | Extract from river sediment [54] |
| Hg         | In situ Cu, Pb (II), Cd (II), Zn (II) | 6·10⁻¹¹ (Zn); 2·10⁻¹¹ (Cd); 1·10⁻¹¹ (Pb); 5·10⁻¹¹ (Cu) | 0.025 M KCl (pH 3.5) + 0.3 gL⁻¹ Hg (II) | DP ASV | + | Sea waters [55] |
| Hg         | Ex situ Cu (II) | 2·10⁻⁸ | 0.1 M HNO₃ | SQW ASV | – | Waters, pharmaceutical preparations [56] |
| Hg         | Ex situ Pb (II) | 5·10⁻⁹ | 2.5 M NaCl + 0.25 M asc. ac. + 0.24 M NaOH | DP ASV | + | Soil, air [57] |
| Hg         | Ex situ Tl (I) | 1·10⁻⁹ | 0.13 M EDTA + 0.58 M asc. ac. + 0.7 M NaOH | DP ASV | + | Soils [58] |
| Hg         | Ex situ Tl (I) | 5·10⁻¹⁰ | 0.17 M EDTA + 2 mM HCl + 0.03 M asc. ac | LS ASV | + | Natural waters [59] |
| Modifier | Manner | Analyte | Detection limit (M) | Supporting electrolyte | Sweep mode | Purge | Sample | Reference |
|----------|--------|---------|---------------------|-----------------------|------------|------|--------|-----------|
| Hg       | Ex situ| Ba (II), Pb (II) | $7 \times 10^{-10}$ (Ba); $5 \times 10^{-10}$ (Pb); | $0.1 \ M \ HClO_4$ or $80\%$ ethanol $+ 0.1 \ M \ TBAP$ | DP ASV | + | BGD | [60] |
| Hg       | Ex situ| Pb (II), Cu (II), Cd (II) | $6 \times 10^{-11}$ (Pb); $2 \times 10^{-10}$ (Cu) | $0.01 \ M \ NH_4Ac\cdot HCl + 1.2 \times 10^{-4} \ mM \ NaSCN \ (pH \ 3.4)$ | DP ASV | – | Sea water | [61] |
| Hg       | Ex situ| Pb (II), Cu (II), Cd (II) | $10^{-9}$ | $0.05 \ M \ HCl + 70\%$ methanol (pH 4–6) | DP ASV | + | Foodstuffs | [62] |
| Hg       | Ex situ| Zn (II), Cu (II), Pb (II), Cd (II) | $5 \times 10^{-10}$–$1 \times 10^{-9}$ | $0.1 \ M \ KNO_3 + 2 \times 10^{-4} \ M \ HNO_3$ | SQW ASV | – | Waste water | [63] |
| Hg       | Ex situ| Zn (II), Cu (II), Pb (II), Cd (II) | $4 \times 10^{-7}$ (Zn); $2.7 \times 10^{-9}$ (Cd); $6.8 \times 10^{-9}$ (Pb); $4 \times 10^{-9}$ (Cu) | $0.2 \ M \ HNO_3$ | SQW ASV | – | Sweet water | [64] |
| Hg       | Ex situ| Zn (II), Cu (II), Pb (II), Cd (II) | $8 \times 10^{-9}$ (Zn); $9.7 \times 10^{-9}$ (Cu); $1.6 \times 10^{-8}$ (Pb); $8.6 \times 10^{-9}$ (Cd) | $0.01 \ M \ LiCl \ (pH \ 2.9)$ | SQW ASV | + | Fuel | [65] |
| Hg       | Ex situ| Cu (II), Pb (II), Cd (II), Zn (II) | $1 \ ng \ g^{-1}$ | $0.075 \ M \ NaNO_3$ | LS ASV | + | Sugar, syrup | [66] |
| Hg       | Ex situ| Cu (II), Pb (II), Cd (II), Zn (II) | $10^{-8}$–$10^{-9}$ | $0.1 \ M \ citric \ acid + 1 \times 10^{-4} \ M \ Fe \ (III)$ | LS ASV | – | BGD, extracts from turf | [67] |
| Hg/Cu    | Ex situ/in situ | Se (IV) | $1 \times 10^{-9}$ | $0.1 \ M \ HClO_4 + 1 \ mg\ L^{-1} \ Cu \ (II) + 0.02 \ M \ NaSCN + 5 \times 10^{-3} \ M \ EDTA$ | DP CSV | + | BGD | [68] |
| Hg, 8HXQ | In situ | Mo (VI) | $5 \times 10^{-9}$ | $0.2 \ M \ NaAc \ (pH \ 5.25) + 5 \times 10^{-5}$ | DP CSV | + | Biomaterials and background objects | [69] |
| Hg, DMG  | In situ | Ni (II) | $1.3 \times 10^{-10}$ | $0.1 \ M \ KNO_3 + 2 \times 10^{-4} \ M \ Hg(NO_3)_2 \ (pH \ 9)$ | SQW CSV | – | Soils | [70] |
| Hg/RSH   | Ex situ | Cd (II) | $4 \times 10^{-12}$ | $0.01 \ M \ NaAc \ (pH \ 3.0)$ | SQW CSV | + | Sea water | [71] |
| Hg, catechol | In situ | Sn (IV), Pb (II) | $5 \times 10^{-9}$ (Pb); $4 \times 10^{-9}$ (Sn) | $0.1 \ M \ NaAc \ (pH \ 4.5) + 5 \times 10^{-4}$ | DP CSV | + | Biomaterials, foodstuffs, background objects | [72] |
| Element | Form | Condition | Reagent | Dilution | Use | Source |
|---------|------|-----------|---------|----------|-----|--------|
| Hg/EDA | Ex situ/ in situ | Cu (II) | 0.01 M HCl + 3·10^{-3} M EDA | SQW ASV | Sea water | [75] |
| Hg/DMG | Ex situ/ in situ | Ni (II) | 10^{-6} | LS CSV | BGD | [76] |
| Hg/DMG | Ex situ/ in situ | Pb (II) | 1·10^{-4} | SQW ASV + BGD | | [77] |
| Hg/18C6 | Ex situ/ in situ | Co (II), Ni (II) | 1·10^{-9} | DP CSV + Model mixtures | | [78] |
| Hg/CHD or DMG | Ex situ/ in situ | Co (II), Ni (II) | 5·10^{-9} (Ni); 2·10^{-9} (Co) | SQW CSV | Biological liquids | [79] |
| Hg/DMG (1), Hg/8HXQ (2) | Ex situ/ in situ | Ni (II) (1), Cu (II) (2) | 9·10^{-10} (Ni), 1·10^{-9} (Cu) | SQW CSV | BGD | [80] |
| Au | Ex situ | As (III) | 1·6·10^{-8} | HCl + Na₂SO₃ | DP ASV + | Natural waters | [81] |
| Au nanoparticles | Ex situ | As (III) | 1·3·10^{-10} (LS ASV); 2·10^{-10} (SQW ASW) | 1 M HCl | LS ASV | River waters | [82] |
| Au | Ex situ | CH₃Hg⁺ | 2·10^{-8} | 0.01 M NaN₂₀₃ + 0.14 M HNO₃ | DP ASV | Model solution | [83] |
| Au | Ex situ | Se (IV), Te (IV) | 1·6·10^{-10} (Te) | 0.1 M HNO₃ | DP ASV | Copper | [84] |
| Au/PVP | Ex situ | Hg (II) | 5·10^{-10} | 0.025 M H₂SO₄ + 0.05 M KCl | SQW ASV | Natural waters | [85] |
