Mixed-Valent Ruthenium Oxide–Ruthenium Cyanide Inorganic Film on Glassy Carbon Electrodes as an Amperometric Sensor of Aliphatic Alcohols

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A mixed-valent ruthenium oxide–ruthenium cyanide film on glassy carbon (GC/mvRuO–RuCN) electrode exhibits excellent electrocatalytic activity toward oxidation of simple aliphatic alcohols and polyhydric compounds in acidic media. Electrochemical formation of the ruthenium oxide-based chemically modified electrode can be accomplished by potential cycling or potentiostatic control in diluted sulfuric acid solutions. The attractive electrooxidation capabilities of hydroxyl-containing compounds at this modified electrode are highlighted in terms of sensitivity, stability, and catalytic action. Remarkably, the molar response of the catalytic oxidation increases on increasing the chain length of aliphatic alcohols. For example, the molar response ratio between 1-butanol and methanol is 37 in 25 mM sulfuric acid. Chromatographic separations with electrochemical detection using the GC/mvRuO–RuCN modified electrode allow very simple quantitation of aliphatic alcohols in real samples with linear calibration plots over about 3 orders of magnitude. The detection limits for ethanol, 1-propanol, 1-butanol, and 1-pentanol are 4, 0.8, 1, and 2 nmol injected (S/N = 3), respectively.

Simple aliphatic alcohols (AAs) such as methanol, ethanol, propanol, and so on, which are of industrial, clinical, and forensic significance, exhibit a large overpotential toward oxidation at common carbon surfaces; thereby they are not suitable for quantitation with electrochemical (EC) detection in batch or flow injection analysis (FIA). Previous efforts toward enhancing the detection of aliphatic alcohols include the use of platinum and gold electrodes. However, in order to maintain a stable and reproducible response, a dedicated instrumentation for pulsed amperometric detection (PAD) has been developed by Johnson and co-workers.[1-3] The main drawback of these noble metal electrodes is the need for multistep potential waveforms, which incorporate cleaning and activation steps along with detection.

Chemically modified electrodes (CMEs)[4-7] are very promising for minimizing the overpotential effects, and some examples have

been proposed for the determination of simple alcohols. These include ruthenium dioxide carbon paste electrodes[8] and nickel hydroxide adsorbed on a glassy carbon surface.[9] Yet both these modified electrodes can only be exploited in strongly alkaline solutions where high-valent surface species are formed and electrooxidation of several scarcely electroactive compounds is allowed.[10,11]

In the last few years, there has been a growing interest in metal hexacyanometalate complexes that form an electroactive polymeric film on electrodes surfaces.[12-34] Since the pioneering work of Neff et al.[12] and Itaya et al.[13] on Prussian Blue [iron(III)–hexacyanoferrate(II)] modified electrodes, several polynuclear transition metal cyanides have been successfully applied in

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electrocatalysis and determination of organic and inorganic species.[7] We describe here the analytical application of a CME obtained by modifing a glassy carbon electrode with an electrochemically grown thin film of ruthenium oxide and ruthenium cyano bridges that exhibits strong electrocatalytic activity toward aliphatic alcohol oxidation, especially the primary alcohols. Early investigations on the electrocatalytic capabilities of these polymeric films focused on the oxidation of inorganic species such as As-(III)[16,31] and thiocyanate[21] and organic compounds such as methanol,[17,31] methionine,[26] insulin,[23,34] hydrazine and hydrazine derivates,[22] glutathione,[25] and sulfur-containing amino acids.[25,27]

This mixed-valent RuO−RuCN film enables the electrooxidation of aliphatic alcohols to proceed effectively in acidic media, so we have considered the application of this modified electrode for the electrocatalytic determination of ethanol in real samples following chromatographic separations using diluted sulphuric acid as mobile phase.

EXPERIMENTAL SECTION

Reagents and Materials. Methanol HPLC grade (E. Merck), ethanol and 1-butanol (Carlo Erba) sorbitol (Sigma Chemical Co.), 1-propanol, 2-propanol, 1-pentanol, 3-methyl-1-butanol (isopentanol), 1,2-ethanediol (ethylene glycol), 1,2,3-propanetriol (glycerol), 2,3-butanediol, tert-butyl alcohol, meso-erythrytol, xylitol, ruthenium(III) chloride hydrate, and potassium hexacyanoruthenate(II) hydrate (Aldrich Chemical Co.) were used as received. Stock solutions of aliphatic alcohols were prepared in pure water just prior to use. Other chemicals employed were of analytical grade (Aldrich) and were used without further purification. Deionized−double distilled water was used for preparing the solutions.

