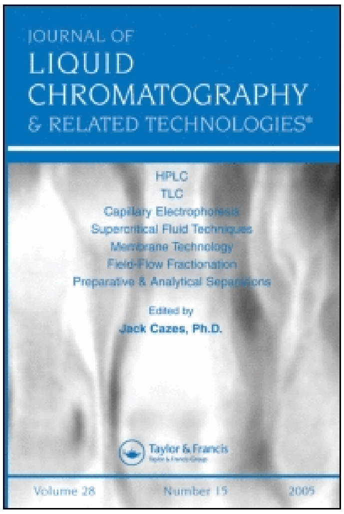

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Fabrication and Characterisation of Leak-Tight Glassy Carbon Electrodes, Sealed in Glass Employing Silicon Coating, for Use in Electrochemical Detection

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FABRICATION AND CHARACTERISATION OF LEAK-TIGHT GLASSY CARBON ELECTRODES, SEALED IN GLASS EMPLOYING SILICON COATING, FOR USE IN ELECTROCHEMICAL DETECTION

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SUMMARY

Glassy carbon discs have been coated with silicon in a chemical vapour deposition process to obtain leak-tight electrodes, sealed in glass. Electrodes with coatings thicker than 5 μm prove to be leak-tight in contrast with uncoated ones. Silicon-coated electrodes show faster decay of charging current, less noise and decreased background current. Leak-tightness and electron microscope information correlate well with the electrochemical data. All results can be ascribed to the absence of a void between glassy carbon and glass at Si-coated electrodes. By silicon coating, signal-to-noise ratios are improved with a factor of about 5, as is demonstrated for catecholamines and metabolites in liquid chromatography with electrochemical detection.

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INTRODUCTION

Electrochemical flow-through detectors are widely used for low-level, selective and inexpensive analysis of a large variety of substances. Nowadays those which employ some form of carbon as working electrode constitute the majority, being used for mainly oxidative detection in liquid chromatography.

From experience it is known that new electrodes behave differently from repolished ones. This (long-term!) deterioration, being reflected in more noise and a higher background current, is known as "aging" and is of extreme importance for lowest-level determinations. Since it was believed that electrode fabrication plays an important role in aging, this aspect of electrochemical detection has been studied in detail.

There are several ways to fabricate glassy carbon (GC) electrodes for detectors. Electrodes can be press-fitted or sealed in Kel-F, Teflon, plexiglas or glass. In the PB-2 confined wall-jet flow-through detector [1], the GC working and auxiliary electrodes (WE resp. AE) are sealed in holders of borosilicate glass (Fig. 1). The coefficient of thermal expansion of the glass matches that of the used GC within a narrow range (resp. 32 and 35 x 10^{-7}/°C).

With these electrodes used directly after fabrication, very low detection limits can be obtained [1]. In the time, however, electrochemical behaviour gradually deteriorates. We have observed even faster deterioration in organic solvents like acetonitrile and methanol, eventually leading to cracking of the glass holder. Mostly, the initial electrode characteristics can not be recovered by repolishing. It appears that solvents can penetrate in a thin void between the GC and glass in spite of the matched expansion coefficients. Similar aging behaviour has been observed by us with GC electrodes, press-fitted or glued in Kel-F.

According to Levy and Farina [2], leak-tight electrodes can be obtained by coating the GC with silicon (Si). For the same purpose SiO and SiO_2 coating techniques have been described [3,4]. These GC electrodes, sealed in glass, have been developed for and only applied (as far as we know) in high temperature electrochemical studies (ca. 500 °C). It seemed likely to us that Si-coated electrodes would offer comparable advantages in aqueous and organic solvents at room temperature.

In the present work Si-coated GC electrodes, sealed in glass, are manufactured and compared with conventional ones. The influence of the thickness of the coating on charging and background currents, noise and long-term stability is studied in batch and flow experiments. The electrochemical results are correlated with leak-tightness and electron microscope (EM) information.