| Cd | In situ | Hg (II) | 4·5·10^{-9} | 0.1 M Na₂Br + 1·10^{-8} M Cd (II) | LS ASV | Natural waters | [86] |
| Cu (1); Au (2); Se (3) | In situ | Se (IV), Au (III) | 3·8·10^{-5} (Se), 1·5·10^{-5} (Au) | 0.1 M HClO₄ + 1·1·10^{-4} M Cu(II) (Au(III)) (Se); 0.1 M HClO₄ + 10 mgL⁻¹ Se (IV) (Au) | SQW CSV | Vitamins | [87] |
| Pb | In situ | Ni (II), Co (II) | 1·6·10^{-9} (Ni); 1·10^{-9} (Co) | 0.1 M PIPES + 5·10^{-3} M DMG + 2·5·10^{-5} M Pb(NO₃)₂ (pH 6–9) | SQW CSV | SS of water and tea leaves | [88] |
| Pt nanoparticles | In situ | As (III) | 2·8·10^{-8} | 1 M HClO₄ | LS ASV | Drinking water | [89] |
| Bi | In situ | In (III) | 10^{-8} | 0.1 M NaAc (pH 4.5) + 0.1 M KBr + 200 µgL⁻¹ Bi (III) | SQW ASV | Model solutions | [90] |
| Bi | In situ | Zn(II), Cd (II), Pb (II) | 1·10^{-9} (Pb); 2·10^{-9} (Cd); 1·10^{-9} (Zn) | 0.1 M NaAc + 500 µgL⁻¹ Bi (III) | SQW ASV | Tap water, biomaterials | [91] |
| Bi | Ex situ | Cu (II) | 7·8·10^{-8} | 0.1 M acet. buff. (pH 4.75) + 2·5·10^{-4} M Ga (III) | SQW ASV | Model solution | [92] |
| Bi | Ex situ | Cd (II), Pb (II) | 5·10^{-7} | 0.05 M NaAc | SQW ASV | BGD | [93] |
| Bi | Ex situ | Zn (II), Cd (II) | 4·3·10^{-7} (Zn); 5·9·10^{-9} (Cd) | 0.1 M NaAc | SQW ASV | BGD | [94] |
| Bi | Ex situ | In(III), Ti(IV), Cu(II), Cd(II) | 10^{-7} | 0.1 M NaAc (pH 4.5) | SQW ASV | BGD | [95] |
| Modifier | Manner | Analyte | Detection limit (M) | Supporting electrolyte | Sweep mode | Purge | Sample | Reference |
|----------|--------|---------|---------------------|------------------------|------------|------|--------|-----------|
| Bi/CMA  | Ex situ/ in situ | V (V)  | 2·10⁻⁸  | 0.1 M acet. buff. (pH 5.5) + 50 μM CAA + 4 mM KBrO₄ | SQW CSV | – | Groundwater | [97] |
| Bi/DMG  | Ex situ/ in situ | Co (II) | 1.8·10⁻¹¹ | 0.0125 M PIPES + 0.002 M HEPES + 75 μg L⁻¹ CTAB + 2.4·10⁻⁴ M DMG (pH 6.5) | DP CSV | + | Tea leaves, natural and drinking waters | [98–99] |
| Bi/CF   | Ex situ/ in situ | Cr (VI) | 2·10⁻⁹  | 0.01 M PIPES + 0.2 M KCl + 0.1 mM CF | SQW CSV | – | Tap water, soils | [100] |
| Bi/TEA  | Ex situ/ in situ | Fe (III) | 7.7·10⁻⁹ | 0.1 M NaOH + 0.01 M TEA + 5·10⁻³ M KBrO₄ | DP CSV | + | Standard sample of river water | [101] |
| Bi/DTPA | Ex situ/ in situ | Cr (VI) | 3·10⁻¹⁰ | 0.1 M NaAc (pH 4.5) + 0.25 M KNO₃ + 1·10⁻⁶ M DTPA | SQW CSV | + | River waters | [102] |
| Bi/CMA  | Ex situ/ in situ | Ni (II) | 1.2·10⁻⁹ (Co); 1.7·10⁻⁶ (Ni) | 2.5·10⁻⁹ M DMG | SQW ASV | – | Ore, river water | [103] |
| Bi/cupferron | Ex situ/ in situ | Mo (VI) | 2·10⁻⁹ | 0.05 M acet. buff. (pH 5.5) + 5·10⁻⁵ M CAA | SQW CSV | – | Sea water | [104] |
| Bi/CMA  | Ex situ/ in situ | U (VI)  | 4·10⁻¹⁰ | 0.01 M PIPES + 0.05 M KCl + 0.1 mM cupferron | SQW CSV | – | Sea water | [105] |
| Pb-Cu/DMG + NO₂⁻ | In situ | Co (II) | 1·10⁻¹¹ | 0.2 M (NH₄)₂SO₄ + NH₄OH + 0.5 M NaNO₂ + 2·10⁻² M DMG + 5·10⁻⁷ M Cu (II) + 1·5·10⁻⁷ M Pb (II) (pH 8.5) | SQW CSV | – | SS, water | [106] |
| 8HXQ    | In situ | Sn (II) | 2·10⁻⁶  | 0.1 M NaAc (pH 6) + 8HXQ | SQW | + | Tooth paste, pharmaceutical preparations | [107] |
| HEPES   | In situ | U (VI) | 1·10⁻⁹ | 0.02 M HClO₄ (pH 4) + 2·10⁻⁵ M HEPES | SQW CSV | + | Food stuffs, fertilizers, cement | [108] |
| TMAC    | In situ | Al (III), Mg (II) | 5·10⁻¹¹ (Al); 4·10⁻¹⁰ (Mg) | 0.01 M KNO₃ (pH 5.0) + 0.02 M TMAC | SQW ASV | + | Food stuffs, fertilizers, cement | [109] |
| DFO     | In situ | Al (III) | 2·10⁻⁷ | 0.05 M amm. buff. (pH 8.3–8.9) + (10⁻⁸–10⁻⁵) M DFO, THMP, DHP | DP ASV | – | Natural waters, biological liquids | [110] |
| DDTACD  | Ex situ | Au (III) | 8·3·10⁻⁸ | 0.1 M NaCl + 0.01 M NaAc (pH 4) | SQW CSV | – | Geological samples | [111] |
| 8MQN    | Ex situ | Ag (I)  | 2·7·10⁻¹¹ | 0.1 M NaAc (pH 4.3) (accumulation), 0.1 M HNO₃ + 0.05 M KBr (sweep) | LS ASV | – | Sea waters, rice | [112] |
| PAN     | Ex situ | Cd (II) | 5·10⁻¹⁰ | 0.1 M NaH₂PO₄ | LS ASV | – | Model solution | [113] |
| ARS     | In situ | Cu (II) | 1·10⁻⁶ | 0.1 M NaH₂PO₄ + 0.1 M ARS | CV | – | BGD | [114] |
| Alizarin| Ex situ | Cu (II) | 1·10⁻⁴ | 0.5 M Na₂SO₄ (pH 4) | CV | – | BGD | [115] |
| BPD     | In situ | Fe (II) | 10⁻⁷ | 0.025 M KCl + 1 g L⁻¹ BPD | DP AVA | + | Soils | [116] |
| Dithizone| Ex situ | Hg (II) | 5·10⁻¹⁰ | 0.1 M KJ (pH 2) | LS ASV | – | Sea water | [117] |
| MAA     | Ex situ | Hg (II) | 4·10⁻² | 0.1 M HNO₃ | LS ASV | – | BGD | [118] |
| BPD     | Ex situ | Pb (II) | 1·10⁻⁷ | 0.1 M NaAc (pH 4.5) | LS ASV | + | Model solutions | [119] |
Humic acids Ex situ Fe(II), Cu(II), Ni(II) 2.0·10⁻⁶ (Fe); 6.0·10⁻⁷ (Cu); 6.0·10⁻⁶ (Ni) 0.1 M KHPH (Fe, Cu); 0.1 M Na₂SO₄ (Ni) SQW ASV – BGD [120]