Instrumentation. Cyclic voltammetry was performed with an Amel Instruments Model System 5000, equipped with a Linseis $X-Y$ recorder, Model LY 18100. Electrochemical experiments were made at room temperature (20 ± 1 °C) with an EG&G Princeton Applied Research Model K0062 conventional single-compartment glass cell (10 mL). All potentials below are quoted with respect to a saturated calomel reference electrode (SCE) using a platinum wire as counter electrode. The glassy carbon disk electrode (3-mm diameter) used in cyclic voltammetry was purchased from Amel Model 493.

Amperometric detection in a flowing stream was performed using a PAR Model 400 electrochemical detector and a flow-through thin-layer electrochemical cell with a single glassy carbon working electrode (MP 1305), Ag/AgCl reference electrode, and stainless steel auxiliary electrode. The detector time constant was set at 1 s. The output signal was recorded by a $X-t$ Amel Model 868 recorder. The chromatographic system consisted of a Hewlett-Packard 1050 pump equipped with an on-line degasser system and a Rheodyne (Berkeley, CA) Model 7125 injector using a 10-μL sample loop. Chromatographic separations of aliphatic alcohols were effected at room temperature using a 10-μm macroporous styrene/divinylbenzene ion-exchange and reversed-phase column Polipore H 220 × 4.6 mm i.d. (Applied Biosystems, Inc.) with 25 mM H_2SO_4 as eluent and 0.4 mL·min^{-1} flow rate. Flow injection studies were done with a Varian 2510 pump using an injection loop of 50 μL and the thin-layer electrochemical detector interconnected by 0.30 mm i.d. Teflon tubing.

Electrode Modification Procedures. Prior to its modification, the glassy carbon (GC) electrode was polished with 0.05-μm α-alumina suspension on a microcloth polishing pad, washed
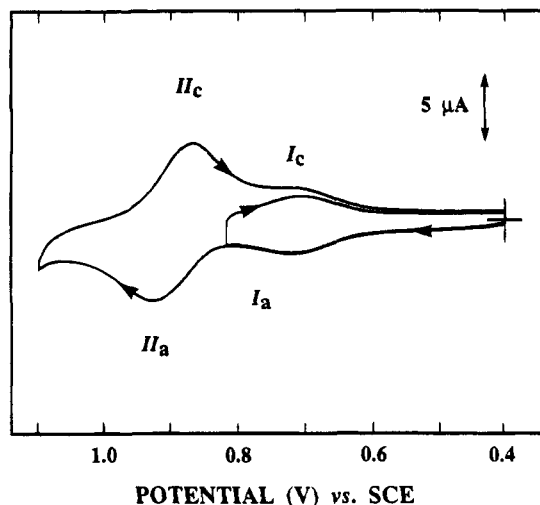

Figure 1. CVs of a mixed-valent RuO−RuCN electrode recorded at 5 mV·s^{-1}; surface coverage, $\Gamma = 5 \times 10^{-9}$ mol·cm^{-2}. The inorganic polymeric film was prepared by cycling the potential of a glassy carbon electrode (7.1 mm^2) 25 times between −0.20 and +1.10 V at 50 mV·s^{-1} in a 0.5 M KCl/HCl pH 2 solution. The modified electrode was washed and transferred to a 0.1 M Na_2SO_4/H_2SO_4 pH 2 solution to record the voltammograms shown. The arrows indicate the direction of scans.

with water, and sonicated for a few minutes in distilled water to remove trace of allumina particles. Two methods of electrochemical deposition were used. The first procedure is similar to that described by Cox and Kulesza[16,17,26] and involved the potential cycling of a clean glassy carbon disk electrode between −0.20 and +1.10 V at 50 mV·s^{-1} in freshly prepared solutions containing 1 mM Ru^{3+} and $Ru(CN)_6^{4-}$ in 0.5 M KCl/HCl at pH 2. No action was taken to remove oxygen from the solutions. Cyclic voltammograms were characteristic of surface deposition of electroactive species with increasing surface coverage with time. Usually, after 25 potential cycles the electrode was removed from the solution and rinsed with water; a dark violet film was visible on the electrode surface. The modified electrodes used in batch experiments were conditioned by cycling in 0.1 M Na_2SO_4 (adjusted to pH 2.0 with H_2SO_4) between −0.20 and +1.10 V at 50 mV·s^{-1} for several cycles until a steady-state voltammetric profile was observed. Coverage of the modified electrode was determined by measuring the charge under the voltammetric waves for the hexacyanoruthenate(II/III) redox process at about +0.72 V. Typical coverages employed were in the (1−5) × 10^{-9} mol·cm^{-2} range. In the second method, the mvRuO−RuCN films were prepared by potentiostatic deposition in freshly prepared Ru^{3+}/$Ru(CN)_6^{4-}$ solutions with an applied potential ranging from +1.00 to +1.10 V. Thus, GC electrodes potentiostated at +1.05 V for 5−30 min in a plating solution allow the formation of a stable, compact, and electroactive film. This procedure was always adopted for the GC electrode assembled in the flow cell. Amperometric measurements were made by applying the desired working potential and allowing the background current to decay to a steady-state value. Normally, this conditioning step took 10−20 min.