EXPERIMENTAL

Electrode fabrication

Circular GC discs (V10, Le Carbone Lorraine, Paris, France) with a diameter of 10 mm, all made from a single plate, were ground with 40 µm carborundum powder and cleaned ultrasonically in methanol before coating.

The discs were placed in a cold wall chemical vapour deposition reactor, operating at atmospheric pressure with hydrogen as carrier gas, and brought to 1250 °C by an inductively heated graphite susceptor. Polycrystalline Si coatings were deposited by thermal decomposition of trichlorosilane (2% by volume). The growth rate of the Si layers amounted to 3 µm/min. Si coatings of 5, 15 and 40 µm were prepared. The thermal expansion coefficient of Si is 30×10^{-7}/°C.

Next, the discs were sealed in tubes of borosilicate glass (Duran 8330, Jena Glaswerk, Mainz, GFR). Si was removed from the frontside by grinding. The surface was polished to a mirrorlike finish with 6 and finally with 1 µm diamond spray (Engis Ltd., Maidstone, U.K.). Electrical contact (shielded cable) was established with silver paint (Elecolit 325, 3M, Leiden, The Netherlands). The connection was mechanically fixed with a non-conductive resin (Araldite, AW 136/HY 994, Ciba Geigy, Arnhem, The Netherlands). Electrodes without Si coating were prepared in an identical manner. For EM studies, unpolished dummy electrodes were made by cutting off the glass holder just above the GC.

Electrode characterisation

All electrodes have been checked for leak-tightness with a helium leak detector (Leybold-Heraeus, Köln, GFR). With an EM (Cambridge S180) secondary electron image (SEI) and backscattered electron image (BSEI) pictures of the dummy electrodes were made for surface and material contrast information respectively. A thin layer of gold has been sputtered onto the samples to prevent charging of the glass.

Electrochemical measurements were performed with a Bruker E310 modular research polarograph (Bruker, Brussels, Belgium). The currents in the chronoamperometric experiments were sampled and digitized by a MINC-11/03 microcomputer (Digital Equipment Corporation, MA, USA). Data-acquisition and -processing was controlled by a Fortran program and curves were plotted with a HP 7220C plotter (Hewlett Packard Company, San Diego, CA, USA).

The GC AE (diameter 10 mm and coated with 40 µm Si), the SCE reference electrode (home made) and one of the WE's were placed in the PB-2 detector

(Fig. 1). In the batch experiments a 0.05 M phosphate buffer of pH 3.5 containing 0.1 M $NaClO_4$, and methanol with 0.1 M $NaClO_4$ as supporting electrolyte, acidified to "pH" 1.5 with $HClO_4$ were used. The distance between WE and AE was about 1 cm.

Chromatography

Polygosil 60-5C8 (5 µm, Machery-Nagel & Co., Düren, GFR) was packed in a stainless steel Valco column (100x3.0 mm i.d.) and coated in situ with tri-n-butyl-phosphate (TBP). The eluent, saturated with TBP and thermostatted at 25 °C, was an aqueous 0.05 M phosphate/0.1 M $HClO_4$ solution, adjusted to pH 3.5 with NaOH [6]. About 10 mg of EDTA per litre eluent was added in order to decrease the (steady-state) background current.

An Orlita 1515 reciprocating pump (Giessen, GFR) and an injection valve with fixed loop (Rheodyne 7010, Berkeley, CA, USA) were used. In the chromatographic experiments, the distance between WE and AE was 50 µm, adjusted with a PVC spacer.

Mixtures of noradrenaline HCl (Sigma), adrenaline bitartrate (Boehringer-Ingelheim), bis(4-hydroxy-3-methoxy)phenylglycol piperazine salt (Sigma) and 3-hydroxytyramine HCl (Aldrich) were prepared in 1 M $NaClO_4$ aqueous solutions, acidified to pH 3.0 with $HClO_4$.

The chromatographic conditions of the recordings of brain tissue (Fig. 7) are described by Van Valkenburg et al. [7].