PCC Ex situ Ce(III) 2.0·10⁻¹⁰ 0.1 M NaOH DP ASV + SS, hair [121]
KF-222 Ex situ Hg(II) 10⁻¹² 0.01 M NaAc (pH 4) + 0.1 M NaClO₄ SQW ASV – Sea and waste waters, saliva [122–123]

CA Ex situ Hg(II) 2.5·10⁻⁸ 0.1 M H₂SO₄ + 0.01 M NaCl SQW ASV + Natural waters [124]

TCA Ex situ Cu(II) 2.10⁻⁹ 0.1 M B₃R (pH 4.5) DP ASV + Natural waters [125]

TCA Ex situ Pb(II), Cd(II) 2.10⁻⁸ (Cd); 8.10⁻⁹ (Pb) 0.1 M acet. buff. DP ASV + Natural waters [126]

Nafion Ex situ Pb(II) 5·10⁻⁹ 0.1 M NaCl+ 0.05 M HCl SQW ASV – Standard sample TMDA-52.2 [127]

Nafion Ex situ Sn(IV) 8·10⁻¹⁰ 0.01 M NaCl + HCl (pH 1.9) LS CSV – Hair [128]

Nafion Ex situ CH₃Hg⁺ 4.5·10⁻⁸ 0.01 M HClO₄ SQW AV + BGD [129]

Nafion Ex situ Fe(III), Fe(II) 10⁻⁹ (0.03–0.3) M HCl SQW DDV + Interstitial waters [130–131]

Nafion /Hg Ex situ Cd(II) 1·10⁻¹⁰ 0.01 M NaAc LS ASV + Blood [132]

Nafion /Hg Ex situ Cu(II) 1.6·10⁻⁶ 0.1 M HNO₃ SQW ASV + Beer [133]

Nafion /Hg Ex situ Cu(II) 1.5·10⁻⁸ 0.1 M acet. buff. (pH 3.5) DP ASV + Estuarial water [134]

Nafion /Hg Ex situ Pb(II) 2.10⁻⁷ 0.1 M TRIS + 0.6 M NaCl SQW ASV + BGD [135]

Nafion /Hg Ex situ Pb(II) 1·10⁻⁷ 0.02 M KNO₃ (pH 5) DP ASV + Model solution [136]

Nafion /Hg Ex situ Pb(II) 1.2·10⁻⁹ 0.1 M NaAc (pH 4.6) + 85.7 mM Hg (II) SQW ASV – Simulated saliva [137]

Nafion /Hg Ex situ/ in situ Pb(II), Cd(II) 2·10⁻⁹ M (Cd); 4·10⁻⁹ M (Pb) 0.1 M KNO₃ + 2 mM HNO₃ + 1·10⁻⁴ M Hg (II) SQW ASV – Waste water [138]

Nafion /Hg Ex situ/ in situ Pb(II), Cd(II) 3·10⁻¹¹ (Pb), 5·10⁻¹¹ (Cd) 0.1 M NaAc (pH 4.6) SQW ASV – BGD [139–140]

Nafion /Hg Ex situ Pb(II), Cd(II) 9·10⁻⁹ (Cd), 1·10⁻⁷ (Pb) 0.12 M NaAc (pH 7.7) SQW ASV + Sweet water [141]

Nafion /Hg Ex situ Pb(II), Cu(II) 2·10⁻⁸ (Pb), 6·10⁻⁸ (Cu) 0.1 M KNO₃ + 5 mM HNO₃ DP ASV – Service waters [142]

Nafion /Hg Ex situ Cd(II), Pb(II) 4.5·10⁻⁸(Cd); 4.8·10⁻⁸(Pb) 0.1 M NaAc (pH 4.5) + 9.41·10⁻⁵ M FA DP ASV + Model solutions of fulvic acids [143]

Nafion /Hg Ex situ Cu(II), Pb(II), Cd(II) 1.6·10⁻⁸ (Cu); 4.8·10⁻⁸ (Pb); 8.9·10⁻⁹ (Cd) 0.1 M NaAc (pH 4.5) SQW ASV + Food stuffs [144]

Nafion /Hg – Cu Ex situ Pb(II) 4·10⁻¹⁰ 5 mM HNO₃ + 0.1 M KNO₃ SQW ASV + Natural waters [145]

Nafion /Bi Ex situ/ in situ Pb(II), Cd(II) 4.8·10⁻⁸ 0.1 M NaAc (pH 4.5) + 400 µg L⁻¹ Bi (III) SQW ASV – Model solutions of SAS [146]

Nafion /Bi Ex situ/ in situ Pb(II), Zn(II) 5·10⁻¹⁰ (Pb); 9·10⁻¹⁰ (Cd); 6·10⁻⁹ (Zn) 0.1 M acet. buff. SQW ASV – Tap water, urine, wine [147]
Table 1 (continued)

