REVIEW

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Thick-film graphite electrodes in stripping voltammetry

Abstract Various types of modified thick-film graphite electrodes are reviewed. Two modification options are available: either *in situ* modified or beforehand. Electrodes modified *in situ* by various organic compounds were used for the determination of W, Mo, Cr, Ni and Mn by adsorptive stripping voltammetry. Insoluble inorganic salts, insoluble organic complexes or soluble compounds protected with Nafion were used for modification of the electrode surface beforehand. These pre-conditioned electrodes permit quantification of Pb, Cd, Cu, Zn, Sn, As and Hg ions. The detection limits of these elements were in the sub-µg/L range. The relative standard deviation did not exceed 10–15%. Measurements were made without deaeration of test solutions and normally without destroying small organic matter found in surface waters. A number of characteristics, such as the formation of well-shaped peaks and stable increments of peaks after standard additions, as well as elimination of the mechanical surface regeneration stage and metallic mercury or its soluble salts from the analytical procedure and a long shelf-life of the electrodes make them promising for electroanalysis and for application in portable field instruments.

Introduction

Although papers dedicated to electroanalysis and, in particular, stripping voltammetry have been abundant, this method has not acquired the significance in analytical chemistry which would adequately reflect its capabilities. In this review we shall address only one of its variants: stripping voltammetry with solid-state electrodes. The most common solid-state electrodes in stripping voltam-

metry are glassy carbon and impregnated graphite electrodes [1], thin-film screen-printed electrodes [2–4] and thick-film graphite electrodes (TFGE) [5–7].

The latter consist of a hardened paste containing graphite particles and a polymer. The paste is applied on polymer or ceramic substrates.

TFGEs give cyclic voltammograms for reduction-oxidation of Cc^+ (Cc-cobaltocene). These cyclic voltammograms have a sigmoidal shape similar to those obtained with the use of a platinum microdisk (d = 10 µm) electrode. This fact and the results of electron microscopic studies [5] suggested that TFGEs may be regarded as random array electrodes. The net effect of the microelectrode array feature is analytically advantageous, particularly in stripping voltammetry, for the following reasons:

- high scan rates with a superior Faradaic to charging current ratio;
- no need to remove oxygen from the solution.

The possibility to modify the molecular matrix of the electrode or its surface has led to an "outburst" of chemically modified electrodes. Carbon paste [8] or thick-film graphite [7] electrodes have been used as the basis of these electrodes.

Two different methods of electrode surface modification will be considered:

- modification *in situ* with mercury or an organic agent, which is selective to the ions being determined. This method known as adsorptive stripping voltammetry (AdSV) has been described using mercury drop [9], impregnated graphite [10] and thick-film graphite electrodes [6];
- the surface is modified beforehand by insoluble organic or inorganic compounds, and also by soluble compounds, which are protected with Nafion. A thick-film graphite electrode serves as the substrate. Some researchers [11] have tried to modify beforehand the surface of a glassy carbon electrode. But this operation is inconvenient since it is time- and laborintensive.

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Chemicals and instruments

Chemicals. Sodium diethyldithiocarbaminate (pro analysis) and DIN buffer 38406E 16 were used as received from Merck. Nafion 117 (purum) was taken from Fluka. The reagents – salts, acids and organic compounds of p.a. and s.p. grades – were available from Merck, Fluka Co. and various suppliers in Russia. Three-times distilled water was used for the preparation of solutions.

Instruments. A 693 VA processor with a 694 VA Stand, a 685 Dosimat and a 700 Dosino from Metrohm (Switzerland), and an IVA-stripping voltammetric analyzer from IVA (Ekaterinburg, Russia) were used. DP voltammograms were recorded using the VA processor and derivative voltammograms with linear scans were obtained on the IVA analyzer.

Organic compounds present in some waste waters were decomposed by UV-digestion (705 UV digester, Metrohm Ltd., Switzerland); in surface waters the metals were determined without sample preparation. The biological material (olive leaves) was treated by wet digestion with sulfuric acid and H_2O_2 using a Digesdahl digestion apparatus (Hach Company, Belgium). The food samples were decomposed in accordance with GOST 26929 "Sample Preparation. Mineralization for the Determination of Toxic Elements" [12] or in the above-mentioned apparatus.

Electrodes. A graphite rod was used as the auxiliary electrode. A silver-silver chloride electrode in a saturated KCl solution served as the reference electrode. TFGEs (IVA, Ekaterinburg, Russia) [6] were used as the substrate for thick-film modified graphite electrodes (TFMGEs). Three types of TFMGEs were manufactured [6, 7]:

- electrodes modified by insoluble inorganic salts,
- electrodes modified by an insoluble organic complex,
- electrodes modified by a soluble inorganic compound protected with Nafion.

The diversity of these electrodes is illustrated in Fig. 1.

Thick-film graphite electrodes modified *in situ*

TFGEs modified *in situ* by mercury [5, 6, 13]

The detection limit of metal ions determined with the use of TFGEs modified *in situ* by mercury is 1 µg/L for Cu, 0.5 µg/L for Pb, 0.3 µg/L for Cd, 2 µg/L for Zn, 5 µg/L for Sn, and 1 µg/L for Bi.

TFGE's plated with mercury *in situ* are less sensitive to surfactants than solid and mercury electrodes. They have been used successfully for blood analysis without chemical preparation of samples [13].

TFGE's plated with mercury *in situ* combine advantages of solid and mercury electrodes: they operate in a broad working range of potentials and their surface can be adequately reproduced. No intermetallic interaction usually takes place at these electrodes.

TFGEs modified *in situ* by organic reagents

Adsorption of organic compounds or their complexes on the electrode surface is used for accumulation and deter-