All chemicals were reagent grade and used as received. Demineralized water was additionally purified by a Milli-Q Water Purification System (Millipore, Bedford, MA, USA).

RESULTS AND DISCUSSION

Leak-tightness of the electrodes

The influence of the thickness of the Si coatings on the leak-tightness was investigated by a helium leak test and EM. Both methods reveal that 5µm of Si is not sufficient to obtain leak-tight seals. From the EM results it seen that the carbon surface at the side is not entirely covered with Si. Polishing and a better controlled coating procedure would probably give better results. Electrodes with 15 and 40 µm Si coatings were leak-tight in all cases.

The uncoated electrode leaked; on the EM picture (Fig. 3), it can be seen that a void of about 1 µm is present between GC and

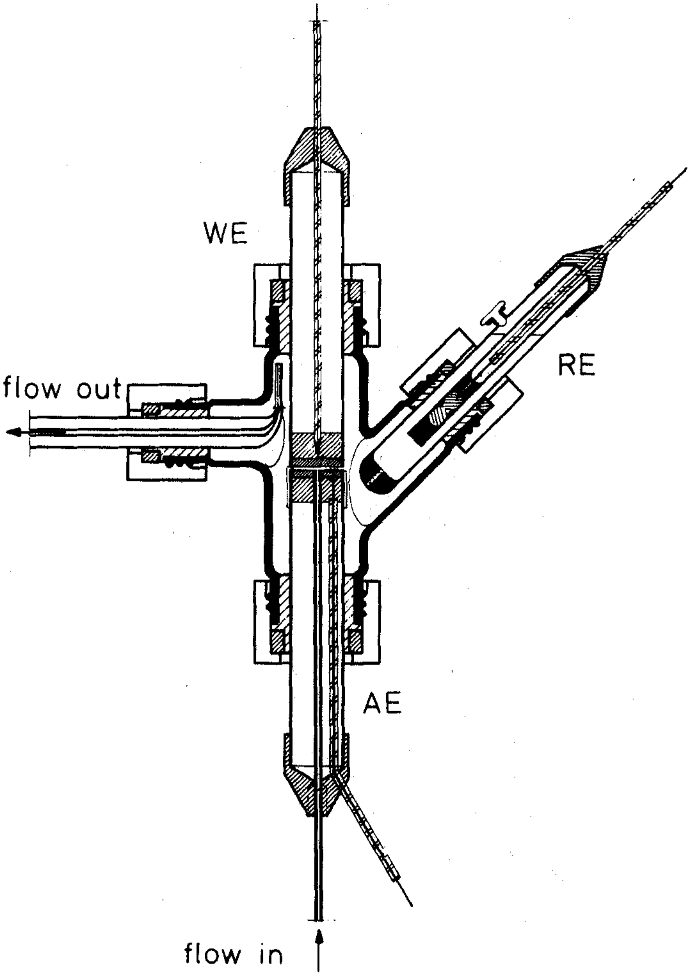

Fig. 1. The PB-2 confined wall-jet detector.