| Modifier | Manner | Analyte | Detection limit (M) | Supporting electrolyte | Sweep mode | Purge | Sample | Reference |
|----------|--------|---------|---------------------|-----------------------|------------|-------|--------|-----------|
| Naflon + HgCl₂ | Ex situ | Pb (II), Cu (II) | 5.8 × 10⁻⁹ (Pb); 5 × 10⁻⁸ (Cu) | 0.1 M citric acid + 0.03 M Na₂HPO₄ + 0.1 M KCl | LS ASV | – | Sea water | [148] |
| Naflon + KF-222 (1); Naflon + terpene (2) | Ex situ | Hg (II); Fe (II) | 3.8 × 10⁻⁹ (Hg); 2.5 × 10⁻⁷ Fe (II) | 0.025 M H₂SO₄ + 0.1 M NaCl (Hg); 0.1 M sulphate buffer (pH 3) (Fe) | SQW ASV | – | BGD | [149] |
| Naflon + Na-DDC (1); Naflon + 18C6 (2) | Ex situ | Pb (II), Cu (II), Cd (II), Hg (II) | 1 × 10⁻⁸ (Hg) (1); 1 × 10⁻⁹ (Cu, Pb, Cd) (2) | 0.1 M KNO₃ (pH 2.0) (1); 0.1 M NaAc (2) | DP ASV | + | BGD | [150] |
| Naflon + tobramycin | Ex situ | Cu (II) | 5 × 10⁻¹⁰ | Acet. buff. (pH 4.6) | DP ASV | – | Water samples, analytical salts | [151] |
| Naflon + BPD/Hg | Ex situ | Pb (II) | 5 × 10⁻¹⁰ | 0.07 M phosphate buffer (pH 4) | SQW ASV | – | Drinking water | [152] |
| Naflon + DAB /Hg | Ex situ | Se (IV) | 6 × 10⁻⁹ | 0.1 M NaClO₄ | SQW CSV | – | Natural waters | [153] |
| Naflon + 8HXQ /Hg | Ex situ | Te (IV) | 1.6 × 10⁻⁹ | 0.1 M NaClO₄ (pH 2.5) + 0.01 M EDTA NH₄Cl buffer (pH 9) | SQW CSV | + | BGD | [154] |
| Nontronite /naflon /Hg | Ex situ | Cu (II) | 10⁻⁷ | 0.01 M KNO₃ | SQW ASV | + | Natural waters | [156] |
| Tosflex | Ex situ | Cu (II) | 9.4 × 10⁻⁶ | 0.5 M NaCl + 0.1 M NaAc (pH 5) | LS ASV | + | BGD | [157] |
| Tosflex | Ex situ | Hg (II) | 2 × 10⁻¹⁰ | 0.5 M NaCl + 0.01 M HCl | DP ASV | + | Natural waters | [158–159] |
| Tosflex /Hg | Ex situ | Bi (II) | 3 × 10⁻⁹ | 0.5 M KCl (pH 1.4) | SQW ASV | + | Waters | [160] |
| Tosflex /Hg | Ex situ | Ti (III) | 5 × 10⁻¹⁰ | 0.5 M KCl (pH 5.6) | SQW ASV | – | Model solutions | [161] |
| Tosflex /Hg | Ex situ | Zn (II) | 1.5 × 10⁻⁹ | 0.02 M H₂SO₄ | SQW ASV | + | Model solutions | [162] |
| Tosflex + DAB /Hg | Ex situ | Se (IV) | 1.3 × 10⁻⁹ | 0.1 M KCl | SQW CSV | + | Sea and sweet natural waters | [163] |
| Tosflex + 8HXQ /Hg | Ex situ | Te (IV) | 1.6 × 10⁻⁹ | 0.1 M KCl (pH 3) | SQW CSV | + | Model solutions | [164] |
| PPG | Ex situ | Sb (III) | 4.1 × 10⁻¹⁰ | 0.04 M NaAc (pH 5.5) (accumulation); 1 M HCl (sweep) | DP ASV | + | Sea water, hair | [165] |
| PPD | Ex situ | Hg (II) | 1 × 10⁻¹⁰ | 0.5 M NaCl + 0.01 M HCl | DP ASV | + | Interstitial waters | [166] |
| PP + PDDT | Ex situ | Cu (II) | 1 × 10⁻⁶ | 0.1 M NaAc | CV | – | Model solution | [167] |
| PMR | Ex situ | Hg (II) | 4.4 × 10⁻¹¹ | B-R buff. (pH 2.56) | LS ASV | – | Like water | [168] |
| CA | Ex situ | Pb (II), Cd (II) | 2 × 10⁻⁷ | 0.1 M NaAc | DP ASV | + | Model solution | [169–170] |
| Nontronite/CA | Ex situ | Cu (II) | 2.7 × 10⁻⁸ | amm. buff. (pH 10) | SQW ASV | – | Natural waters | [171] |
| OxPPh or Morin hydrate | Ex situ | Sn (II, IV), Sb (III) | 5 × 10⁻⁸ (Sn); 5 × 10⁻⁸ (Sb) | 0.5 M HCl + 1.5 M NaCl | LS ASV | – | Natural waters | [172–173] |
| Method       | Substrate                | pH        | Buffer        | Supporting Electrolyte | Description        | Reference |
|--------------|--------------------------|-----------|---------------|------------------------|--------------------|-----------|
| PVP + KF222  | Ex situ                  |           |               |                        | DP ASV – BGD       | [176]     |
| PVP /Hg      | Ex situ                  |           |               |                        | SQW ASV – Subsoil waters | [177]     |
| PVP /Hg      | Ex situ                  |           |               |                        | SQW ASV – Subsoil waters | [178]     |
| CA/Hg        | Ex situ                  |           |               |                        | DP ASV + Model solutions | [179]     |
| PP /Hg       | Ex situ                  |           |               |                        | SQW ASV + BGD      | [180]     |
| PESA /Hg     | Ex situ / in situ        |           |               |                        | SQW ASV – Model solutions of SAS | [181] |
| PSSF /Hg     | Ex situ                  |           |               |                        | SQW ASV – Natural waters | [182-184] |
| PSSF /Hg     | Ex situ                  |           |               |                        | SQW ASV + Model solutions | [185]     |
| CNT          | In situ                  |           |               |                        | LS CSV + BGD      | [186]     |
| CNT          | Ex situ                  |           |               |                        | DP ASV – Lake water | [187]     |
| CNT          | Ex situ                  |           |               |                        | DP ASV – Lake water | [188]     |
| CNT + Nafion | Ex situ                  |           |               |                        | DP ASV – Water samples | [189]     |
| GCM-Au/MWCNT | Ex situ                  |           |               |                        | DP ASV – BGD      | [190]     |

*CAA Chloramline acid, 8HMQ 8-hydroxyquinoline, DMG dimethylglyoxime, RSH 8-mercapto-carboxylic acid, EDA ethylenediamine, 18C6 18-crown-6-ether, CHD 1,2-cyclohexanedione dioxime, PVP poly(4-vinylpyridine), CAA chloramine acid, CF cupferon, TEA triethanolamine, DTPA diethylene triamine pentacetic acid, TMAC tetramethylammonium chloride, DFO diferrinoxamine, DDTC/DACD 8,9,17,18-dibenzo-1,7-dioxo-10,13,16-triazacyclooctadecane, 8MQN 8-mercaptoquinoline, PAN polyacrylonitrile, ARS alizarin red S, BPD 2,2'-bipyridyl, PCC pyrocatechol, KF-222 Cryptofix-222, MAE 8-mercaptoacetic acid, CA calix[6][arene], TCA p-tert-butylthiophen-4carboxylate, DDC diethyldithiocarbamate (e.g., Na, Zn), DAB 3,3'-diaminobenzidine, PPG polypyrrolol, HEPES N-(2-hydroxyethyl)piperazine-N'-3-propane sulfonic acid, PDDT pyridyl-5,6-diphenyl-1,2,4-triazine, PMR polymethyl-red, CA cellulose acetate, OxPPh oxidized phenylphthalein, EDTA ethylenediaminedimercaptotetraacetic acid, PDDS poly(3-A'-diami-no-2,2',5',2"-terthiophen), PESA polyester sulfonic acid, PSSF poly(styrene sulfonate), PLL-PSS poly-4,4'-bipyridyl-5,6-diphenyl-1,2,4-triazine, PMR polymethyl-red, CA cellulose acetate, OxPPh oxidized phenylphthalein, EDTA ethylenediaminedimercaptotetraacetic acid, PDDS poly(3-A'-diami-no-2,2',5',2"-terthiophen), PESA polyester sulfonic acid, PSSF poly(styrene sulfonate), PLL-PSS poly-4,4'-bipyridyl-5,6-diphenyl-1,2,4-triazine, PMR polymethyl-red.|

*Ammonium buffer, ascorbic acid, TRAP tetraphenylammonium perchlorate, SDS sodium dodecyl sulfate, PIPES piperazine-N,N'-bis(2-ethane sulfonic acid), CTAB cetyl trimethylammonium bromide, THIMP 3-hydroxy-2-methyl-4H-pyrane-4-one, DHP 2,3-dihydroxyxypyridine, KHPh potassium hydroxylate, acet. buffer, tetraethylammonium bromide, 8,9,17,18-dibenzo-1,7-dioxo-10,13,16-triazacyclooctadecane, 8MQN 8-mercaptoquinoline, PAN polyacrylonitrile, ARS alizarin red S, BPD 2,2'-bipyridyl, PCC pyrocatechol, KF-222 Cryptofix-222, MAE 8-mercaptoacetic acid, CA calix[6][arene], TCA p-tert-butylthiophen-4carboxylate, DDC diethyldithiocarbamate (e.g., Na, Zn), DAB 3,3'-diaminobenzidine, PPG polypyrrolol, HEPES N-(2-hydroxyethyl)piperazine-N'-3-propane sulfonic acid, PDDT pyridyl-5,6-diphenyl-1,2,4-triazine, PMR polymethyl-red, CA cellulose acetate, OxPPh oxidized phenylphthalein, EDTA ethylenediaminedimercaptotetraacetic acid, PDDS poly(3-A'-diami-no-2,2',5',2"-terthiophen), PESA polyester sulfonic acid, PSSF poly(styrene sulfonate), PLL-PSS poly-4,4'-bipyridyl-5,6-diphenyl-1,2,4-triazine, PMR polymethyl-red, CA cellulose acetate, OxPPh oxidized phenylphthalein, EDTA ethylenediaminedimercaptotetraacetic acid, PDDS poly(3-A'-diami-no-2,2',5',2"-terthiophen), PESA polyester sulfonic acid, PSSF poly(styrene sulfonate), PLL-PSS poly-4,4'-bipyridyl-5,6-diphenyl-1,2,4-triazine, PMR polymethyl-red.|

*LS Linear sweep, ASV anodic stripping voltammetry, SQW square wave, DP differential pulse, AC alternating current, CSV cathodic stripping voltammetry, CV cyclic voltammetry, AVA anodic voltammetry, DDV double differential voltammetry, MSWV multiple square wave voltammetry.|

*Supporting electrolyte, SS standard sample, SAS surface active substances.
groups were synthesized on GCE. The response selectivity is efficiently improved by the “guest–host” interaction. Properties of crown ethers acting as host molecules for ions of guest metals were used [77, 112, 108–109, 148–149, 176] for measurements of Au (III), Hg (II), Cu (II), Pb (II), and Cd (II) ions on electrodes modified by crown-ether adsorption and a nafion film with immobilized macrocycles.