Fig. 1 TFGEs modified by different methods
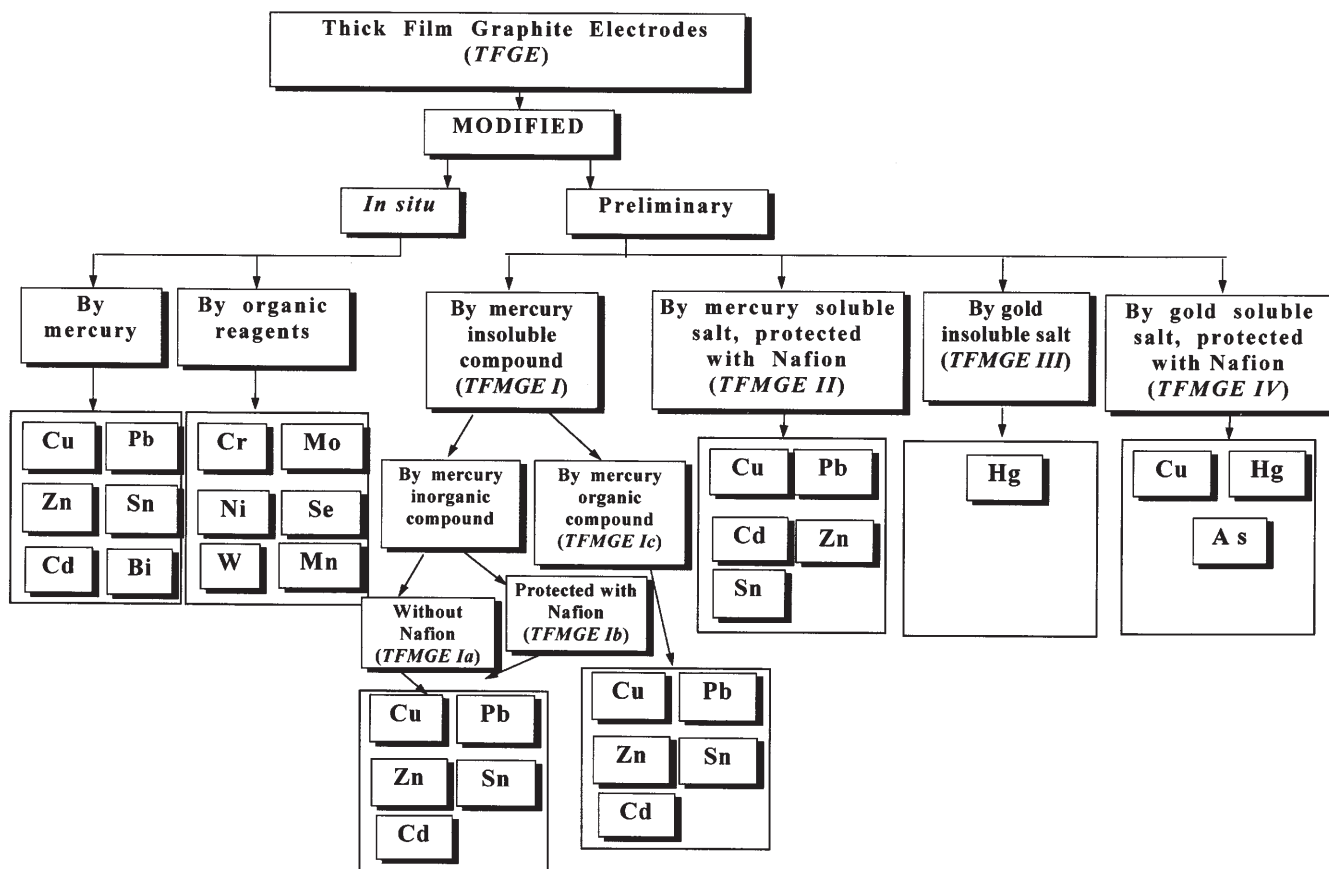
mination of some elements in adsorptive stripping voltammetry. Adsorptive processes of several types are used for accumulation and determination of elements in AdSV:

Type I: The element to be determined is electrochemically reduced or oxidized, which is accompanied by formation of an insoluble compound with an organic reagent on the electrode surface. These processes are used for determination of, e.g., W, Mo and Mn.

Type II: Formation of a complex in the solution and its adsorption. These processes underlie determination of Cr and Se.

Type III: Adsorption of a ligand followed by formation of a complex on the electrode surface. Most likely, this process cannot be realized in a pure form. Probably, a mixed mechanism of accumulation takes place: a surface active complex is formed both in the solution and on the electrode surface. Nickel is probably accumulated by this combined process.

In the following sections we shall consider these adsorptive processes in actual determinations of specific elements.
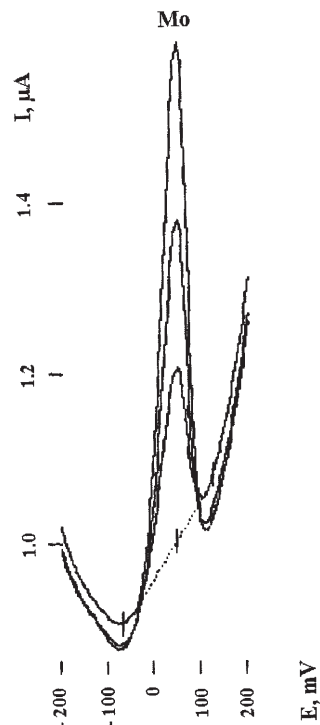
Determination of Mo

A comprehensive stripping study of Mo(VI) compounds with heterocycles (caproluctum, pyramidone and antipyrine) has been reported [14, 15]. An impregnated graphite electrode (ultra trace electrode of Metrohm) was used as the working electrode. Molybdenum is concentrated on the electrode surface after reduction to Mo(V) as an insoluble ternary complex in the presence of rhodanide ions and antipyrine (ANT). The following reaction scheme was proposed [14] to visualize the electrochemical concentration of Mo(VI) on the graphite electrode:

$$MoO_2^{2+} + e \rightarrow MoO_2^+ \tag{1}$$

$$MoO_2^+ + 3\ SCN^- + 3\ ANT + 2H^+ \rightarrow MoO(SCN)_3 ANT_3 \downarrow + H_2O \tag{2}$$
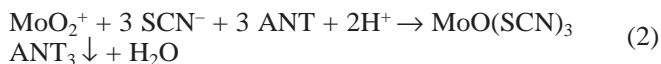
The peak of the anodic current of the compound deposited on the graphite electrode surface serves as the analytical signal (response). A disadvantage of the method [14, 15] is the necessity to clean the electrode surface mechanically each time a voltammogram has been recorded. In our study we have attempted to eliminate this drawback by introducing a method that would provide electrochemical regeneration of the electrode surface.

A TFGE was taken as the working electrode. DP-voltammograms of Mo are shown in Fig. 2. The optimal conditions for molybdenum determination with the TFGE are as follows: 0.5 M HCl (0.25 M H$_2$SO$_4$) + 0.03 M NH$_4$SCN + 0.05 M ANT at the preconcentration potential of –0.3 V. Under these optimal conditions a directly proportional dependence between the anodic current of the compound electrotransformation and the Mo(VI) concentration of the solution is observed in the range 0.2–25 μg/L, provided the preconcentration time is chosen correctly and passivation of the electrode is excluded. The detec-

Fig. 2 DP-voltammograms of Mo recorded using a TFGE modified *in situ* by organic reagents. Electrolyte: 0.5 M HCl + 0.05 M ANT + 0.03 M NH$_4$SCN + x μg/L Mo(IV), x = 2, 4, 6, E_{acc} = –0.3 V; t_{acc} = 90 s

tion limit for Mo(VI) is 0.1 μg/L (RSD = 20%) at the preconcentration time of 300 s.