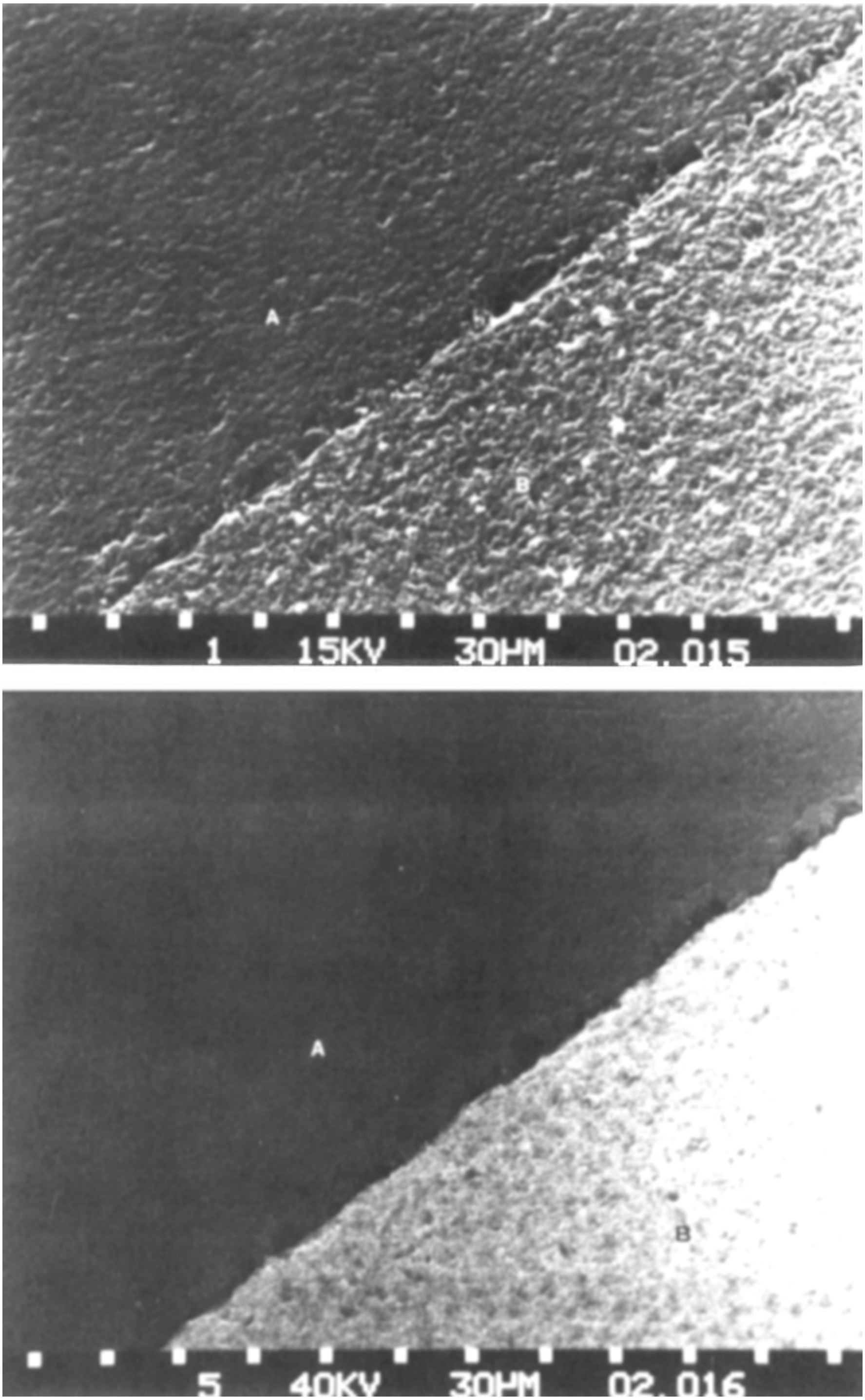

Fig. 2. EM photographs of an uncoated electrode. SEI (upper) and BSEI (lower) pictures of the interface between GC (A) and glass (B). The surface is not polished.

