

Electrocatalysis and amperometric detection of alditols and sugars at a gold–nickel composite electrode in anion-exchange chromatography

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Abstract

A novel Au–Ni composite electrode prepared by cathodic precipitation/deposition of nickel hydroxide on the gold surface was characterised. The resulting composite electrode was evaluated as an amperometric sensor in flow injection analysis and anion-exchange chromatography for the quantitation of alditols and simple carbohydrates. Constant potential detection at +0.6 V vs Ag/AgCl and a pulsed detection mode were employed, and their applicability and usefulness discussed. The detection limits ($S/N = 3$) for all investigated compounds, in both modes of detection, ranged between 1.5 and 7.5 pmol injected. Linear dynamic ranges spanned over four and three orders of magnitude when the composite electrode was used in the DC or pulsed mode. The main advantage of the Au–Ni composite electrode is that detection selectivity can be tailored by the choice of the detection mode and by the polarisation potential. As an example, we show how to detect common carbohydrates in tea powder using the constant potential detection mode. ©1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Several transition metal electrodes (Au, Pt, Ni, Cu, Co, Ru etc.) exhibit a good degree of electroactivity toward sugars and are extensively used as electrode material in liquid chromatography with electrochemical detection (LC-EC) [1–5]. Perhaps one of the dominant themes in electrochemical research has been to regulate the structure and reactivity of the electrode/solution interface by derivatisation or chemical modification of the traditional electrode surface. Indeed, in the last decade there has been a growing interest in chemically modified electrodes (CMEs) and their potentially attractive applications as electrochem-

ical sensors. Metal species electrodeposited or entrapped in thin organic/inorganic layers appear as microparticles three-dimensionally dispersed in the polymer matrix with highly active electrode surface, suitable for efficient electrocatalysis [6–8]. In addition, CMEs containing surface-confined chemical functionalities have shown advantages over conventional bare electrode in terms of mechanical stability, improved selectivity and protection from potential fouling effects. Carbon paste electrodes, containing active metal particles and specific binding agents, are characterised by low residual current and good mechanical stability when used in flowing streams as amperometric sensors [9–12].

An alternative strategy in which the electrocatalytic performance may be improved is to employ underpotential deposition of heavy metals ad-atoms, or by co-deposition of transition metals on the elec-

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trode surface. Enhancement of the catalytic activities has been interpreted in terms of decreased electrode poisoning, stabilisation of the redox mediator or synergistic activity among different metal particles. In this respect, metal alloy or composite electrodes such as platinum–palladium, nickel–chromium, nickel–titanium and gold–copper have been proposed as sensing probes for the determination of several organic molecules in flowing streams [13–16].

Recently, a composite bimetallic electrode prepared by electroprecipitation of nickel hydroxide microparticles onto the surface of a bare gold electrode (Au–Ni) has been characterised by electrochemical and X-ray photoelectron spectroscopic techniques [17]. Although this electrode configuration does not possess any synergistic interaction between the gold substrate and nickel oxohydroxide species towards the electrocatalytic oxidation of glucose, the concomitant presence on the electrode surface of both Au(OH)_{ads} and NiOOH leads to an extended range of the potential window in which the Au–Ni electrode exhibits good catalytic activity. In addition, the absence of NiO on the electrode surface provides good conducting properties of the nickel-based film with the subsequent absence of any passivation or screening effects on the catalytic activity.

In the present study, the Au–Ni composite electrode is further characterised and used as a sensing electrode in flowing streams. The applicability and usefulness of constant-potential (DC) and pulsed amperometric detection (PAD) methods for the analysis of some common carbohydrates has been investigated.

2. Experimental

2.1. Reagents

Solutions were prepared from analytical reagent-grade chemicals without further purification. Twice distilled and de-ionized water was used throughout. Individual solutions of alditols and carbohydrates (Aldrich Chemie) were prepared daily in distilled water. Appropriate dilutions were made with 0.2 M NaOH and water for flow injection analysis (FIA) and liquid chromatography (LC), respectively. Unless otherwise specified, experiments were performed by using 0.2 M NaOH as background electrolyte. Dur-

ing cyclic voltammetry experiments, solutions were protected from oxygen by purging with high-purity nitrogen. All experiments were carried out at ambient temperature. Before injection onto the column, samples of tea (1.79 g) were treated in 100 ml of boiling distilled water and shaken vigorously for a few minutes. The suspension was filtered through filter paper, the resulting solution was diluted 1:200 with water and injected.