The proposed method can be used for the determination of Mo(VI) in the presence of excess 1×10^5 Ni(II), 2×10^3 V(V), Zn(I), Cr(III); 1×10^3 Ti(IV); 6×10^2 Mn(II), Co(II), Zr(IV); 4×10^2 Sn(IV), 3×10^2 Pb(II); 2×10^2 W(VI), Fe(III); 1×10^2 Cu(II). When the concentration of Cu(II) in the sample is 100 times or more higher than the concentration of Mo(VI), Cu ions have to be bound with thiourea. The interfering effect of up to 2×10^5-fold excess Fe(III) is eliminated by reduction to Fe(II) with ascorbic acid. Organic compounds present in samples (e.g., natural waters) have an interfering effect. Therefore, they have to be decomposed by UV digestion. The high selectivity and the low detection limit of the method permit determination of Mo(VI) in various materials.

Determination of W

A selective and sensitive stripping method was proposed for determination of W(VI) using an ultra trace electrode [16]. Since W(VI) can form low-water soluble compounds such as ion associates with antipyrine (ANT), pyramidone (PYR) and its derivatives in the presence of rhodanide ions, W(VI) was concentrated on the electrode surface by electrochemical reduction of W(VI) and binding of the electrode reaction product W(V) into the low-soluble ternary compound WO(SCN)$_3$ANT$_4$ or WO(SCN)$_3$PYR$_3$ using ANT or PYR in addition to rhodanide. The scheme of W(VI) accumulation on the graphite electrode surface is similar to that given by Eqs. 1 and 2 for Mo.

Fig. 3 DP-voltammograms of W(VI) recorded with a TFGE modified *in situ* by organic reagents. Solution: 0.9 M H₂SO₄ + 0.066 M NH₄SCN + 0.0265 M ANT + x µg/L W(VI), (x = 2, 4, 6). E_{acc} = –0.5 V, t_{acc} = 60 s
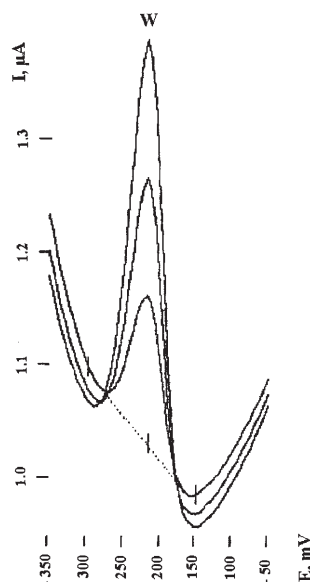
The applicability of these processes in stripping voltammetry with TFGEs is illustrated by DP voltammograms given in Fig. 3. The proposed method can be used for the determination of W(VI) in the presence of excess 5×10^4 Ni(II); 3×10^4 Cr(III); 2×10^4 Cd(II) and Mn(II); 5×10^3 Pb(II) and Zn(II); 2×10^3 Mn(VII) and Co(II); 1000 Cr(VI); 100 Mo(VI) and Cu(II); and 50 Fe(III). The interference due to higher concentrations of Cu(II) is eliminated with thiourea. Fe(III) is reduced with ascorbic acid to Fe(II), which does not interfere with tungsten determination at a 10^5-fold excess. The detection limit of W(VI) is 0.5 µg/L (RSD = 15%) at the preconcentration time of 180 s. The method permits determination of W(VI) in various materials.
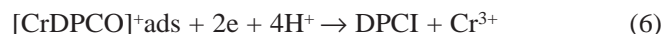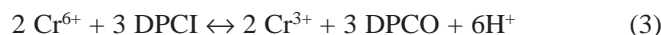
Determination of Mn

The TFGE surface was modified *in situ* at the accumulation potential of 0.5 V from the test solution containing diphenylcarbazone, the ammonia chloride buffer (pH 9.2) and different amounts of manganese (II) ions as described elsewhere [17]. At the above potential the following processes take place on the electrode: adsorption of the organic reagent, oxidation of manganese(II) and interaction of the oxidized form of manganese with diphenylcarbazone. The peak of manganese reduction is observed in the potential range –0.25 to 0 V. The directly proportional dependence between the value of the cathodic signal of manganese and the concentration of Mn(II) ions in the test solution is preserved over a wide range of concentrations: 10^{-9}–10^{-7} M. The detection limit of Mn(II) is 0.3 µg/L (RSD = 9%) at the accumulation time of 300 s.

A TFGE modified *in situ* by diphenylcarbazone is selective to manganese (II) ions and may be used in stripping analysis of different materials for the determination of manganese in the presence of excess 10^4 Cu(II), Ce(IV), Tl(I), Al(III); 10^5 Cl⁻, F⁻, NO₃⁻; 10^3 Zn(II),

Te(IV), Hg(II); 3×10^2 Bi(III), Cd(II); 2×10^2 As(III), As(V), Ga(III); 100 Cr(VI), V(V); 70 MnO₄⁻, 60 Fe(III), Fe(II), Sb(III); 50 Sn(II).

Determination of Cr

Cr(VI) undergoes a redox reaction with 1,5-diphenylcarbazide (DPCI) and forms a chromium (III) complex with diphenylcarbazone (DPCO) in 10–15 min at room temperature. This complex is adsorbed on the graphite electrode and can be stripped from the graphite surface during cathodic sweep [18]. The scheme of the processes that occur in the solution and on the electrode during determination of Cr(VI) can be given by the following equations:

$$2\ Cr^{6+} + 3\ DPCI \leftrightarrow 2\ Cr^{3+} + 3\ DPCO + 6H^+ \tag{3}$$

$$Cr^{3+} + DPCO \leftrightarrow [CrDPCO]^+ + 2H^+ \tag{4}$$

$$[CrDPCO]^+\ sol \rightarrow [CrDPCO]^+ads \tag{5}$$

$$[CrDPCO]^+ads + 2e + 4H^+ \rightarrow DPCI + Cr^{3+} \tag{6}$$

The directly proportional relationship between the maximum cathodic current of the chromium complex reduction (E_p = 0.1 V) and the concentration of chromium (VI) ions is preserved over a wide interval of concentrations: 1×10^{-9} to 1×10^{-6} M using a 0.15 M H₂SO₄ and 2×10^{-5} M diphenylcarbazide containing supporting electrolyte. The detection limit of Cr(VI) is 0.2 µg/L (RSD = 20%) at the accumulation time of 300 s and the accumulation potential of 0.35 V.