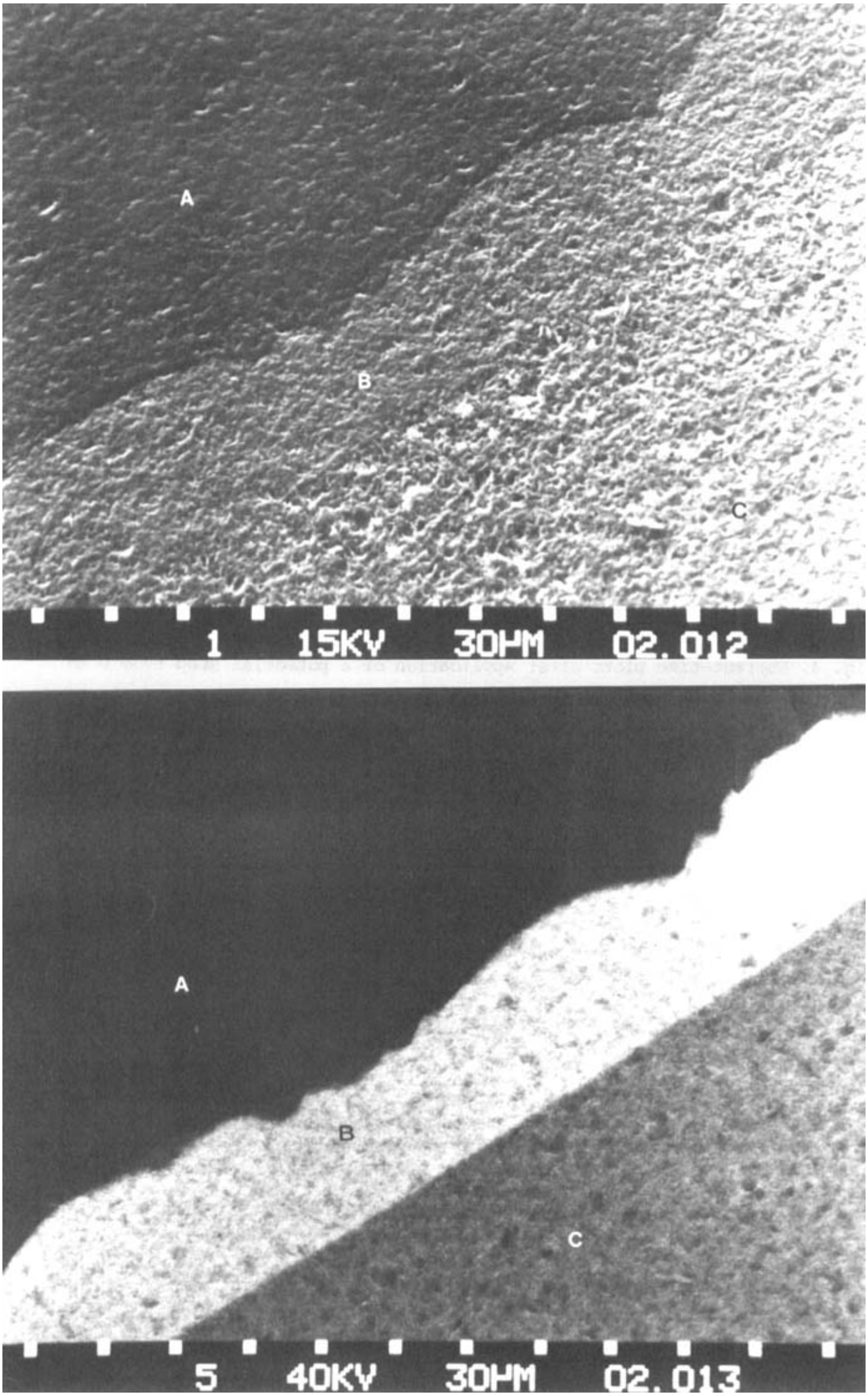

Fig. 3. EM photographs of a 40 µm Si-coated electrode. SEI (upper) and BSEI (lower) pictures of the interface between GC (A), Si (B) and glass (C). The surface is not polished.