2.2. Apparatus

A Model 273 Princeton Applied Research (PAR EG&G) potentiostat/galvanostat was used for electrochemical measurements. Cyclic voltammetry (CV) was done in a three-electrode cell using the Au–Ni working electrode, a SCE (4 M KCl) reference electrode and a platinum foil counter electrode. The gold electrode used in CV (geometric area 0.125 cm²) was purchased from PAR. All current densities are quoted in terms of mA cm⁻² of apparent geometric area of the gold electrode.

Amperometric measurements in flowing streams were performed using a PAR Model 400 Electrochemical Detector and a flow-through thin-layer electrochemical cell consisting of the Au–Ni as working electrode, an Ag/AgCl (4 M KCl) reference electrode and a stainless steel counter electrode. The output signal was recorded by a Model Servogor 120 BBC recorder. Flow injection experiments were carried out by a Varian 2510 pump equipped with a Model 7125 Rheodyne injector using a 50 μ l sample loop. The mobile phase was purged from oxygen by an on-line degasser system (Hewlett Packard Series 1050).

Chromatographic separations were performed either by a CarboPac PA1 (Dionex) anion-exchange column (250 \times 4 mm i.d. with particle size 10 μ m) coupled with a CarboPac PA1 (50 \times 4 mm i.d.) guard column, or a CarboPac PA100 (Dionex) anion-exchange column (250 \times 4 mm i.d.) with particle size 8.5 μ m).

2.3. Electrode preparation

Prior to each electrode modification, traces of nickel species were removed from the gold surface by soaking the electrode in concentrated nitric acid (70%, w/w) for a few minutes. The electrode was then

polished with 0.05 μm α -alumina powder on a polishing micro-cloth and washed with water. The gold electrode was electrochemically conditioned in 0.2 M NaOH by cycling the potential between -0.25 V and $+0.6$ V vs. SCE (50 mV s^{-1}) for 20 cycles. Films of nickel hydroxide were deposited either by voltage cycling (50 mV s^{-1}) between 0.0 and -0.5 V vs. SCE or at constant potential of -0.3 or -0.4 V vs. SCE. The depositions were performed using non-de-aerated 50 mM $\text{Ni}(\text{NO}_3)_2$ solutions maintained at pH 7.5. Subsequently, the modified electrode (Au–Ni) was washed with water and conditioned by continuous CV, cycling the potential between -0.25 and 0.6 V for 35–40 min (about 140 cycles) at 100 mV s^{-1} in 0.2 M NaOH.

The surface concentration of nickel sites (Γ_{Ni}) was evaluated by integration of the cathodic wave centred at about $+0.35$ V corresponding to the $\text{Ni}^{\text{III}} \rightarrow \text{Ni}^{\text{II}}$ reduction process, assuming that all the nickel redox sites are electroactive on the voltammetric time scale. Unless otherwise specified, all experiments were performed with nickel surface loadings at the Au–Ni composite electrode of $5\text{--}7 \text{ nmol cm}^{-2}$.

3. Results and discussion

3.1. Voltammetry

Representative cyclic voltammograms at a bare gold electrode and at the Au–Ni electrode ($\Gamma_{\text{Ni}} \cong 6.2 \text{ nmol cm}^{-2}$) in 0.2 M NaOH are reported in Fig. 1. The voltammetric profile of the modified electrode (solid curve) seems to be the weighted sum of the electrochemical behaviour of bare gold and of nickel catalyst in alkaline medium. As can be seen, two redox transitions, Ia_1/Ic_1 , and Ia_2/Ic_2 , are present. While the Ia_1/Ic_1 process is related to gold oxide formation and subsequent reduction to Au^0 [18–20], the Ia_2/Ic_2 couple is due to the redox transition $\text{Ni}^{\text{II/III}}$ [21–23]. The loading of nickel and the number of potential cycles in alkaline solution affect the voltammetric behaviour of this last couple in terms of peak potential, separation and peak current. These findings may be explained by considering the occurrence of slow and continuous crystallographic $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations of the nickel film during pro-