RESULTS AND DISCUSSION

Cyclic Voltammetry at a mvRuO−RuCN CME. Figure 1 shows cyclic voltammograms (CVs) recorded with a mixed-valent ruthenium oxide−ruthenium cyanide (mvRuO−RuCN) chemically
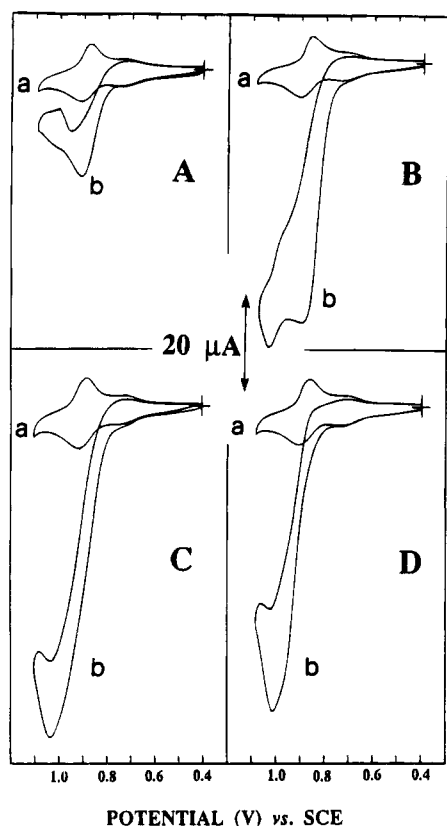
POTENTIAL (V) vs. SCE

Figure 2. Catalytic oxidation of (A) 100 mM methanol, (B) 43 mM ethanol, (C) 13 mM 1-butanol, and (D) 13 mM 1-pentanol (curves b) at a mvRuO—RuCN CME in CV. Curve a represents the CVs recorded in the blank. Experimental conditions: scan rate, 5 mV·s^{-1}; supporting electrolyte, 0.1 M Na$_2$SO$_4$/H$_2$SO$_4$ at pH 2.

modified electrode on glassy carbon at 5 mV·s^{-1} in the blank solution of 0.1 M sodium sulfate at pH 2 by sulfuric acid. As suggested by Cox and Kulesza et al., the mixed-valence ruthenium-based inorganic polymeric film is probably formed by ruthenium oxide stabilized with the residual cyano groups of the hexacyano complex.[17,20,26,31] At low scan rates (2−20 mV·s^{-1}), the film displays two well-defined sets of redox transitions, labeled as I$_a$/I$_c$, and II$_a$/II$_c$, respectively (see Figure 1). Previous voltammetric studies on the electrode modification with Ru(III) + Ru(CN)$_6^{4-}$ in acidic solutions have attributed the first process (I$_a$/I$_c$) at +0.72 V to the reversible behavior of the hexacyanoruthenate(III,II) in the polymeric film,[14,16,20] while the anodic peak observed at +0.93 V was assigned to the oxidation of ruthenium in the ruthenium oxide portion of the modified electrode,[16] probably from Ru(III) to Ru(IV). The loading of mv ruthenium oxide−hexacyanoruthenate film on GC, estimated by integration of the anodic and cathodic waves (I$_a$/I$_c$), gave an average charge value of 35 μC, corresponding approximately to 5 × 10^{-9} mol·cm^{-2} of polymeric film.

In Figure 2 are compared CVs of the GC/mvRuO−RuCN CME recorded at 5 mV·s^{-1} in the blank supporting electrolyte (curves a) and in the presence of 100 mM methanol, 43 mM ethanol, 13 mM 1-butanol, and 13 mM 1-pentanol, curves b. As can be seen, upon alcohol addition there is a marked increase in current in the anodic region corresponding to the second oxidation wave (II$_a$) of the modified electrode, and as would be expected for an electrocatalytic oxidation, the corresponding reduction wave of the modified electrode disappeared. Therefore, the specific catalytic activity of the mixed-valent ruthenium-based electrode is presumably related to the presence of a ruthenium oxy species

in the polymeric film. It is worthwhile to remark that the catalytic current in the presence of AAs did not reach a plateau at low scan rates either, indicating that the reaction rate is probably controlled by the mediated oxidation of substrate by the high-valent species of ruthenium (i.e., Ru(IV)) in the ruthenium oxide portion of the inorganic film.[31]

Surprisingly, the catalytic action is more effective on increasing the chain length of aliphatic alcohols (see Figure 2), the highest electrocatalytic response being observed with 1-butanol and 1-pentanol. The enhancement of response on increasing the number of aliphatic carbons of the AAs will be corroborated in flow injection experiments. Different interactions of single alcohols with the ruthenium-containing inorganic film rather than their steric hindrance may account for the slight variation in peak potential (+0.92 V for methanol, +0.85 and +1.05 V for ethanol, +1.03 V for 1-butanol, and +1.02 V for 1-pentanol) and the intensity of catalytic current. Note that aliphatic alcohols are not effectively oxidized at unmodified glassy carbon electrodes.