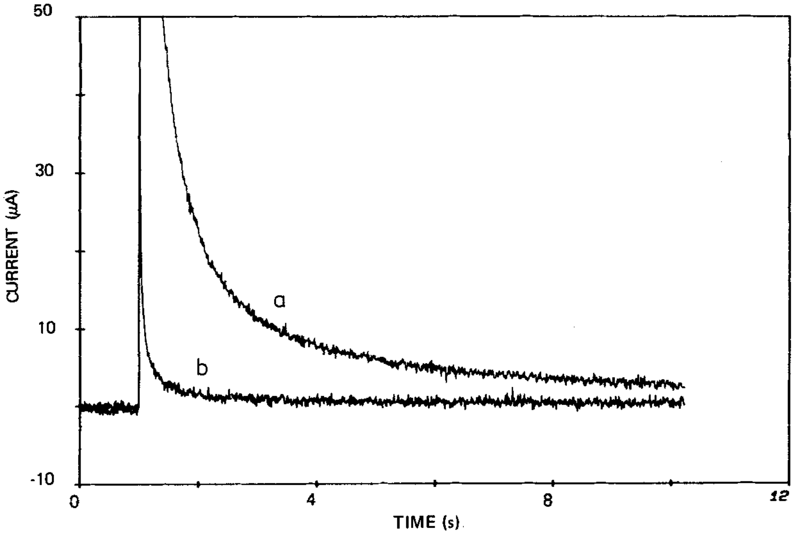

Fig. 4. Current-time plots after application of a potential step from 0 to + 0.5 V vs. SCE for an uncoated (a) and 40 μm Si-coated (b) electrode, directly after fabrication, both recorded in phosphate buffer. Sampling frequency: 100 Hz. Data have not been averaged.

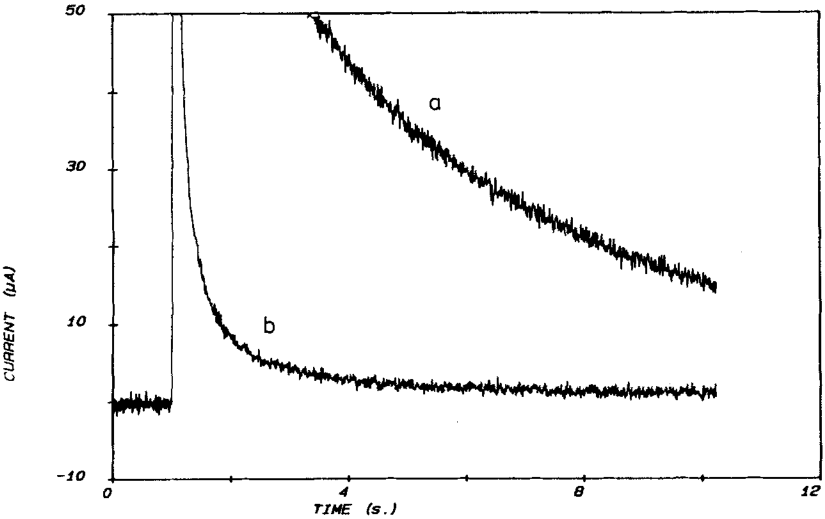

Fig. 5. Current-time plots for the uncoated (a) and 40 μm Si-coated (b) electrode, recorded after been in use for 100 h at + 0.8 V vs. SCE. Experimental conditions as in Fig. 4.

glass. In electrochemical experiments leakage of methanol was observed.

In Figure 3, the 40 µm Si-coated electrode is shown. The EM pictures indicate that the seals between GC and Si and between Si and glass are very good. The good seal between Si and GC can be ascribed to the formation of a thin layer of silicon carbide (SiC) during the coating process. The sealing between Si and glass is ascribed to the fact that Si is well wetted by glass, due to formation of SiO_2 at the surface in contact with air.

The long-term stability of the electrodes (>5 µm Si) proved to be good. In the period between fabrication and this moment (8 months), none of the Si-coated electrodes broke down and all are still leak-tight.

Influence of Si coating on the charging current

The influence of the thickness of the Si coating on the magnitude and decay of the charging current in the phosphate buffer and the methanolic solution was investigated by chronoamperometry. A potential step from 0 to + 0.5 V vs. SCE was applied. The resulting currents are entirely due to recharging of the electrical double layer and to formation/oxidation of surface groups of the electrode material itself [5].