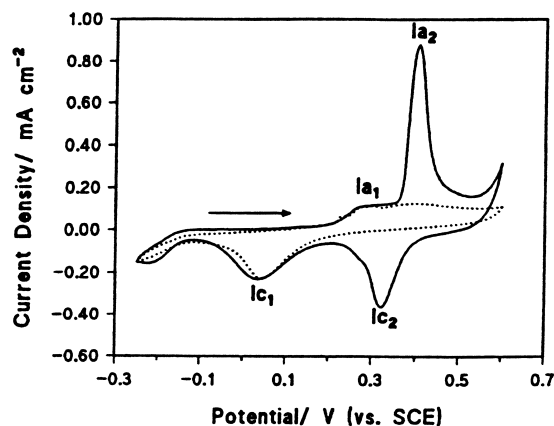


Fig. 1. Steady-state cyclic voltammograms (140th cycles) at a gold electrode (dashed curve) and the Au–Ni composite electrode ($\Gamma_{\text{Ni}} \cong 6 \text{ nmol cm}^{-2}$) in 0.2 M NaOH. Scan rate, 50 mV s^{-1} .

longed potential cycling [17,21–25]. Such crystallographic transformations do not seem to be complete, so that mixed allotropic forms of nickel oxide-hydroxide species are likely co-exist under steady-state conditions. However, the resulting nickel-oxide-hydroxide film deposited cathodically on the gold surface exhibits good electrical properties as peak currents and potentials relevant to Ia_1/Ic_1 are virtually identical to those observed for the bare gold electrode. When nickel loadings higher than 16 nmol cm^{-2} were considered, a decrease equal to 8–12% of the charge under the wave Ic_1 was observed. Apparently, the very low screening effect on gold activity is due to good conductivity and ion-permeability of the nickel film. In addition, the Au–Ni composite electrode exhibits a remarkable stability in alkaline solutions. Upon continuous potential cycling in 0.2 M NaOH, over 8 h, the charges under waves Ia_1/Ic_1 and Ia_2/Ic_2 compared very well with those obtained during the first hour of potential scanning. The only modification of the voltammogram profile was a slight shift of the Ia_2/Ic_2 couple to more positive potentials and an increase of the peak separation ($\text{Epa}_2\text{--Epc}_2$).

Fig. 2 (solid line) shows a representative cyclic voltammogram recorded with a composite electrode in 0.2 M NaOH containing 3.5 mM xylitol. As can be seen, in the positive potential scan two well developed oxidation peaks appear at about $+0.15$ V (Peak B) and $+0.40$ V (Peak C), while during the reverse

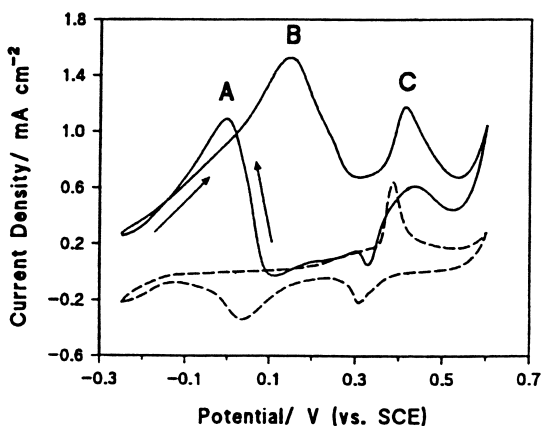


Fig. 2. Cyclic voltammogram (10th cycle) of 3.5 mM xylitol at the Au-Ni electrode ($\Gamma_{\text{Ni}} \cong 5.3 \text{ nmol cm}^{-2}$) (solid curve). Dashed curve corresponds to voltammogram run in blank 0.2 M NaOH. Scan rate, 50 mV s^{-1} .