The determination of Cr(VI) is not hindered by 1000-fold excess Pb(II), Cd(II), Zn(II), Ni(II), Mn(II), Sb(III), S₂O₈²⁻; 1000-fold excess Hg(II), Co(II), Fe(III); 500-fold excess V(V), Mo(VI), Sn(II); 50-fold access S²⁻; 10-fold excess Mn(VII), J⁻; 5-fold excess Fe(II). Thanks to the adequate selectivity and the low detection limit, this method was used for determination of Cr(VI) in natural and waste waters.

Determination of Se

Se(IV) forms a complex with 2,3-diaminonaphthalene (DAN) (4,5-benzopiazselenol) in 5–15 min during heating in a water bath. The current of electrochemical transformations of this complex serves as the analytical signal of selenium. The processes of accumulation and determination of selenium (IV) have been described elsewhere [19].

$$Se(IV) + DAN = PIAZSELENOL \tag{7}$$

$$PIAZSELENOL\ ads + 4e + 4H^+ \rightarrow Di\text{-}imine + H_2Se \tag{8}$$
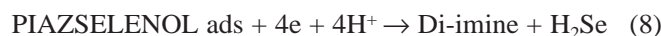
The maximum cathodic current of the adsorbed complex reduction is directly proportional to the Se(IV) concentration in the solution and serves as the analytical signal.

The directly proportional relationship between the maximum cathodic current of the complex reduction (E_p = 0.05 V) and the selenium (IV) concentration in a solution

containing 0.1 M HCl and 6.3×10^{-5} M DAN is observed in the concentration range 1.0 to 50 µg/L. The detection limit of selenium (IV) with a TFGE is 1.0 µg/L at the accumulation potential of – 0.2 V and the accumulation time of 300 s.

The determination of selenium (IV) is not hindered by Pb(II), Cd(II), Zn(II), Co(II), Sb(III), Mn(II) and Ni(II) in the ratio 10000:1; Ce(IV), As(III), Hg(II), Cr(III), Te(IV), Bi(III), Sn(II), Mo(VI) and Ti(IV) in the ratio 1000:1; Cu(II), Fe(II) and (III), and V in the ratio 100:1; Cr(VI) and Mn(VII) in the ratio 10:1. The analysis of solutions containing over 10 mg/L organic carbon causes certain difficulties, because destruction of organic matter is accompanied by oxidation of Se(IV) to Se(VI). The latter cannot be quantitatively transformed to Se(IV).

Determination of Ni

Ni(II) is accumulated on the surface of a TFGE as a complex with dimethylglyoxime [20] and can be determined using the reduction peak in the cathodic stripping voltammogram. The maximum cathodic current of nickel using a supporting electrolyte containing 0.1 M KCl and 2.5×10^{-4} M DMG is observed in the potential range -1.1 ± 0.05 V. The linear dependence of the analytical signal of nickel on the concentration of nickel (II) ions in the solution is preserved over the range of 0.5 to 60 µg/L. The detection limit of Ni is 0.05 µg/L (RSD = 20%) at the accumulation potential of –0.75 V and the accumulation time of 300 s.

The determination of nickel is hindered by Zn(II), Cr(VI), Al(III) and MnO_4^- in the ratio $10^4:1$; Pb(II), Hg(II), Mn(II), Fe(II), Fe(III), and SCN^- in the ratio $10^3:1$. The largest interference comes from cobalt, cadmium and copper. The addition of pyridine as the masking reagent decreases the interfering effect of these elements [20]. Table 1 shows Me/nickel ratios that do not interfere with the determination of nickel. The interfering effect of organic compounds was found to occur at concentrations of organic carbon exceeding 10 mg/L. This interfering effect is obviated by additional electrochemical treatment of samples. This method of nickel determination with the help of TFGEs was used for analysis of various environmental materials and foodstuffs [20]. An advantage of the TFGE modified by an organic compound consists in complete elimination of mercury from the analytical procedure.

Table 1 Metal/nickel ratios that do not interfere with the determination of nickel

Interfering ions	In the absence of pyridine	In the presence of pyridine
Co(II)	5:1	25:1
Cd(II)	30:1	100:1
Cu(II)	15:1	100:1

Thick-film graphite electrodes modified beforehand (TFGMEs)

The problem of elimination of mercury or its soluble salts from the analytical procedure can be solved with the help of electrodes modified beforehand. Inorganic compounds, such as Hg_2Cl_2, $Hg_2(SCN)_2$, $AuCl_3$, $Hg(NO_3)_2$, and organic compounds such as nitrosonaphthol, rhodamine B, xylenol orange tetrasodium salt, sodium diethyldithiocarbaminate (DDC), pyrrolidinedithiocarbamate (PDC) and antipyrine, were tested as modifiers of the electrode surface.

In some cases and, particularly, when soluble compounds were used, Nafion served as protection of the modifying layer.

Suitable reagents were selected considering the criteria of the electrode operation:

- high hydrogen overvoltage;
- low electrical resistance;
- stable increment in the analyte metal peak when a standard addition of metal ions is introduced;
- minimum pollution of the waste solution with mercury ions after the analysis.

The reagent concentration was chosen considering the following factors:

- absence of a visible residue on the electrode surface;
- the amount of mercury on the surface should be sufficient to obtain well-shaped voltammograms of analyte metals;
- stoichiometric correlation between the mercury salt and the organic reagent.

The above requirements were satisfied most by Hg_2Cl_2, DDC, PDC and soluble salts of mercury and gold.

The proposed electrodes can be divided into four types:

- electrodes modified by insoluble mercury compounds: both inorganic mercury compounds (TFMGE Ia, TFMGE Ib) and organic mercury compounds (TFMGE Ic);
- electrodes modified by soluble mercury salts protected with Nafion (TFMGE II);
- electrodes modified by insoluble gold salts (TFMGE III);
- electrodes modified by soluble gold salts protected with Nafion (TFMGE IV).

The main distinctive feature of electrodes modified by insoluble mercury compounds as compared to mercury electrodes or electrodes modified by mercury *in situ* is their ecological safety: the amount of mercury transferred to the solution during the analysis is several orders of magnitude lower.

Electrodes modified by an insoluble mercury compound (TFMGE I)

Electrodes of this type were prepared by consecutive application of reagents on the working surface of TFGEs.