Although most previous applications of mv-Ru-based electrodes[16,17,21−23,25−27,31] have usually been performed in sodium or potassium buffered solutions at pH 2−3, modified electrodes prepared in 25 mM H$_2$SO$_4$ as supporting electrolyte, displayed a similar voltammetric profile at low scan rates with the reversible redox couple (I$_a$/I$_c$) at +0.76 V and the second oxidation peak (II$_a$) at +0.96 V. The fact that the presence of alkali ions[16,26,31] plus H$^+$ or H$^+$ alone in the supporting electrolyte does not impart significant changes in the voltammetric behavior is recognized as due to the non-size-selective structure of the mvRuO−RuCN film. Moreover, the catalytic action is also very active on polyhydric compounds, such as glycerol, 2,3-butandiol, erythritol, and to a lesser extent on ethylene glycol, as illustrated in the CVs of Figure 3. These experimental results demonstrate that the ruthenium-based electrode is particularly effective for the electrooxidation of mono- and polyhydric compounds regardless of the presence of alkali ions in the supporting electrolyte. Since our main objective entailed the application of this CME in liquid chromatography with EC detection of low molecular weight AAs, and considering that these organic compounds can be separated on a hydrogen form macroporous resin using pure water or diluted acidic mobile phases, sulfuric acid was preferred for their sensitive monitoring with amperometric detection.

Flow Injection Studies. Amperometric detection of aliphatic alcohols in flowing streams can greatly benefit from the electrocatalytic response. Thus, a conventional glassy carbon thin-layer electrochemical cell with a mixed-valent RuO−RuCN modified electrode was used.

The effect of flow rate on the Ru CME response for ethanol in FIA is shown in Figure 4. The flow injection peak area is strongly dependent upon flow rate with a sharp decrease in current on increasing the flow rate from 0.2 to 2.0 mL·min^{-1}. Apparently, the reason for decreased response may be due to the rate of the catalytic reaction between the modified electrode and analyte. In agreement with the voltammetric response, the catalytic oxidation is relatively slow to produce appreciable currents during fast passage of the sample plug, and mass transfer to the electrode surface has a negligible effect on the catalytic current. Depending on the experimental needs, relatively low flow rates (0.2−0.5 mL·min^{-1}) can be used in chromatographic separation in order to obtain lower detection limits and higher column efficiency,
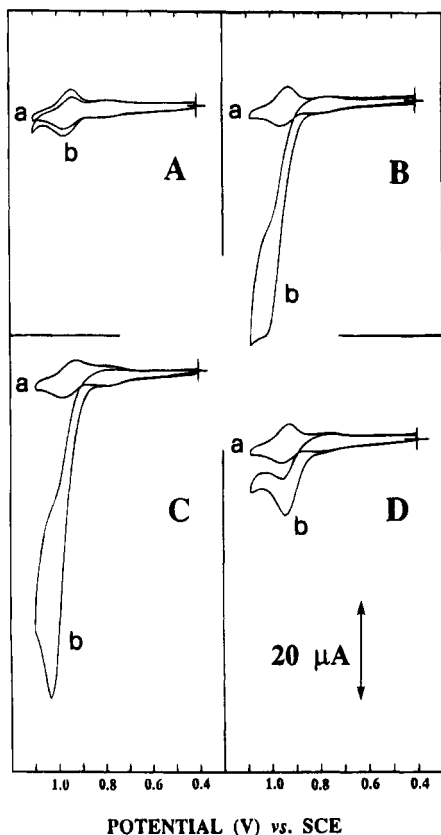
Figure 3. CVs at a mvRuO−RuCN CME showing the catalytic oxidation of polyhydric compounds: (A) 100 mM ethylene glycol; (B) 50 mM 2,3-butandiol; (C) 50 mM glycerol; (D) 50 mM erythritol in 25 mM H_2SO_4 (curves b). Constant-potential film deposition using a solution of 1 mM of $RuCl_3$ + 1 mM of $Ru(CN)_6^{4-}$ in sulfuric acid. Scan rate, 5 $mV \cdot s^{-1}$.
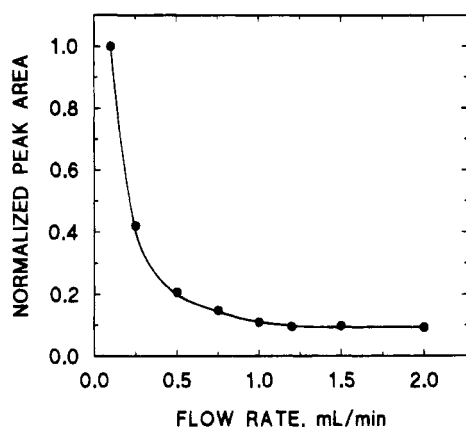
POTENTIAL (V) *vs.* SCE