scan a single oxidation peak at about -0.05 V (peak A) is observed. Peak height is proportional to analyte concentration up to about 6, 10 and 18 mM for peaks A, B and C, respectively. In the range of potential from -0.3 to $+0.2 \text{ V}$ the oxidation of xylitol is sustained by the electroactive species of gold, that is $\text{Au}(\text{OH})_{\text{ads}}$ [4,18–20], while at higher potentials (i.e. between $+0.3$ and $+0.6 \text{ V}$) the electrooxidation process is sustained by NiOOH [2,17,21–25]. Similar current-potential curves were observed for other examined compounds such as mannitol, glucose and sucrose, the only differences being the current ratios (A : B : C) and the positive shift of peaks B and C for sucrose. With regard to the electrocatalytic oxidation of carbohydrates, no evidence of synergistic interactions between the gold substrate and nickel oxyhydroxide species was noted [17]. We wish to emphasise, however, that the concomitant presence on the electrode surface of two active catalysts, AuOH and NiOOH, leads to a greater extension of the potential window in which the electrooxidation process is operative (i.e. between -0.2 and $+0.6 \text{ V vs SCE}$).

The effect of nickel loading on the height of peaks A, B and C was examined by cyclic voltammetry using glucose as a model compound. Fig. 3 shows the variations of the current densities of peaks A, B and C as a function of nickel loading on the gold substrate. The current density of peak C increases proportionally with nickel loading up to a maximum value

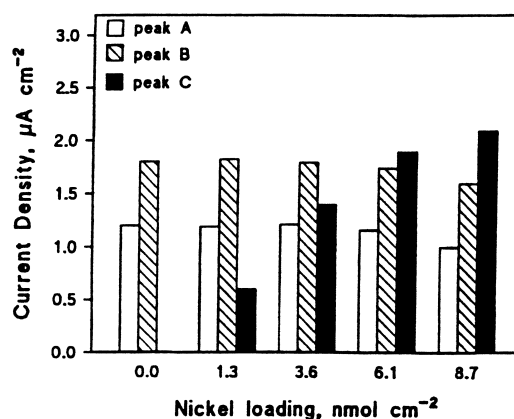


Fig. 3. Influence of the oxidation current of Peaks A, B and C on the nickel loading at the Au-Ni electrode for 5.0 mM glucose in 0.2 M NaOH solution. The peak currents were determined by CV at 50 mV s^{-1} .

of about 6 nmol cm^{-2} , while the current densities of peaks A and B exhibited just a slight decrease. Notably, a composite electrode having a nickel loading of 8.7 nmol cm^{-2} , when compared with a conventional gold electrode, exhibits a decrease of peaks A and B of 13 and 9%, respectively. This result is in agreement with the above voltammetric data, thus suggesting that the transport of the glucose (and its oxidation products) within the nickel film seems to occur very easily. Therefore, to obtain the highest electrode sensitivity over the entire range of explored potentials (i.e. $-0.2 - +0.6 \text{ V}$), all experiments were carried out with a nickel surface coverage of $5-7 \text{ nmol cm}^{-2}$.

3.2. FIA measurements

A gold-nickel composite electrode ($\Gamma_{\text{Ni}} = 6 \text{ nmol cm}^{-2}$) was evaluated as an amperometric sensor in flowing streams using a conventional thin-layer cell configuration. To optimise the amperometric detection conditions in terms of applied potential, the hydrodynamic voltammogram (HDV) for the oxidation of 0.5 mM xylitol was accomplished at 50 mV increments between 0.0 and $0.65 \text{ V vs. Ag/AgCl}$. Fig. 4A shows the resulting HDV obtained under constant-potential operation (DC mode). The amperometric signal increases significantly between 0.4 and 0.6 V while for higher potentials exhibits a marked abatement. Similar behaviour was observed for the electrooxidation