Table 2 Results of Cd(II), Pb(II), Cu(II) and Zn(II) determination with a TFMGE Ia ($n = 3$)

Analyte	E_{acc}, V	E_p, V	Concentration, µg/L	
			Added	Found
Cd(II)	−1.1	−0.65	1	1.17 ± 0.06
Pb(II)	−1.1	−0.50	1	1.16 ± 0.13
Cu(II)	−1.1	−0.30	2	2.23 ± 0.11
Zn(II)	−1.3	−1.10	10	10.76 ± 1.24

TFGEs modified by an insoluble inorganic mercury compound without Nafion (TFMGE Ia)

The determination of Cu, Pb, Cd and Zn by anodic stripping voltammetry is possible using a TFMGE Ia. The solution of 0.1 M HCl served as the supporting electrolyte for determination of Cu, Pb, Cd and 0.1 M NaCl + 0.1 M NaAc for determination of Zn. The concentrations of Cu, Pb, Cd and Zn determined in recovery studies are given in Table 2.

A significant feature is the opportunity of determining tin and lead when they are present in the test solution simultaneously. In the supporting electrolyte containing 4.6 g/L NH_4Cl + 9.6 g/L $(NH_4)_2C_2O_4$ + 9.4 g/L (w = 0.3) HCl + 10 mg/L methylene blue [21] these elements give separate peaks at a TFMGE Ia (Fig. 4).

The detection limit of the elements at a TFGE modified by an inorganic mercury compound without Nafion is 1 µg/L (RSD = 7.6%) for Cd, 1.0 µg/L (RSD = 6.8%) for Pb,

2 µg/L (RSD = 5.2%) for Cu and 5 µg/L (RSD = 9.7%) for Sn at the accumulation time of 60 s. A considerable drawback of this electrode is that the mercury chloride precipitate is coarse and adheres poorly to the electrode surface. This complicates storage and transportation of electrodes and impairs reproducibility of measurement results.

TFGEs modified by an insoluble inorganic mercury compound protected with Nafion (TFMGE Ib)

The surface of electrodes modified by an insoluble inorganic mercury compound (calomel) protected with Nafion is finer and more uniform. As a consequence, results obtained with different electrodes of this type are reproduced well. Moreover, the metrological characteristics of electrodes which were kept in storage for a year were not inferior to those of freshly prepared electrodes. Responses of Cb, Pd, Cd, Zn and Sn recorded with a TFGE modified by an insoluble inorganic mercury compound protected with Nafion are similar to those depicted in Fig 4.

TFGEs modified by an insoluble organic mercury compound (TFMGE Ic)

The electrode surface is modified by insoluble complexes: mercury-diethyldithiocarbaminate (Hg-DDC) [7] or mercury pyrrolidinedithiocarbamate (Hg-PDC) [21]. Good results are obtained by these electrodes for the determination of Zn, Cd, Pb, and Sn. A linear calibration graph is

Fig. 4 DP-voltammograms of Sn and Pb recorded with a TFGE modified by an insoluble inorganic mercury compound without Nafion. Solution: 4.6 g/L NH_4Cl + 9.6 g/L $(NH_4)_2C_2O_4$ + 9.4 g/L (w = 0.3) HCl + 10 mg/L Methylene blue + x µg/L Sn(IV) + y µg/L Pb(II) (x = 10, 20, 30; y = 2, 4, 6). E_{acc} = −1.2 V, t_{acc} = 60 s
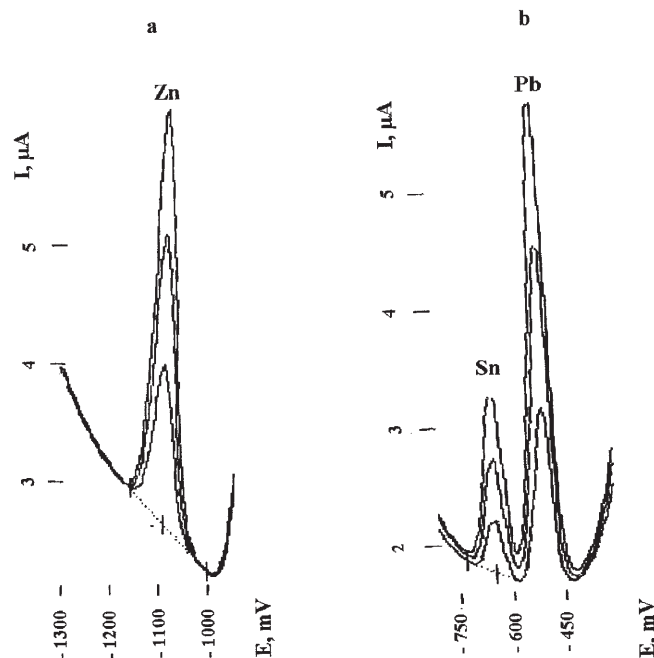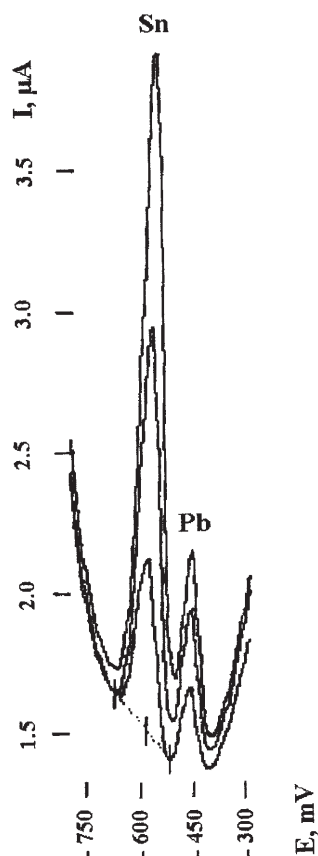

Fig. 5a, b DP-voltammograms of Zn (**a**) and Sn, Pb (**b**) recorded with a TFGE modified by an insoluble organic mercury compound. Solutions: DIN buffer (0.15 M KCl + 0.05 M NaAc) + 100 µg/L Ga(III + x µg/L Zn(II) (x = 10, 20, 30) (**a**) and 4.6 g/L NH_4Cl + 9.6 g/L $(NH_4)_2C_2O_4$ + 9.4 g/L (w = 0.3) HCl + 10 mg/L Methylene blue + y µg/L Sn(IV) + z µg/L Pb(II) (y = z = 10, 20, 30) (**b**). E_{acc} = −1.4 V (**a**) and −1.2 V (**b**), t_{acc} = 60 s

observed up to 2 mg/L Pb and 0.8 mg/L Cd. The detection limit found according to the 3σ-criterion is 0.5 µg/L for Cd and 0.5 µg/L for Pb at the accumulation time of 60 s. Up to 10 determinations can be made using one and the same electrode. Figure 5 shows DP-voltammograms of zinc, tin and lead registered with a TFMGE Ic.