One more method for improvement of the voltammetric selectivity is the use of electrodes with monolayers of organic molecules self-organized on the electrode surface [72, 193–194]. For example, ω-carboxylic acids with hydrocarbon chains of different lengths can arrange themselves to the Langmuir palisade on gold or mercury surfaces. While possessing discrimination properties, functionalized layers can change the transport of depolarizer particles to the electrode surface not only due to different charges, but also due to the hydrophobic effect.

The pioneering studies concerned with the use of nanotube-modified GCE include the research performed by a group of Taiwan investigators [187, 188]. Such electrodes provided sufficiently low detection limits for elements. However, the introduction of these electrodes to the analytical practice requires solving the problem of structural ordering in the nanotube layer which influences the reproducibility of measurement results.

A serious problem in the use of GCE is the degradation of the modified surface showing up as the displacement of the current peak potential of the determined element, the distortion of the peak shape, and the emergence of additional peaks [195]. To make the GCE surface reproducible, it is prepared and cleaned by a great variety of methods such as mechanical polishing [108], treatment with reagents [76], electrochemical treatment by polarization at high anode potentials [36, 186], and exposure to microwaves or ultrasound [29, 40, 131]. Mechanical polishing of the surface with abrasive diamond or Al₂O₃ powders or special polish cloths is in most common use. This surface treatment method is not only laborsome and time-consuming, but what is the worst does not guarantee that the surface properties will be reproducible. This problem was attacked by development of automatic devices for cleaning of the solid electrode surface [116], but they have been used on a narrow scale because of their complexity and high cost. The original approach has been used [190] to modify GC with glassy carbon spheres covered by nanoparticles of precious metals and multiwalled nanotubes.

**Carbon-paste electrodes**

In 1958, Adams described a new type of the carbon-paste electrode (CPE) for voltammetry. This electrode was
Table 2 Modified carbon paste electrodes