Figure 4. Plot of normalized peak area vs flow rate at a GC/mvRuO−RuCN modified electrode. Experimental conditions: applied potential, +1.00 V vs Ag/AgCl at a thin-layer electrochemical cell; carrier electrolyte, 0.1 M Na_2SO_4/H_2SO_4 pH 2; concentration of ethanol injected, 100 mM; loop, 50 μL.

whereas high flow rates can be exploited in FIA for higher sample throughput.

Figure 5 shows the hydrodynamic voltammograms (HDVs) obtained under flow injection conditions for methanol, ethanol, and 1-propanol. Although the HDVs show a maximum response between +0.95 and +1.15 V, in accordance with the CV behavior, a constant potential in the range between +1.00 and +1.05 V was usually chosen both to maintain a low background current and to increase long-term stability of the modified electrode.
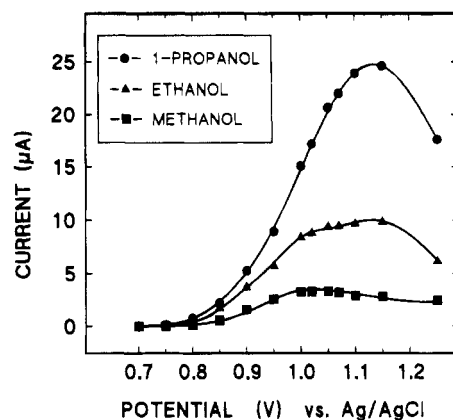

Figure 5. Hydrodynamic voltammograms of 100 mM methanol, 100 mM ethanol, and 95 mM 1-propanol in FIA at the mvRuO−RuCN CME. Flow rate, 0.5 $mL \cdot min^{-1}$. Other experimental conditions as those described in Figure 4.
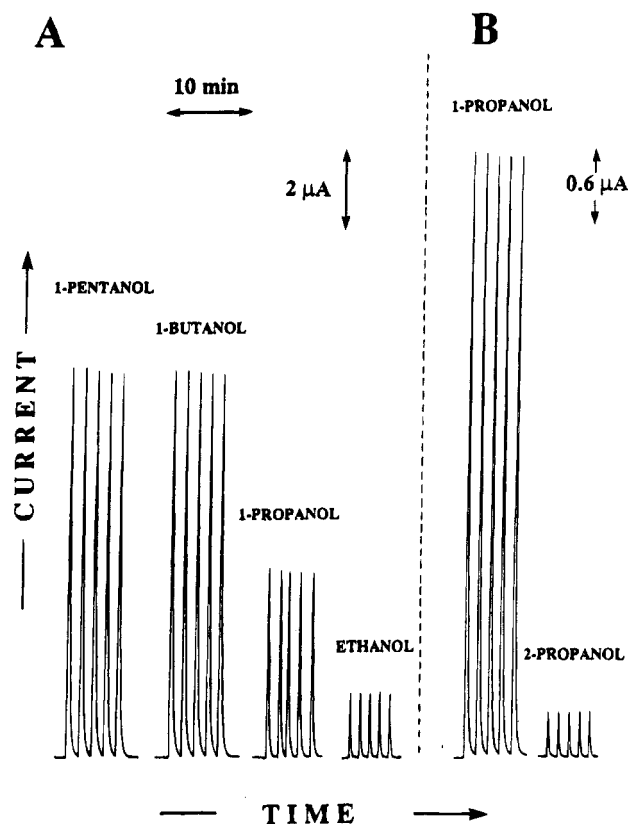

Figure 6. (A) Multiple flow injection peaks at GC/mvRuO−RuCN modified electrode of 10 mM ethanol, 10 mM 1-propanol, 10 mM 1-butanol, and 10 mM 1-pentanol. (B) Comparison between the molar response of 10 mM 1-propanol and 15 mM 2-propanol: Sample injected, 50 μL; electrolyte and carrier, 25 mM H_2SO_4 at 0.5 $mL \cdot min^{-1}$; applied potential, +1.05 V vs Ag/AgCl.