When a TFMGE Ic is used, the dependence of the response on the concentration of metal ions in the solution is linear at 1–100 µg/L Zn and 1–100 µg/L Sn. The tin detection limit of the PDC-Hg-modified electrode is 0.9 µg/L at the accumulation time of 120 s. The standard deviation for 10 determinations made with the same electrode using 50 µg/L tin is 1.8%. The zinc detection limit of the TFMGE Ic is 1 µg/L at the accumulation time of 60 s. For Cu determination using these electrodes certain difficulties are caused by oxygen reduction in the potential range of Cu oxidation and a high stability of the Cu DDC complex as a consequence, Cu accumulates on the electrode

surface and difficulties are encountered in regenerative stripping of ion from the electrode surface.

TFGEs modified by a soluble mercury salt protected with Nafion (TFMGE II)

Figure 6 (a,b,c) shows DP-stripping-voltammograms of copper, lead, cadmium and tin recorded using a TFMGE II. It is seen that metal responses are well defined and standard additions of metal ions provide a proportional growth of their responses. At 60 s accumulation time this type of modified electrode ensures the following detection limits of metals: 2 µg/L Cu, 1 µg/L Pb, 1 µg/L Cd, 2 µg/L Zn, 1 µg/L Sn. As distinct from TFMGE I electrodes, a small quantity of Hg(II) passes to the test solution from TFMGE II electrodes and by the end of the measuring procedure the mercury (II) concentration of the solution becomes $\approx 10^{-4}$–10^{-3} g/L. Note also that the shelf-life of TFMGE II electrodes is short.

TFGEs modified by an insoluble organic gold salt (TFMGE III)

Au(III) and pyrrolidinedithiocarbamate (PDC) form strong, water-insoluble complexes which were used [22] to mod-

Fig. 6 a–c DP-voltammograms of copper (**a**), lead and cadmium (**b**), tin and lead (**c**) recorded with a TFGE modified by a soluble mercury salt protected with Nafion. Supporting electrolyte: 1 M HCl + x µg/L Cu(II) (x = 5, 10, 15) (**a**), 0.2 M HCl + y µg/L Pb(II) + z µg/L Cd(II) (y = 5, 10, 15; z = 2, 4, 6) (**b**), 1 M CH₃COONa + 0.2 M CH₃COOH + 0.6 M KCl + f µg/L Pb(II) + e µg/L Sn(II) (f = 2, 4, 6; e = 10, 20, 30) (**c**): E_{acc} = –0.9 V(**a**), –1.2 V (**b**), –1.4 V(**c**); t_{acc} = 60 s
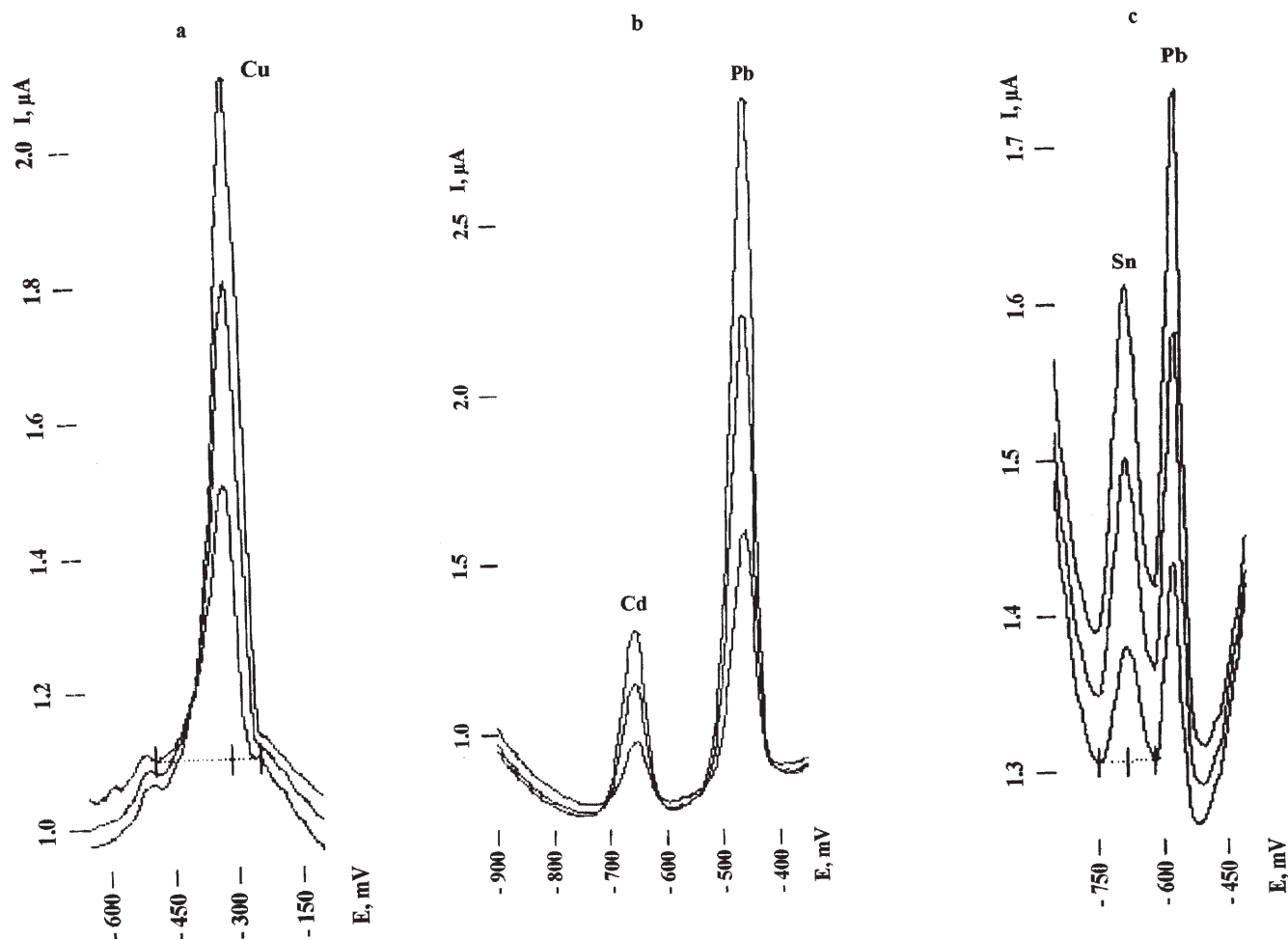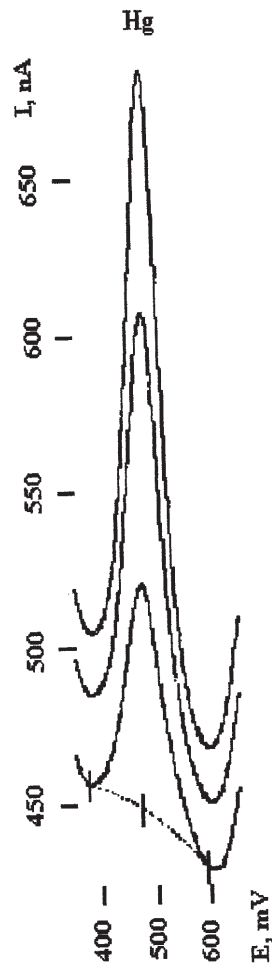
Fig. 7 DP-voltammograms of mercury recorded using a TFGE modified by an insoluble organic gold salt. Supporting electrolyte: 0.1 M H_2SO_4 + 0.004 M HCl + x µg/L Hg(II) (x = 1, 2, 3). E_{acc} = –1.2 V; t_{acc} = 120 s