| Modifier | Manner | Analyte | Detection limit (M) | Supporting electrolyte | Sweep mode<sup>b</sup> | Purge | Sample | Reference |
|----------|--------|---------|---------------------|------------------------|-------------------------|-------|--------|-----------|
| Au_dano  | Ex situ| As (III)| 3·10<sup>-9</sup>  | 0.1 M HNO<sub>3</sub> | SQW ASV – | BGD, mineral water | [202–203] |
| Au       | Ex situ| As (III, V)| 4·10<sup>-8</sup> As (III); 7·10<sup>-9</sup> As (V) | 1 M HClO<sub>4</sub> + 0.2 M HCl + 5·10<sup>-9</sup> | LS ASV + | River water | [204] |
| Au_ductums | In situ| Au (III)| 1·10<sup>-6</sup>  | 0.2 M H<sub>2</sub>SO<sub>4</sub> | CVA – | Model mixtures | [205] |
| Au       | In situ| Hg (II)| 2·5·10<sup>-10</sup> | 0.1 M HNO<sub>3</sub> + 0.02 M KCl + 5·10<sup>-9</sup> | DP ASV – | Drinking water | [206] |
| Bi       | In situ| Zn (II), Pb (II), Cd (II)| 1.5·10<sup>-8</sup> (Pb)  | 0.1 M NaAc (pH 4.5) + 0.5 mg L<sup>-1</sup> Bi (III) | SQW ASV – | Model solutions | [207] |
| Bi       | Ex situ| Cd (II), Pb (II)| 9·10<sup>-9</sup> (Cd); 4·10<sup>-9</sup> (Pb) | 0.2 M acet. buff. (pH 4.25) | SQW ASV or DP ASV – | Tap, sea waters | [208–209] |
| Bi<sub>2</sub>O<sub>3</sub> or Bi | Ex situ| Zn (II), Pb (II), Cd (II)| 4·4·10<sup>-8</sup> (Cd); 2·4·10<sup>-8</sup> (Pb) | 0.1 M NaAc (pH 4.5) | DP ASV – | Waters | [210–211] |
| Hg       | In situ| Zn (II)| 1·3·10<sup>-7</sup>  | 0.1–0.2 M amm. buff. + 2·10<sup>-5</sup> M Hg(NO<sub>3</sub>)<sub>2</sub> | DP ASV – | Drinking water | [212] |
| Hg       | Ex situ| Cu (II), Pb (II), Cd (II)| 5·10<sup>-9</sup>  | Ammonium acetate buff. (pH 4.5) | DP ASV – | Fish muscles and water samples | [213] |
| Wax + Hg oxalate | Ex situ| Cu (II), Pb (II), Cd (II), Zn (II)| 3·10<sup>-9</sup> (Cd) | 0.1 M KCl or acet. buff. (pH 3.8) | DP ASV or LS + | Medicinal plants, tablets | [214] |
| Pt nanoparticles | Ex situ| Cu (II)| 3·9·10<sup>-9</sup> | 0.1 M acet. buff. (pH 5.9) | LS ASV – | Urine | [215] |
| DB18C6 (1), CuO (2) | Ex situ| Pb (II)| 2·10<sup>-9</sup> (1); 2·5·10<sup>-9</sup> (2) | 0.1 M NaCl + 10<sup>-3</sup> M 18C6 (1); 0.1 M NaCl (2) | DP ASV – | Soil, snow, air, waters | [216] |
| DB18C6 | Ex situ| Cu (II), Pb (II)| 9·5·10<sup>-9</sup> (Cu); 2·10<sup>-9</sup> (Pb) | 1 M NaAc (pH 5–6) | LS ASV – | Waste waters | [217] |
| Aza-crown compound | Ex situ| Ni (II), Co (II)| 4·10<sup>-8</sup> (Ni); 1·2·10<sup>-7</sup> (Co) | 0.1 M NaCl (accumulation); 0.1 M KOH (sweep) | DP ASV – | BGD | [218] |
| DB18C6 and its analogs | Ex situ| Au (III), Pt (IV), Pd (II)| 8·10<sup>-9</sup> (Au); 3·10<sup>-7</sup> (Pt); 2·10<sup>-9</sup> (Pd) | 0.1 M HCl | DP ASV – | SS of ore | [219] |
| B15C5 | Thiacrown compounds | Cu (II)| 8·10<sup>-7</sup> | Water-ethanol (40%) solutions | DP ASV – | Strong drinks | [220] |
| Thiacrown compounds | Cu (II)| 5·10<sup>-7</sup> | NaClO<sub>3</sub> (accumulation); 0.1 M NaAc (sweep) | DP ASV – | BGD | [221] |
| calix[4]arene | Cu (II)| 2·10<sup>-8</sup> | Acidified sample (accumulation); 0.1 M HCl (sweep) | DP ASV – | Tap water | [222] |
| a-CD & b-CD | Pb (II)| 6·3·10<sup>-7</sup> (Pb); 2·0·10<sup>-6</sup> (Cd); 1 M HClO<sub>4</sub> | ASV – | BGD | [223–] |
| Modifier | Manner | Analyte | Detection limit (M) | Supporting electrolyte | Sweep mode | Purge | Sample | Reference |
|----------|--------|---------|---------------------|-----------------------|------------|-------|--------|-----------|
| Zeolite  | Ex situ| Cu (II)| 1.5·10^{-8} | 0.05 M NaNO₃          | DP ASV     | +     | Dried tomoay, bakosel capsule | [225] |
| Silica   | Ex situ| Cu (II)| 2·10^{-9}  | 0.1 M NH₂OH           | LS ASV,    | –     | Subsoil, sea waters            | [227] |
| Silica   | Ex situ| Hg (II)| 2·10^{-9}  | Solution pH 4–7       | SQW ASV    | –     | Real Samples                  | [230] |
| Silicas  | Ex situ| Cu (II)| 3·10^{-9}  | 0.1 M HNO₃            | DP ASV     | –     | Tap water                      | [231] |
| Silicas  | AMT    | Hg (II)| 5·10^{-10}| Sample (pH 2) (accumulation); 0.05 M KNO₃ (sweep) | DP ASV     | –     | Natural waters                 | [232] |
| AMT (1); | Ex situ/ in situ | Cu (II); Ni (II) | 3.1·10^{-8} (Cu); 2·10^{-9} (Ni) | Ethanolic solution (accumulation); 0.1 M NH₄Cl + 2.5·10^{-3} M DMG (pH 9 for Ni) | DP ASV (1) | –     | Ethanol fuel samples            | [233] |
| AMT/    | thio- | groups | Ex situ | Cd (II) | 1·10^{-7} | 0.1 M phosphate buffer (pH 4) | DP ASV     | +     | Natural waters                  | [235] |
| DMG (2) | Ex situ | Hg (II) | (2.5–6.5)·10^{-8} | HNO₃ (pH 3.0) (accumulation); 0.01 M KNO₃ (sweep) | DP ASV     | –     | BGD, natural water             | [236] |
| ex situ | Pb (II); Hg (II) | 2·4·10^{-9} (Pb); 1.5·10^{-8} (Hg) | 0.2 M HNO₃ | SQW ASV | –     | BGD                            | [238] |
| Mercapto- | ex situ | Hg (II) | 1·10^{-6} | pH 1 (accumulation); 0.1 M HCl + 5% thiourea (sweep) | DP ASV     | –     | BGD                            | [239] |
| groups | CPA | ex situ | U (VI) | 1·10^{-7} | 0.05 M CH₃COONa (pH 5) (accumulation); 0.2 M HNO₃ (sweep) | DP ASV     | –     | BGD                            | [240] |
| Monsil  | Ex situ | Cd (II); Pb (II); Cu (II) | 8.9·10^{-8} (Cd); 4.8·10^{-8} (Pb); 1.6·10^{-7} (Cu) | 0.1 M NaClO₄ + 1.5 M HClO₄ (Hg, Ag, Pb); 0.1 M KCl + 1.0 M HCl (Cu) | CVA        | +     | BGD                            | [242] |
| ZrPH    | Ex situ | Cd (II) | 2·10^{-9} | 0.05 M B-R buff. (pH 3) (accumulation); 0.1 M citrate buff. (pH 3.5) (sweep) | DP ASV     | –     | Artificial synthetic samples   | [243] |
| Vemiculite | Ex situ | Cu (II) | 5·10^{-9} | 0.04 M B-R buff. (accumulation); 0.1 NaNO₃ + 0.02 M B-R buff. (sweep) | SQW ASV DP ASV | –     | SRM 1643b (SS)               | [244–245] |
| Vemiculite | Ex situ | Cu (II); Ag (I) | 1.9·10^{-5} (Ag); 3.1·10^{-6} (Cu) | 0.01 M NaClO₄ | DP ASV | –     | BGD                            | [246] |
| Vemiculite | Ex situ | Hg (II); Ag (I) | 5.7·10^{-8} (Hg); 6.3·10^{-8} (Ag) | B-R buff. – pH 7 (Hg), pH 6 (Ag) (accumulation); B-R buff. (pH 5) + 0.05 M NaNO₃ (sweep) | SQW ASV | –     | Model solutions                | [247] |
| Montmorillonite | Ex situ | Cu (II) | 4·10^{-8} | NaAc (pH 5.5) | DP ASV | –     | Model solutions                | [248] |
| Montmorillonite | Ex situ | Bi (III) | 1·10^{-10} | 0.1 M HCl | DP ASV | –     | Water, nikel metal            | [249] |
| Sample Type | Ex situ/In situ | Element | Concentration | Precipitation Solution | Assay | Source |
|-------------|-----------------|---------|---------------|------------------------|-------|--------|
| Montmorillonite | Ex situ | Hg (II) | 1·10^{-10} | 0.1 M tartaric acid | ASV | BGD [250] |
| | Ex situ | Hg (II) | 5·10^{-8} | 1 M KCl (pH 2) | DP ASV | Natural water [251] |
| | Ex situ | Fe (III) | 3·6·10^{-6} | 0.05 M KCl (pH 3.2) | DP CSV | BGD [252] |
| | Ex situ | Hg (II) | 5·10^{-10} | Sample (pH 2–5) (accumulation); 0.05 M KNO₃ (sweep) | ASV | Natural water [253] |
| TZT-HDTA-clay | Ex situ | Hg (II) | 5·10^{-10} | 0.1 M CH₃COONa (pH 6.8) | DP CSV | Model solutions [254] |
| Dowex CGC241 | Ex situ | Cu (II) | 6·25·10^{-5} | 0.01 M KNO₃ (accumulation); 0.1 M HCl (1 M KNO₃) (sweep) | DP ASV | Waste waters [255] |
| Dowex 50W-8X | Ex situ | Cu (II) | 1·10^{-7} | 0.1 M HCl (1 M KNO₃) (sweep) | LS ASV | River waters [256] |