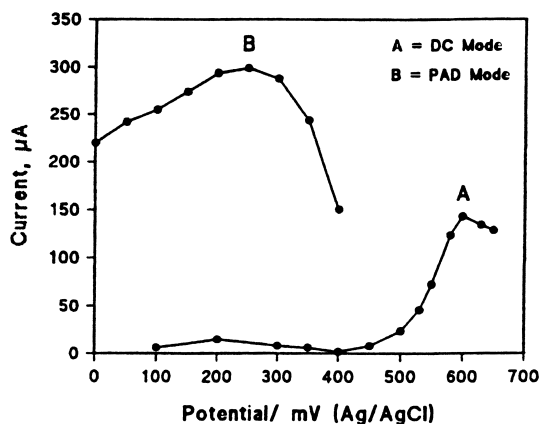


Fig. 4. Hydrodynamic voltammograms of 0.5 mM xylitol, obtained by FIA at the Au–Ni composite electrode. Curve A, constant applied potential (DC). Curve B, pulsed amperometric detection using the following potential time settings, $E_{\text{red}} = -0.2$ V with $t_{\text{red}} = 0.2$ s, $E_{\text{ox}} = 0.65$ V with $t_{\text{ox}} = 0.2$ s, $t_{\text{det}} = 0.4$ s with E_{det} as reported in the graph. Sample loop, 50 μl ; flow rate, 1.0 ml min^{-1} .

of alditols at other nickel-based modified electrodes [26,27]. In agreement with voltammetric results (see Fig. 2), the catalytic currents observed between 0.5 and 0.6 V are sustained by the NiOOH formed on the electrode surface. For potentials lower than 0.4 V, the amperometric response of the Au–Ni composite electrode is very low and, more importantly, it exhibits a continuous decrease during the first 10–12 repetitive injections of xylitol. As expected, the strong adsorption of intermediates and/or oxidation products on the gold catalytic sites led to irreversible fouling with a severe attenuation of the electrode reactivity [1,4,5]. In these cases, PAD techniques are successfully employed to preserve the integrity of the catalytic activity. The accomplishment of PAD employing noble metal electrodes for the detection of organic compounds is due to the multistep potential waveform, which manages sequentially the process of detection followed by oxidative and reductive reactivation of the electrode surface [1,4,5,28,29]. Thus, between 0.0 and 0.4 V vs. Ag/AgCl, an appropriate waveform for triple-pulse amperometry was employed. The relevant HDV for 0.5 mM xylitol is reported in Fig. 4B. The following values of the potential-time waveform were considered as optimal in terms of signal and background stability, sensitivity and temporal reproducibility; reductive potential ($E_{\text{red}} = -0.2$ V, time ($t_{\text{red}} = 0.2$ s, oxidative po-

tential ($E_{\text{ox}} = 0.65$ V, time ($t_{\text{ox}} = 0.2$ s, and detection potential ($E_{\text{det}} = 0.2$ V, time ($t_{\text{det}} = 0.4$ s). The hydrodynamic voltammograms reported in Fig. 4 confirm the composite character of the gold–nickel electrode, which combines the catalytic activity of gold species at low potentials (i.e. 0.1–0.3 V), and that of NiOOH at higher polarisation potentials (i.e. 0.55–0.65 V).

Electrode stability was tested in flowing streams by measuring the change of signal upon injections of 0.1 mM xylitol using an applied potential of +0.6 V in the DC mode. A carrier electrolyte consisting of 0.2 M NaOH at a flow rate of 1.0 ml min^{-1} was used. After the initial 10–12 min, the background current (about 0.5 μA) and the electrode response were sufficiently stable for several hours. During more than 24 h of continuous operation the amperometric signal decreased by about 15–20%. Noticeably, repetitive changes in the detection mode at the Au–Ni composite electrode from DC to PAD and vice versa (performed over 6 h) did not cause appreciable lowering of the catalytic performance.

3.3. Calibration data, reproducibility and limits of detection

Anion-exchange chromatography (AEC) under alkaline conditions represents a particularly valuable technique for the separation of weakly ionisable compounds, such as alditols and carbohydrates. The requirement of alkaline conditions has also a favourable effect on the catalytic activity of both gold and nickel catalytic species. Standard mixtures of some representative alditols and sugars were separated with an alkaline mobile phase (0.2 M NaOH) using two different anion-exchange columns. Fig. 5 shows two chromatograms, A and B, of the same standard mixture of carbohydrates obtained with the Au–Ni composite electrode in DC (+0.6 V vs. Ag/AgCl) and PAD modes, respectively, using a CarboPac PA100 column. Similarly, other carbohydrates and alditols were separated with a CarboPac PA1 column (chromatograms not shown). Analytical results in terms of limit of detection (LOD), linear range and sensitivity are summarised in Table 1. The LODs range from 1.5 pmol for glucose obtained in DC to 7.5 pmol for maltose obtained in PAD. Generally, a linear response was obtained over a range of approximately three and four