ify the TFGE surface. These electrodes were used to record mercury responses, which were directly proportional to the concentration of mercury (II) ions in the solution (Fig. 7).

The concentration dependence of the mercury response is directly proportional over the range 0 µg/L to 10 µg/L at the accumulation time of 60 s, and 0 ng/L to 1000 ng/L at the accumulation time of 120 s. The mercury detection limit with the TFMGE III is 5 ng/L at the accumulation time of 300 s. Determination of mercury at the electrodes modified by an insoluble organic gold salt is not hindered by 1000-fold excess Al(III), Cd(II), Co(II), Ni(II), Mo(VI), Sn(IV), V(V), and Zn(II); 100-fold excess Bi(III), Cr(III), Pb(II), and Tl(I); 10-fold excess Cu(II), Fe(III), Se(IV) and Ag(I) interfere with determination of Hg at the concentration ratio Me:Hg = 1:1.

TFGEs modified with a soluble gold salt protected with Nafion (TFMGE IV)

Electrodes of type TFMGE IV were used to test solutions for the content of mercury (II), copper and arsenic ions (see Fig. 8 a,b,c). The detection limits of copper, arsenic and mercury are 1, 1 and 0.1 µg/L at the accumulation
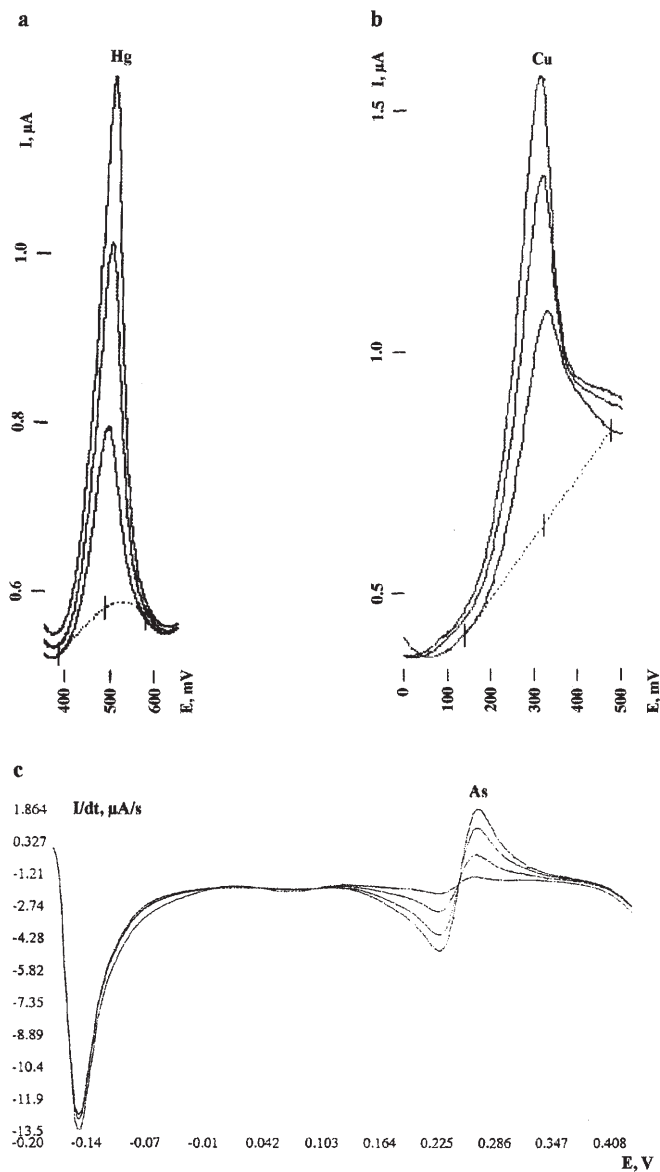
Fig. 8 a–c DP (**a, b**) and derivative (**c**) voltammograms of Hg (**a**), Cu (**b**) and As (**c**) recorded with a TFGE modified by a soluble gold salt protected with Nafion. Solutions: 0.1 M HCl + x µg/L Hg(II) (x = 5, 10, 15) (**a**) and 0.1 M HCl + y µg/L Cu(II) (y = 10, 20, 30) (**b**); 2 M HCl + z µg/L As(III) (z = 0, 5, 10, 15) (**c**). E_{acc} = –0.2 V (**a**), –0.5 V (**b**), and –1.0 V (**c**); t_{acc} = 60 s (**a, b**) and 15 s (**c**)

time of 60, 60 and 300 s respectively. A virtue of TFMGE III and TFMGE IV electrodes is the possibility of their repeated use.