In Fig. 4, the results in the phosphate buffer for uncoated and 40 µm Si-coated electrodes (new ones) are shown. No significant differences between the current-time curves recorded in methanol and phosphate buffer were observed. The curves for 5 and 15 µm Si-coated electrodes very much resemble the one with 40 µm Si. The experiments were repeated with the uncoated and 40 µm Si-coated electrode after both had been in use for about 100 h at + 0.8 V vs. SCE (Fig. 5). The conclusion is that there are important differences in decay between uncoated and Si-coated electrodes. This difference is already significant directly after fabrication, but becomes more pronounced when the electrodes have been in use for some time.

Comparable differences in charging current were observed in cyclic voltammetry and in differential pulse amperometry (DPA). In DPA, e.g., the recorded background current of a 40 µm Si-coated electrode is 4 times smaller than of an uncoated one. These differences in behaviour are explained by the absence of the extra impedance due to the void between GC and glass. Accumulation of impurities and electrolyte in the void may also contribute to the observed deterioration. Nevertheless, some residual current persists at GC electrodes, even in absence of a void, because of micropores in the material and of formation/oxidation of surface groups [5].

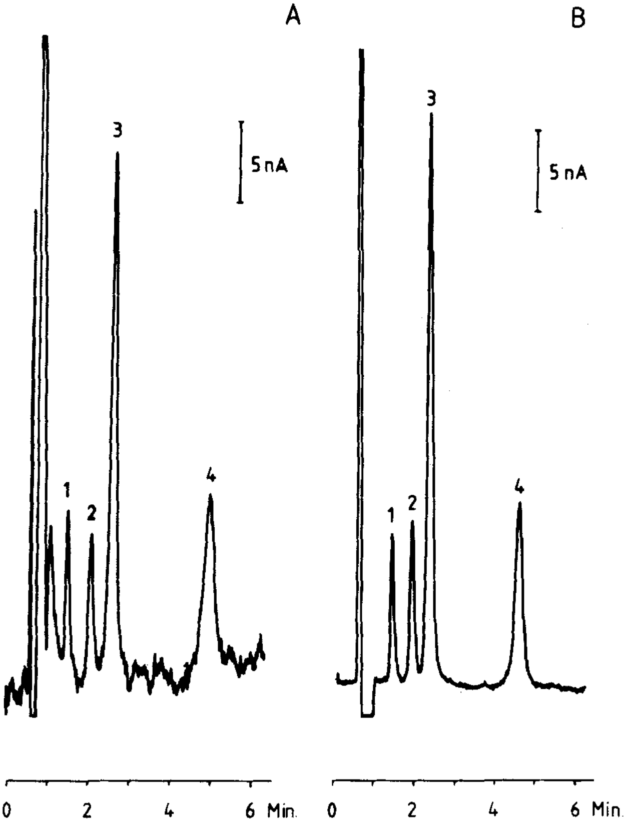

Fig. 6. Chromatograms of a mixture of 1.6 ng 3-methoxy-4-hydroxyphenylethyleneglycol (1), 1.0 ng adrenaline (2), 2.8 ng noradrenaline (3) and 1.1 ng dopamine (4) at the uncoated (A) and 40 μm Si-coated electrode (B). The flowrate was 0.7 mL/min and the used time constant was 1.0 s. The peak-to-peak noise levels are about 2.0 (A) and 0.4 nA (B). (E = + 0.8 V vs. SCE, 20-μL loop).