Table 1
Quantitative parameters for alditols and carbohydrates in LC with electrochemical detection at an Au–Ni composite electrode

Analytes	Carbopac PA1 ^a					
	DC			PAD		
	LOD ^b (pmol)	Linear range (μM)	Sensitivity ^c (μA/mM)	LOD (pmol)	Linear range (μM)	Sensitivity ^c (μA/mM)
Xylitol	1.5	0.07–800	46.1	3.5	0.10–500	112.1
Arabinose	1.8	0.07–750	33.4	3.5	0.10–500	84.2
Glucose	1.8	0.06–700	27.7	3.8	0.09–500	94.5
Fructose	2.0	0.07–700	22.5	4.1	0.10–500	70.7
Lactose	2.5	0.08–700	9.6	4.5	0.10–260	84.2
Sucrose	3.8	0.08–750	8.9	5.3	0.11–150	50.9
	Carbopac PA100 ^a					
Rhamnose	3.6	0.08–800	15.2	6.6	0.14–400	142.4
Mannose	3.5	0.07–800	26.0	6.5	0.14–500	175.0
Lactulose	3.0	0.08–900	13.5	7.0	0.15–350	127.2
Sucrose	4.0	0.08–900	11.1	5.5	0.15–150	94.8
Cellobiose	4.1	0.09–1000	10.3	6.0	0.14–200	138.6
Raffinose	4.0	0.09–900	9.2	7.0	0.14–100	110.0
Maltose	3.5	0.09–1000	8.2	7.5	0.15–130	94.1

^a Flow rate, 1.0 and 0.5 ml min⁻¹ for CarboPac PA100 and PA1, respectively. Isocratic elution using 0.2 M NaOH. Sample loop 50 μl. Thin-layer electrochemical cell with a Au–Ni electrode ($\Gamma_{Ni} \cong 6.2 \text{ nmol cm}^{-2}$). DC mode: +0.6 V; PAD mode: $E_{det} = 0.2 \text{ V}$, $t_{det} = 0.4 \text{ s}$, $E_{red} = -0.2 \text{ V}$, $t_{red} = 0.2 \text{ s}$, $E_{ox} = 0.65 \text{ V}$, $t_{ox} = 0.2 \text{ V}$.

^b LOD determined for $S/N=3$ from the lowest injected concentration.

^c From least-squares analysis of seven–eight data points spaced over the linear range. Correlation coefficients were always greater than 0.99.

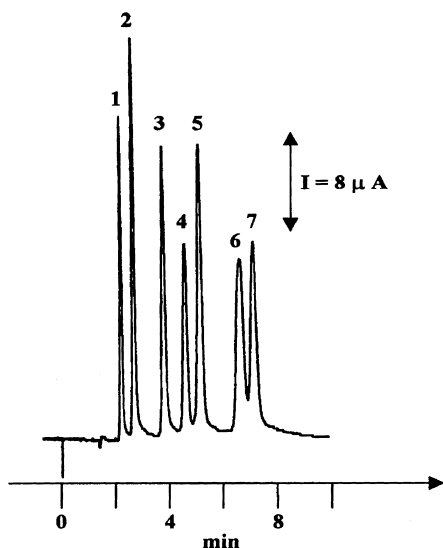


Fig. 5. LC-EC at the Au–Ni composite electrode using DC (A), and PAD modes (B) for a standard mixture containing (1) rhamnose, (2) mannose, (3) lactulose, (4) sucrose, (5) cellobiose, (6) raffinose, and (7) maltose, 150 μM each. Column, CarboPac PA100 (Dionex). Other conditions as in Table 1.

orders of magnitude under the PAD and DC modes, respectively. Note that the linear ranges obtained in the PAD mode, although extending up to three orders of magnitude, are generally lower than those obtained in DC. Moreover, it is interesting to observe that the analytical performances, expressed in terms of LOD and linear range, are generally better or at least comparable with those obtained by other amperometric sensors based on a single metal catalyst, either in the DC or PAD mode [1–4,7,8,15,16,28,30]. Precision expressed as relative standard deviation, obtained by six repetitive chromatographic analyses by DC first and then in PAD mode of a solution containing about 60 μM of each analyte, ranged from 5.9% of cellobiose (PAD mode) to 1.7% of maltose and fructose (DC mode).