| Amberlite IRS 718 | Ex situ | Cd (II) | 4·4·10^{-8} | 1 mM amm. buff. (accumulation); 0.1 M HCl (sweep) | CV | River waters [257] |
| Dyolite GT-73 | Ex situ | Hg (II); CH₃Hg⁺ (I) | 2·0·10^{-8} (Hg); 9·4·10^{-9} (CH₃Hg⁺) | 0.1 M HCl | DP ASV | Drinking water [258] |
| Ion-exchange resin | Ex situ | Cu (II); Pb (II); Hg (II) | 2·4·10^{-7} (Cu); 1·1·10^{-7} (Pb); 5·0·10^{-8} (Hg) | 0.1 M KNO₃ + 5·10^{-3} M CH₃COOH | LS ASV | Catalysts, precious metals [259] |
| Humic acids | Ex situ | Pd (II) | 9·4·10^{-8} | 0.1 M B-R buff. (pH 2.8) (accumulation); 1.0 M HCl (sweep) | DP ASV | SRM 2670 (SS), urine [260] |
| Humic acids | Ex situ | Pb (II); Cu (II); Hg (II) | 4·8·10^{-9} (Pb); 7·9·10^{-9} (Cu); 8·0·10^{-7} (Hg) | 0.1 M KNO₃ | DP ASV | Ores [261] |
| Humic acids + EDA | Ex situ | Au (III) | 5·10^{-8} | 0.35 M HNO₃ (accumulation); 0.8 M HCl (sweep) | DP ASV | River waters [262] |
| Humic acids/amides | Ex situ | Hg (I; II) | 5·10^{-8} | 0.1 M H₂SO₄ (accumulation); 0.5 M H₂SO₄ (sweep) | LS ASV | River waters [262] |
| Soils | Ex situ | Cu (II) | 1·2·10^{-5} | 0.04 M B-R buff. + 0.1 M KNO₃ | DP ASV | Model solutions [263] |
| HSF-Na | In situ | Ag (I) | 2·5·10^{-12} | 0.02 M NaAc + 8·3·10^{-5} M HSF-Na + 3 mM EDTA | DP ASV | Tap water [264] |
| TTCP | In situ | Ag (I) | 1·10^{-4} | 0.2 TBAP + 1·10^{-3} TTCP | CV | BGD [265] |
| BPG | In situ | Bi (III) | 5·10^{-10} | 0.3 M HCl + 2·0·10^{-5} M BPG | ASV | Waters, hair [266] |
| ARS | In situ | Cu (II) | 1·6·10^{-10} | 0.04 M B-R buff. (pH 4.56) + 3·6·10^{-5} M ARS + 1·6·10^{-3} M K₂S₂O₈ | SD CSV | Natural water, soil [267] |
| ARS | In situ | Zr (IV) | 1·10^{-10} | 0.1 M acetic acid + 0.08 M KHP (pH 4.8) + 4·10^{-6} M ARS | SD CSV | Ore samples [268] |
| ARS + CTAB | In situ | Ce (IV) | 6·10^{-10} | 0.1 M HAc-NaAc + 0.2 M KHP (pH 5) + 2·10^{-6} M ARS | SD CSV | Cast iron samples [269] |
| CTAB | In situ | Ti (IV); V (V); Mo (VI) | 2·0·10^{-9} (Ti); 1·4·10^{-9} (V); 4·2·10^{-10} (Mo) | 0.01 M oxalic acid + x mM CTAB; x=0.1 (Ti); 0.25 (V); 0.75 (Mo) | DP ASV | Rock, fuel, steel [270–271] |
| CTAB, Septonex | In situ | Os (IV); Pt (IV); Jr (IV) | 5·10^{-9} (Os); 1·10^{-6} (Pt, Jr) | 0.1 M acet. buff. + 0.15 M NaCl + 1·10^{-5} M CTAB or Septonex (pH 4.5–6) | DP CSV | Industrial waste water [272–273] |
| Modifier | Manner | Analyte | Detection limit (M) | Supporting electrolyte | Sweep mode | Purge | Sample | Reference |
|----------|--------|---------|-------------------|------------------------|-------------|-------|--------|-----------|
| EDTA | In situ | Fe (III) | $2 \times 10^{-7}$ | 0.01 M KCl +3$\times 10^{-8}$ M EDTA (pH 3.0) | DP CSV | + | River and tap waters | [274] |
| DAN | In situ | Se (IV) | $1.3 \times 10^{-7}$ | 0.1 M KCl (pH 2) + 1$\times 10^{-4}$ M DAN (accumulation); 0.1 M HNO3 + 0.1 M KNO3 (sweep) | LS CSV | + | Natural, waste waters | [275] |
| Thioridazine | In situ | Pd (II) | $4.7 \times 10^{-9}$ | 0.08 M HCl +75 mg L$^{-1}$ Thioridazine | DP ASV | + | Drinking water | [276] |
| Mo-GGPA, Mo-SA | In situ | Ge (III); Si (IV) | $0.17 \times 10^{-8}$ (Ge); $0.09 \times 10^{-8}$ (Si) | 0.1 M citrate buff. (pH 2.5) + Mo-GGPA (Mo-SA) | DP CSV | – | Semiconductors, refined waters | [277–279] |
| PEI | In situ | Ag (I); Hg (II); Cu (II); Pb (II); Cd (II) | $0.9 \times 10^{-6}$ (Ag); $1.1 \times 10^{-6}$ (Hg, Cu); $8.0 \times 10^{-7}$ (Pb); $8.4 \times 10^{-7}$ (Cd) | 0.1 M KCl (0.1 M KNO3) + 2% PEI (pH 3 for Pb, Cd and pH 2 for Cu) | LS ASV | – | Tap water | [280–283] |
| IDA | Ex situ | Pb (II) | 25.4 μg/kg | (pH 6) (accumulation); acet.-ammonium buff. (pH 3) (sweep) | DP ASV | – | SS of water | [284] |
| 8HXQ | Ex situ | Tl (I) | $4.9 \times 10^{-9}$ | 0.01 M B-R buff. (pH 7.96) (accumulation); 0.2 M amm. buff. (pH 10) (sweep) | DP ASV | – | USEPA SS (WP 386) | [285] |
| 2-methyl-8HXQ | Ex situ | Cu (II) | $3.3 \times 10^{-9}$ | 0.05 M KSCN+0.05 M HNO3 (accumulation); 0.05 M KSCN + B-R buff. (sweep) | DP ASV | + | SS | [286] |
| 2,3- Dicyano-1,4-naphthoquinone | Ex situ | Ag (I) | $5 \times 10^{-8}$ | 0.1 M KNO3 | LS CSV | – | BGD | [287] |
| N-p-CPCHA | Ex situ | Cd (II) | $5.5 \times 10^{-9}$ | 0.3 M NH4Cl (pH 5) | DP ASV | – | Mineral and drinking waters | [288] |
| N-p-CPCHA | Ex situ | Pb (II) | $10^{-8} - 10^{-9}$ | 0.3 M CH3COONa (pH 6) | DP ASV | – | Drinking water | [289] |
| N-p-CPCHA | Ex situ | Co (II) | $3.3 \times 10^{-7}$ | 0.2 M CH3COONa (pH 6) | DP ASV | – | Vitamin B12 | [290] |
| Dithizone | Ex situ | Pb (II) | $8 \times 10^{-8}$ | Sample pH 12 (accumulation); 0.1 M HCl (sweep) | DP ASV | – | River water | [291] |
| Thiophydrazine | Ex situ | Cu (II) | $8 \times 10^{-9}$ | 0.1 M HCl | CV | – | River waters | [292] |
| BBTSC | Ex situ | Hg (II) | $4 \times 10^{-8}$ | 0.01 M KNO3 (accumulation); 0.1 M HCl (sweep) | SQW ASV | – | River waters | [293] |
| FTHD | Ex situ | Cd (II) | $5 \times 10^{-10}$ | B-R buff. (pH 4) | DP ASV | – | Model solutions | [294] |
| DPCO | Ex situ | Hg (II) | $5 \times 10^{-9}$ | 0.1 M KSCN (pH 2) | DP ASV | – | BGD | [295] |
| PTL derivative | Ex situ | Cu (I) | $5 \times 10^{-9}$ | 0.5 M CH3COONa (pH 6) | DP ASV | – | CO NBS 1643 | [296] |
| PTL + nafion | Ex situ | Fe (II) | $3 \times 10^{-8}$ | B-R buff. (pH 4.5) | DP CSV | – | Waters, SS of alloys | [297] |
| Diacetyldioxime | Ex situ | Pb (II); Cd (II) | $1 \times 10^{-8}$ (Pb); $4 \times 10^{-8}$ (Cd) | 0.1 M NaH2PO4 | DP ASV | – | Natural waters | [298] |
| PAN | Ex situ | Mn (II; VII) | $6.9 \times 10^{-9}$ | Phosphate-borate buffer (pH 8.7) | DP CSV | + | SS, sea water | [299] |
| Compound                  | Method         | Concentration |
|---------------------------|----------------|---------------|
| TDPTA                     | Ex situ        | Co (II)       |
|                          |                | 5.0 x 10^{-10}|
| Thiourea derivative      | Ex situ        | Ag (I)        |
|                          |                | 9.3 x 10^{-8}  |
| Chelate P                | Ex situ        | Cu (II)       |
|                          |                | 3 x 10^{-8}    |
| Cupron                    | Ex situ        | Cu (II)       |
|                          |                | 4.7 x 10^{-9}  |
| Glyoxal derivative       | Ex situ        | Hg (II); Ag (I)|
|                          |                | 1 x 10^{-9} Hg; 1 x 10^{-10} Ag |
| Phenylfluorone           | Ex situ        | Sb (III)      |
|                          |                | 8.2 x 10^{-9}  |
| PPDA                     | Ex situ        | Pb (II)       |
|                          |                | 1 x 10^{-9}    |
| Zn-DDC                   | Ex situ        | Hg (II)       |
|                          |                | 8 x 10^{-10}   |
| DMG + glycerol           | Ex situ        | Hg (II); Ni (II); Co (II); Pd (II) |
|                          |                | 1 x 10^{-8}    |
| TBP                      | Ex situ        | Zn (II); Ga (III) |
|                          |                | 2 x 10^{-6}    |
| Morin                    | Ex situ        | Zr (IV)       |
|                          |                | 1 x 10^{-8}    |
| Lichen                   | Ex situ        | Pb (II); Cu (II) |
|                          |                | 2 x 10^{-6} Pb |
| Lichen                   | Ex situ        | Pb (II)       |
|                          |                | 1 x 10^{-8}    |