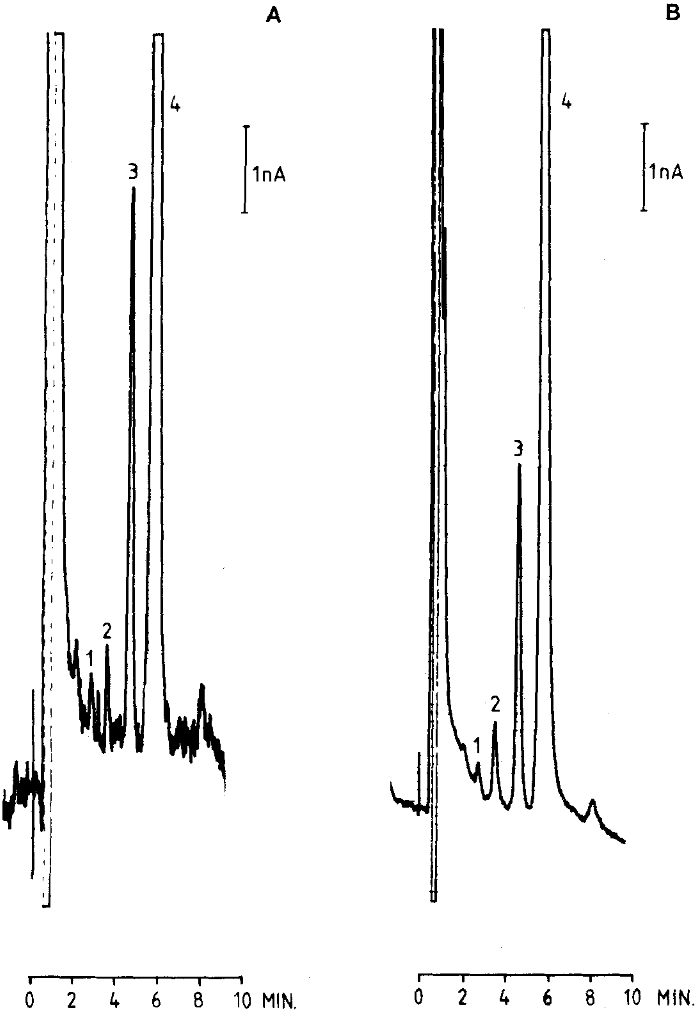

Fig. 7. Chromatograms of a sample obtained from rat tuberculum olfactorium at the uncoated (A) and 40 μm Si-coated electrode (B). The supernatant derived from about 0.5 mg tissue was dissolved in 0.1 M $HClO_4$ and injected. Peaks: noradrenaline (1), homovanillic acid (2), dihydroxyphenylacetic acid (3) and dopamine (4). The flow rate was 0.8 mL/min and the used time constant was 2.2 s. The peak-to-peak noise levels are about 0.5 (A) and 0.1 nA (B). (E = + 0.8 V vs. SCE, 100-μL loop).

Application of the electrodes in electrochemical detection

Si coatings have also a pronounced effect on the noise and S/N ratio. The improvement is illustrated by chromatograms, recorded with an uncoated and 40 µm Si-coated electrode. Both electrodes were repolished after about 200 h of use. Since repolishing, the electrodes had been used for about 50 h at + 0.8 V vs. SCE before the chromatograms were recorded (Fig. 6). Because both electrodes, with equal geometric area, were not pretreated electrochemically, the I/E relationships of the detected compounds may be different, being reflected in differences in sensitivity (Figs. 6 and 7).

Because of the influence of Si coating on the decay of the charging current, the background current at the Si-coated electrode reached a steady state (35 nA) within 30 min, while about 2 h were needed for the uncoated one (55 nA). The electrodes were also compared in the determination of dopamine and its acidic metabolites in rat brain tissue [7]. Both were repolished and the chromatograms were recorded after a 24 h equilibration at + 0.8 V vs. SCE (Fig. 7). The recorded background currents were 95 and 55 nA at the uncoated and coated electrode respectively.

The S/N ratios in both determinations are improved with a factor of about 5 by Si coating.

Preliminary experiments indicate that the electrochemical phenomena, observed at uncoated GC electrodes, sealed in glass, are also more or less present at electrodes, press-fitted or sealed in Kel-F, Teflon and plexiglas. Work on further characterisation of these Si-coated GC electrodes is in progress.

CONCLUSIONS

It is concluded that the noise, background current and decay of charging current, are partly determined by a void between GC and glass, in which electrolyte can penetrate. This void is not present at electrodes coated with 15 µm or more Si, resulting in improved electrode performance. Thus, because of faster decay of charging current, decreased noise and lower background current, Si coating of GC is advantageous in those fields of electrochemistry where low detection limits and/or low charging currents are required, notably, in liquid chromatography with electrochemical detection.

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