Performances of the mvRuO−RuCN CME. The following figures highlight the sensitivity, stability, and catalytic action of the GC/mvRuO−RuCN modified electrodes. Figure 6 illustrates the multiple flow injection peaks of ethanol, 1-propanol, 1-butanol, and 1-pentanol, 10 mM each, and 15 mM 2-propanol, using 25 mM H_2SO_4 as carrier electrolyte. Note that two different current scales are used in Figure 6A and B for reader convenience. Flow rate was 0.5 $mL \cdot min^{-1}$ and the applied potential, +1.05 V vs Ag/AgCl. One of the most interesting aspects of the AAs oxidation at the mvRuO−RuCN CME was that as the number of methylene groups on the homologous series increased, the molar response

Table 1. Molar and Mass Responses of Some Mono- and Polyhydric Compounds at the GC/mvRuO−RuCN Modified Electrode in FIA[a]
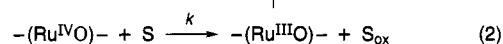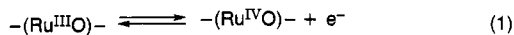
analyte	molar response (μA/mmol)	mass response (nA/mg)
methanol	0.51	15.9
ethanol	3.05	66.3
1-propanol	8.82	147.0
2-propanol	0.47	7.8
1-butanol	18.9	255.4
1-pentanol	19.0	215.9
3-methyl-1-butanol	16.9	192.0
ethylene glycol	0.80	12.9
2,3-butanediol	9.88	109.8
glycerol	8.20	89.1
meso-erythrytol	4.14	33.9
xylitol	1.55	10.2
sorbitol	0.89	4.9

[a] Sample, 50 μL injected at 10 mM concentration; E_{app} = +1.05 V, 0.5 mL·min^{-1} flow rate. The mvRuO−RuCN film was grown electrochemically on a glassy carbon electrode (area 7.1 mm^2) for 15 min at +1.05 V vs SCE in a solution containing 0.5 mM RuCl$_3$ + 0.5 mM Ru(CN)$_6^{4-}$ in 25 mM H$_2$SO$_4$.

also increased and reached a maximum with 1-butanol and 1-pentanol. In addition, primary alcohols were much more easily oxidized than secondary alcohols such as 2-propanol, whereas tertiary alcohols were not at all oxidized. These results are summarized in Table 1. Most likely a hydrogen abstraction from the carbon in the α position to the OH group is involved in the oxidation process. Thus, the catalytic oxidation mechanism is believed to proceed through the oxidation of the COH moiety to aldehyde and carboxyl groups. We understand that the inductive electronic effects of the aliphatic chains probably play an important role in the oxidation process, because steric hindrance of the hydroxy group does not explain the increase of response between 1-propanol and the more bulky 3-methyl-1-butanol (i.e., isopentanol).

In contrast with the noticeable decrease of response observed at a platinum working electrode[35,36] also with pulsed amperometric detection,[3] at the RuO$_2$-containing carbon paste electrode,[8] and at nickel oxy/hydroxide on glassy carbon electrode[9] (these last two CMEs used in alkaline solutions), where the molar response ratios between 1-butanol and methanol are 0.36, 0.22, and 0.8, respectively, in the case of the mvRuO−RuCN electrode, the ratio is 37.0 (see Table 2). These molar response ratios were evaluated in the linear portion of the calibration plots. The reason for this difference in reactivity is not clear at the present time. Unfortunately, AAs with longer aliphatic chains, which would be of interest in this work, are not sufficiently soluble in aqueous solutions.

However, some evidence for the involvement of the steric hindrance is also given by polyhydric compounds. Sorbitol, for instance, demonstrates a molar response of a magnitude comparable with that of methanol; therefore, the presence of additional hydroxy groups significantly affects the electrocatalytic process. The CV behavior of all the examined aliphatic alcohols, which are oxidized in the same potential window where the high-valent species of ruthenium oxide are formed, taken together with the fact that in flowing solutions the response decreases with increasing flow rate, is indicative of a redox process at a catalytically active surface in which the mechanism may be consistent with the following scheme:

$$-(\mathrm{Ru^{III}O})- \rightleftharpoons -(\mathrm{Ru^{IV}O})- + \mathrm{e}^- \qquad (1)$$

$$-(\mathrm{Ru^{IV}O})- + \mathrm{S} \xrightarrow{k} -(\mathrm{Ru^{III}O})- + \mathrm{S_{ox}} \qquad (2)$$

$$\mathrm{S_{ox}} \longrightarrow \mathrm{P} \qquad (3)$$

where $-(\mathrm{Ru^{III}O})-/-(\mathrm{Ru^{IV}O})-$ represents the immobilized redox couple on the electrode surface, presumably Ruthenium(III,IV) oxides, S and $\mathrm{S_{ox}}$ are, respectively, the aliphatic alcohol involved and the intermediate product, and P is the final product. Equation 2, e.g., the chemical oxidation reaction, represents the rate-determining step of the overall process.