The use of thick-film graphite electrodes in analysis

The results of analysis of natural and waste waters, foodstuffs and certified reference samples for the content of various elements, which were obtained in our laboratory using different types of TFGE are given in Tables 3 to 6. The validity of the developed methods for the determina-

Table 3 Results of tungsten and molybdenum determination in waters after UV digestion using a TFGE modified *in situ* by organic reagents

Element	Water source	Introduced, μg/L	Found, μg/L	RSD, %
	municipal waste	–	0	
		2.0	1.89 ± 0.12	6.1
W(VI)	sea	–	0	
		1.0	0.85 ± 0.04	4.5
		5.0	4.56 ± 0.44	9.9
	tap	–	0	
		0.5	0.50 ± 0.04	7.6
		100	96.2 ± 5.15	5.6
	tap	–	1.3 ± 0.1	8.3
Mo(VI)	Iset river	5.0	5.4 ± 0.2	2.8
	Shartash lake	50.0	48.9 ± 4.8	7.9
	municipal waste	10.0	10.1 ± 0.6	4.6
	industrial waste	–	4806 ± 464	7.8

Table 4 Results of W and Ni determination in reference materials after wet digestion using a TFGE modified *in situ* by organic reagents

Sample	Analyte	Stated contents	Found	n	RSD, %
Olive leaves (BCR N 62)	Ni	8 μg/L	7.8 ± 0.5 μg/L	3	2.5
	W	0.2 μg/L	0.19 ± 0.03 μg/L	3	14
Carbon steel Y 58	W	0.028%	0.027 ± 0.001%	5	5

Table 5 Analysis of foods for the content of heavy metals after digestion in accordance with GOST 26929-94 (Russia) with a TFGE modified by mercury insoluble inorganic compound protected with Nafion

Samples	Element	Found in the sample, mg/kg	Spike, mg/kg	Expected concentration, mg/kg	Recoveries, %
Noodles	Cu	2.50	2.50	5.00	98.0
	Pb	0.18	0.20	0.38	100.0
	Cd	0.04	0.04	0.08	100.0
	Zn	2.20	2.10	4.41	99.7
Fish	Cu	0.34	0.34	0.68	92.6
	Pb	0.03	0.03	0.06	100.0
	Cd	0.06	0.08	0.14	92.9
	Zn	4.80	4.50	9.30	118.3
Candies	Cu	9.40	9.40	18.80	90.4
	Pb	0.11	0.11	0.22	118.2
	Cd	0.01	0.01	0.02	100.0
	Zn	12.5	12.5	25.00	96.0

Table 6 Analysis of chemically decomposed canned food for the content of Pb and Sn with a TFGE, modified *in situ* by mercury, after wet digestion

Samples	Element	Found in the sample, mg/kg	Spike, mg/kg	Expected concentration, mg/kg	Recoveries, %
Orange juice with pulp	Sn	250.00	200.00	450.00	98.9
	Pb	0.27	0.20	0.47	112.8
Condensed milk	Sn	15.00	15.00	30.00	106.7
	Pb	0.50	0.50	1.00	95.0
Stewed beef	Sn	18.00	18.00	36.00	102.8
	Pb	1.50	1.50	3.00	103.3
Green peas	Sn	2.90	3.00	5.90	100.0
	Pb	0.31	0.30	0.61	98.4
Canned fish	Sn	0.00	20.00	20.00	102.5
	Pb	0.64	0.60	1.24	101.6

tion of various elements with the use of the TFGE was confirmed by the good results obtained on reference materials and the results of the recovery experiments. It is notable that in some cases the analysis of complicated materials, such as blood [13] or fruit juices [21], with the TFGE does not require sample pretreatment for decomposition of the organic matter.

Thus, all the aforementioned types of TFGEs are undoubtedly of interest for the purposes of electroanalytical chemistry. Basic characteristics of the modified TFGEs are compared in Table 7. As can be seen, each type of TFGEs has its advantages and drawbacks. For example, the mercury complex strongly adheres to the TFMGE Ic surface and therefore it is possible to make 8–10 determinations with a single electrode. In addition, this modified electrode can be stored for a long time. However, it is not advisable to use TFMGE 1c for the determination of copper (II) concentrations in solutions because of a strong Cu-DDC complex. TFMGE Ib, II, IV electrodes are preferable for the determination of copper. Electrodes of the last type do not contain mercury, but their shelf-life is short.

It is worth noting an interesting feature of these electrodes. Organic substances present in waters interfere less in heavy metal determination than mercury electrodes and glassy carbon electrodes. Therefore, it is possible to analyze different kinds of waters and some liquid food without sample preparation.

Thus, considering specific features of each type of TFGEs, it is possible to select an optimal electrode for a specific analytical application.

Conclusions

From the above data it can be concluded that TFMGEs hold the promise of solving certain problems of stripping voltammetry. TFGEs modified by mercury *in situ* can be used instead of conventional glassy carbon or impreg-

Table 7 Comparison of different types of TFGEs

Modification	Electrode type	Analytical elements and their detection limits, µg/L	Number of determinations with a single electrode	Concentration of mercury in the solution after analysis, g/L	Storage time
in situ	TFGE modified by mercury	Cu – 1 Pb – 0.5 Cd – 0.3 Zn – 2 Sn – 5 Bi – 1	1–5	2×10^{-2}	over 1 year
	TFGE modified by organic reagents	Mo – 0.1 W – 0.5 Mn – 0.3 Cr – 0.2 Ni – 0.05 Se – 1.0	1–10 depending on particular element	No	over 3 years
beforehand	TFMGE Ia	Cu – 2 Pb – 1.0 Zn – 2 Cd –1 Sn – 5	1–5	1×10^{-4}	1 week
	TFMGE Ib	Cu – 0.5 Pb – 0.2 Zn – 1 Cd – 0.2 Sn – 5	10–15	2×10^{-5}	1 year
	TFMGE Ic	Pb – 0.5 Cd – 0.5 Zn – 1 Sn – 0.9	8–10	5×10^{-5}	1 year
	TFMGE II	Cu – 2 Pb –1 Zn – 2 Cd –1 Sn – 1	1	3×10^{-4}–1×10^{-3}	1 week
	TFMGE III	Hg – 0.005	10–15	No	1 month
	TFMGE IV	Hg – 0.1 Cu – 1 As – 1	5–10	No	1–3 days

nated graphite electrodes in ASV of heavy metals. TFGEs modified by organic reagents *in situ* are useful in AdSV, providing mercury-free determination of Cr, W, Mo, Ni, Se, and Mn. TFGEs modified beforehand with insoluble organic or inorganic compounds make it possible to eliminate metallic mercury and its soluble salts from the ASV analysis of heavy metals. TFMGEs do not call for mechanical regeneration of the electrode surface.

These electrodes permit development of portable instruments for field applications. Electrodes for such instruments need to maintain good performance over a long period of time and the data of Table 7 confirm stability of the electrode characteristics over a sufficiently long period.

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