For other abbreviations see Table 1.

* HSF-Na Sodium heptyl sulfonate, TTCP 2.5.8-trithio[9]-m-cyclophane, BPG brompyrogallol, DAN diaminonaphthalene, Mo-GGPA molybdenum-germanium heteropolyacid, Mo-SA molybdosilicic acid, PEI polyethylenimine, IDA iminodiacetate, DB18C6 dibenzo-18-crown-6, B15C5 benzo-15-crown-5, α-CD and β-CD α- and β-cyclodextrins, CPA carbamoyl phosphonic acid, AMT 2-aminothiazole, ZrPH zirconium phosphate, KHP potassium biphthalate, TZT-HDTA-clay 2-thiazoline-2-thiol-hexadecyltrimethylammonium-clay, N-p-CPCHA chlorophenyl cinnamohydroxamic acid, BBTSC benzylbisthiosemicarbazone, FTHD 1-furoylthioureas, DPCO diphenylcarbazone, PTL 1,10-phenanthroline, TDPTA 2.4.6-tri(3.5-dimethylpyrazolyl)-1.3.5-triazine, PPDA poly-n-phenylenediamine, TBP tri-n-butylphosphate

CVA Cathodic voltammetry, SD second derivative of voltammogram
conceived because despite good performance capabilities of mercury electrodes with respect to the adsorptive concentration of inorganic ions [196–198], they have some limitations at positive potential range, while many solid electrodes, which are operable over a wide interval of potentials, cannot selectively sorb the required component of the system. Adams’ idea was not overlooked by other investigators, and in 1964, Kuwana et al. performed research making the first contribution to the advancement of chemically modified carbon-paste electrodes, which are described in the reviews [199–201].

CPE is made of a homogenized paste of fine-dispersated coal and a water-immiscible binding liquid. Paraffin, petrolatum, or polychlorotrifluoroethylene oils, silicon fluid, dioctylphthalate, α-bromnaphthalene, tricresyl phosphate, and other materials can be used as the binding liquid. Two types of CPE pastes are available: dry (0.3–0.5 ml of the binding liquid per 1 g of the carbon powder) and wet (0.5–0.9 ml of the binding liquid per 1 g of the carbon powder) pastes. CPE can bear a high residual current caused by oxygen admixed to the paste with carbon powder particles. The residual current can be eliminated if the preheated carbon powder is mixed with wax, paraffin, or petrolatum oil in the nitrogen atmosphere or a lipophilic paste fluid (tricresyl phosphate) is added. The detection limit (LOD) of many inorganic and organic substances on CPE generally is 1·10−9 M. LOD is frequently decreased by activation of the electrode at high negative or positive potentials. The anode activation of the electrode is most efficient because interfering organic substances can be removed from the surface in this case. Sometimes the electrode is “shaken up” through the cyclic polarization between large negative and positive potentials.

When compared to other carbon-containing electrodes, CPE has a well-developed surface with a high adsorptivity of various substances. This property of CPE is used successfully in voltammetry for the modification and the adsorptive accumulation of substances to be measured. A modifier can be immobilized on CPE by several means including sorption, covalent binding, dissolution of a lipophilic modifier in the paste fluid, and direct mixing with the carbon paste. Direct mixing of a modifier with the paste is used most frequently. This modification procedure is very simple: a modifier is added to the paste in the dry form or diluted in a small amount of an organic solvent making the paste more homogeneous. Other methods of the modifier immobilization are used least often. The depolarizer is concentrated on the modified CPE surface through adsorption, chemical, or electrostatic interaction of the element to be measured and the modifier. CPE is modified by various organic substances such as aromatic oxycarboxylic acids, aromatic amine and diimine compounds, azocompounds, dyes, thiocompounds, triazines, and quinoline. In addition to the main hydrocarbon chain, molecules of these organic compounds include nitrogen, sulfur, and oxygen atoms, aromatic and aliphatic cycles containing unbound π-electrons, which can interact, on one hand, with the electrode surface and, on the other hand, with the analyte ensuring a high surface adsorption and strong binding to the substance to be determined.

Every so often, the analyte is concentrated on modified CPE with the circuit open using extraction, sorption, ion exchange, and formation of ion pairs. The measurement stage can be accomplished in another electrolyte. As the electrolyte is replaced, it is possible to optimize the measurement parameters (pH, the ionic force, and the potential) and eliminate the interference of other components of the test solution. Dependences of the current peak of the element to be determined on the concentration and the accumulation time on CPE are flattened-out curves because all functional groups of the modifier are saturated.

Table 2 gives examples of specific applications of modified CPE for the voltammetric determination of metal ions [202–312]. Sometimes CPE is modified by films of metals and their oxides [202–213, 215–216]. The electrode is modified most frequently by crown compounds [216–220], calixarenes [222], cyclodextrins [223–225], nonfunctionalized and functionalized silica [226–243], clay minerals (vermiculite and montmorillonite) [244–253], ion exchangers in the form of artificial resins [254–258, 258–262], natural humic acids and soils [259–263], organic [264–310], and bioactivecompounds [311–312].

Electrodes based on silica with self-organizing monolayers, for example, mesoporous silica modified by acetyl-amide of the phosphonic acid provide accumulation and measurement of Cu, Pb, Cd, and U [240–241]. CPE modified by biocatalysts, which are constituents of α- and β-cyclodextrins [223–225] or natural lichens [311–312] are used for measurement of ions of heavy metals.

Solid depolarizers can be studied after their direct infusion to CPE, which has been called the carbon-paste electroactive electrode (CPEE). The CPEE methodology was recognized to be also suitable for insoluble electroactive compounds. The first studies of metals, metal oxides, chalcogenides, salts, and other compounds by CPEE methodology were reviewed by Brainina et al. [313]. Electrochemical transformations taking place on CPEE provide information about the electrochemical activity of solid compounds, their stoichiometry, the oxidized state of elements, the morphology (the size and the shape of particles, crystal defects), the catalytic activity, etc. The CPEE methodology significantly increased the scope of electrochemistry to poorly conducting and insoluble solids. CPEE is used to analyze lead sulfides, magnetite, oxides of silver, tin, copper, and iron, bromides of rare-earth elements, nickel-containing compounds and other solids,
e.g., ceramics and classes [314–318]. A comprehensive review [319] is dedicated to the electrochemical analysis of solids.

**Conclusion**

Considering the above numerous examples of the electrochemical study and determination of various elements and compounds, it can be concluded that the modification of the surface of solid electrodes by a variety of methods and substances considerably extends the capabilities of voltammetry and ensures a highly sensitive and selective determination of a wide range of elements traces.

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