The stability of coating was tested both in flowing stream operations or by measuring a decrease in the voltammetric currents during potential cycling of the modified electrode. For example, it was noted that when the mixed-valent Ru-based films were stored in sulfate solution at pH 2, the same voltammetric response was observed upon several days. The short-term stability of the mvRuO−RuCN CME in flow injection was investigated using 25 mM sulfuric acid as carrier electrolyte. A series of replicate injections of 10 mM 1-propanol yielded an average 5% decrease in electrode response over a 120-min period, corresponding to about 60 consecutive injections. One of the problems in the use of CMEs for flow-through systems is the gradual change in the mechanical integrity of the catalytic film. It is difficult to maintain a stable electrode structure, chemically or physically, for extended periods of time under constant applied potential. However, the periodical addition of standard solutions for calibration purposes will correct for any changes in the electrode sensitivity. Even with this slight decrease in response, the mvRuO−RuCN sensing electrode demonstrates appreciable stability in flow-through conditions. Under anodic polarization, the modified electrode provides efficient catalytic action for up to

Table 2. Molar Response Ratios of Some Aliphatic Alcohols: Amperometric Detection in Flow Injection Analysis

sensing electrode	detection potential (V vs Ag/AgCl)	flow rate[a] (mL/min)	carrier electrolyte	MRR[b] 1-butanol/ methanol	MRR[b] 1-butanol/ ethanol	MRR[b] glycerol/ methanol	ref
Pt	PAD[c]	0.8 (50)	50 mM HClO$_4$	0.36[d]	0.40[d]	1.95[d]	3
RuO$_2$ CPE[e]	+0.4	0.5 (20)	0.5 M NaOH	0.22[f]	0.58[f]	20.4[f]	8
Ni CMe[g]	+0.5	1.0 (10)	0.2 M NaOH	0.8[d]	1.03[d]	11.4[d]	9
mvRuO−RuCN CME	+1.05	0.5 (50)	25 mM H$_2$SO$_4$	37.0[h]	6.2[h]	16.1[h]	i

[a] Numbers in parentheses are microliters of sample injected. [b] Molar response ratio. [c] Pulsed amperometric detection: E_1 = +300 mV (detection); E_2 = +1400 mV (cleaning); E_3 = −400 mV (activation). [d] Based on the response to injection of 10 ppm solutions. [e] Ruthenium dioxiode-based carbon paste electrode. [f] Solutions injected, 100 mM. [g] Nickel oxy/hydroxide surface modified glassy carbon electrode. [h] Solutions injected, 10 mM. [i] This work.
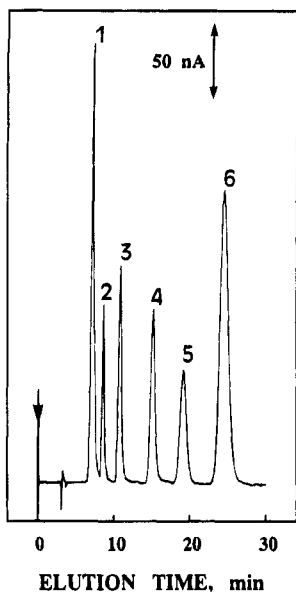
Figure 7. Liquid chromatographic separation with electrochemical detection of a mixture containing (1) 50 nmol of 2,3-butandiol, (2) 500 nmol of ethanol, (3) 100 nmol of 1-propanol, (4) 100 nmol of 1-butanol, (5) 100 nmol of 3-methyl-1-butanol, and (6) 400 nmol of 1-pentanol, at a mvRuO−RuCN CME: column, 10-μm Polipore H 220 × 4.6 mm i.d.; isocratic elution with 25 mM H$_2$SO$_4$ (room temperature); flow rate, 0.4 mL·min^{-1}; loop, 10 μL; thin-layer electrochemical cell with +1.05 V vs Ag/AgCl as applied potential.

2 days of operation time. Repetitive preparations of the ruthenium-based CME result in highly reproducible films in terms of catalytic response. In a series of five deposition trials, the modified electrodes tested in flow injection yielded 4.3 μA as the mean current value for the oxidation of 5 mM 1-butanol, with a range of 3.9−4.6 μA and a relative standard deviation of ±6%.

Liquid Chromatography with Electrochemical Detection of AAs. The most interesting features of the mvRuO−RuCN CMEs is the possibility of using them for amperometric monitoring of mono- and polyhydric compounds following chromatographic separations. Considering that the modified electrode enables the electrooxidation of simple AAs to proceed effectively in relatively dilute aqueous solutions of sulfuric acid, we used a stationary phase able to separate these compounds just in the same media without the presence of alkali ions.