3.4. Analytical applications

To demonstrate the usefulness of the proposed Au–Ni composite electrode as an amperometric sensor in LC, the determination of carbohydrates in a commercial pure tea powder was performed. A sample of tea (1.79 g) was treated for 5 min in 100 ml of boiling distilled water, filtered through filter paper, and before

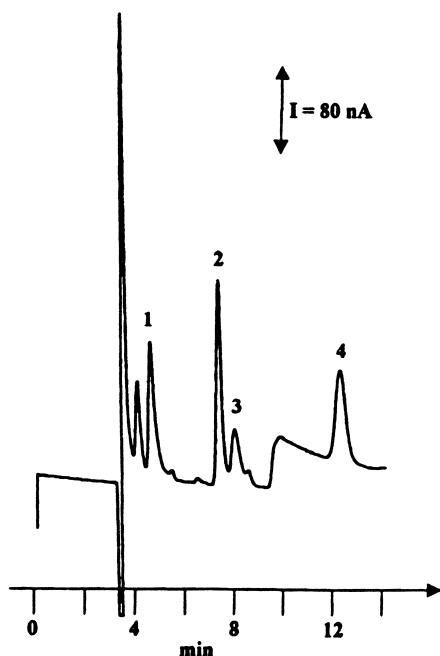


Fig. 6. LC-EC at the Au–Ni composite electrode using the DC detection mode (0.6 V) of a commercial powder tea sample. Peak identification: (1) xylitol, (2) glucose, (3) fructose, (4) sucrose. Chromatographic conditions, Dionex CarboPac PA1 column; flow rate, 0.4 ml min⁻¹, eluent, 0.2 M NaOH, sample loop, 50 μ l.

injection in the column was diluted 1:200 with water. The separation of free carbohydrates was performed with a CarboPac PA1 anion-exchange column with 0.2 M NaOH as the mobile phase. A representative chromatogram of a tea sample obtained in DC detection mode is shown in Fig. 6. Peak identification was based on the retention time of sugar molecules and was confirmed by spiking authentic standard solutions to the sample extract. Concentrations were determined by the standard addition method. In Table 2 are listed the quantitative results.

4. Conclusions

A gold–nickel composite electrode prepared by cathodic precipitation of nickel hydroxide on the gold electrode substrate was characterised. Although no synergistic interactions of the gold substrate and nickel oxohydroxide species in alkaline medium were observed, the concomitant presence on the electrode sur-

Table 2
Quantitative results for the free carbohydrates content (mg g⁻¹) in powdered sample tea by LC-EC^a

	DC	RSD (%)
Xylitol	11.3	4.1
Glucose	7.1	3.8
Fructose	6.7	3.1
Sucrose	13.2	3.6

^a CarboPac PA1 anion-exchange column; mobile phase, 0.2 M NaOH; flow rate, 0.4 ml min⁻¹; DC mode: +0.6 V vs. Ag/AgCl; The concentrations were evaluated by the standard addition method (four additions); The precision expressed as RSD% was obtained from three repetitive analyses.

face of two active catalysts, Au(OH)_{ads} and NiOOH, leads to a greater extension of the potential window in which there are significant catalytic activities towards the oxidation of carbohydrates. The suitability of the Au–Ni composite electrode as an amperometric sensor in flow injection analysis and liquid chromatography using constant and pulse-applied potential was explored. The Au–Ni electrode shows good sensitivity, temporal stability and a wide linear dynamic range for all the examined compounds. Chromatographic analysis of carbohydrates in real matrices has demonstrated the suitability of the Au–Ni composite electrode as an amperometric sensor in LC-EC for routine analytical applications. Further studies regarding the applications and comparison between the DC and PAD mode are currently in progress.

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