A chromatographic separation with EC detection for a sample mixture containing 2,3-butanediol, ethanol, 1-propanol, 1-butanol, 3-methyl-1-butanol, and 1-pentanol is shown in Figure 7. Accordingly, the chromatogram was obtained using 25 mM H$_2$SO$_4$ as mobile phase with a Polipore H column. On the basis of the HDVs, a detector potential of +1.05 V was applied. As expected, the mvRuO−RuCN electrode was able to operate quite efficiently and had no difficulty in detecting simple AAs at low levels. Analytical data of simple AAs are summarized in Table 3. Limit of detections (LODs) evaluated under chromatographic conditions as the concentrations that yielded a signal of 3 times the background noise, were 15, 4, 0.8, 1, and 2 nmol injected, for methanol, ethanol, 1-propanol, 1-butanol, and 1-pentanol, respectively. The sensitivity of calibration plots for all the investigated compounds was constant over about 3 orders of magnitude.

The applicability of the mvRuO−RuCN CMEs to the analysis of real samples such as regular beer (A) and white and red wines

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Table 3. Quantitative Parameters of Aliphatic Alcohols in Liquid Chromatography with Electrochemical Detection at a GC/mvRuO−RuCN CME[a]

alcohol	capacity factor (k')	slope[b] (nA/mM)	linear range (mM)	LOD[c] (nmol)	r^b
2,3-butanediol	1.15	25.8	0.1−100	1	0.9992
methanol	1.42	1.2	1.5−200	15	0.9989
ethanol	1.65	9.1	0.4−200	4	0.9999
1-propanol	2.29	53.2	0.08−100	0.8	0.9996
1-butanol	3.56	41.8	0.1−100	1	0.9992
3-methyl-1-butanol	4.71	34.2	0.2−50	2	0.9989
1-pentanol	6.32	26.6	0.2−50	2	0.9991

^{a} Column, 10-μm Polipore H (220 × 4.6 mm i.d., 10-μm particle size) plus precolumn; mobile phase, 25 mM sulfuric acid; flow rate, 0.40 mL·min^{-1}; loop, 10 μL; dead time, 200 s; applied potential, +1.05 V vs Ag/AgCl. ^{b} Slope and correlation coefficient calculated by linear least-squares analysis (n = 6). ^{c} Limit of detection determined for a S/N = 3 from the lowest injected concentration; average noise, 12 nA.
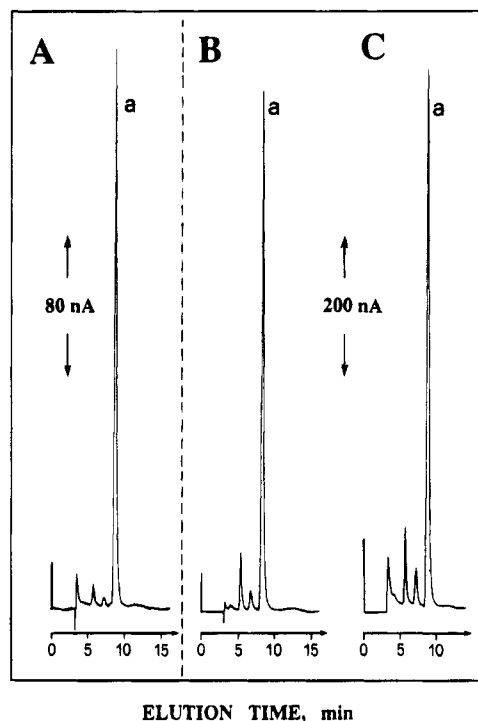

Figure 8. Chromatographic separation and detection of ethanol (a) in real samples: (A) beer, (B) white wine, and (C) red wine. Samples were diluted 1:100 with mobile phase. Conditions were the same as those described in Figure 7.

(B, C), respectively, is demonstrated in Figure 8. No sample preparation was required other than a 1:100 dilution with mobile phase. Within 10 min of chromatographic separation, ethanol is well-resolved and peak intensity allows convenient quantitation in these beverages. Ethanol sample values of 4.7% (A), 10.2% (B), and 11.1% (C) were evaluated from the resulting standard additions plots.

In conclusion, under the acidic conditions employed in this work and necessary for the optimum chromatographic retention and separation of simple AAs, the mvRuO−RuCN inorganic films are highly suitable as amperometric sensors with good sensitivity, providing considerable advantages over the RuO$_2$−carbon paste electrode[8] and Ni(OH)$_2$ adsorbed on GC[9] in detecting low levels of relatively long alkyl chain aliphatic alcohols. In flowing

solutions and under applied potential, it offers good time stability for practical applications. Stable modified electrodes are easy to prepare by simple potentiostatic deposition in diluted solutions of sulfuric acid. Work is in progress in our laboratory for extended applications of these CMEs and for a better understanding of the catalytic oxidation mechanism.