CARBON PASTES FOR VOLTAMMETRIC DETECTORS IN HIGH-PERFOR-MANCE LIQUID CHROMATOGRAPHY

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SUMMARY

Several solid-matrix carbon paste electrodes were tested in thin-layer and wall-jet hydrodynamic systems. Silicone rubber electrodes were unsuitable, but high-molecular-weight polyvinyl chloride and a 1:1 mixture of chloroprene rubber and an alkylphenol resin gave very good electrodes that are readily prepared, can easily be polished, have a lifetime of at least 1 month and exhibit good operating parameters. The residual current and noise are low, there is no baseline drift, the detection limit is in the subnanogram range (adrenaline), the linear dynamic range is broad and the measuring reproducibility is good.

INTRODUCTION

Most common solid electrodes in voltammetric detectors for high-performance liquid chromatography (HPLC) are made of various kinds of carbon. A number of authors have described and compared working electrodes of glassy carbon (*e.g.*, refs. 1–5), pyrolytic graphite (*e.g.*, ref. 6) and various kinds of carbon paste (*e.g.*, refs. 1, 4, 5, 7–9). As shown in our previous work[1], graphite paste electrodes are superior in many respects to other carbon electrodes. They are very cheap, easy to prepare and replace, exhibit very low residual current and noise, so that the detection limit is usually lower than with other electrodes, even when the electrode reactions are generally slower on them than on, *e.g.*, well-polished glassy carbon, and are not damaged by current pulses as often happens with glassy carbon electrodes.

However, classical carbon pastes with liquid diluents (such as Nujol) also have serious drawbacks. It is difficult to make their surfaces sufficiently level and smooth, their cathodic residual current is rather high, chiefly due to adsorption and absorption of traces of oxygen in the paste, they cannot be used for work with organic mobile phases and even in aqueous solution the bleeding of the diluent limits their lifetime to several days. They are not sufficiently mechanically strong for use in wall-jet detectors.

In an attempt to prepare electrodes with the advantages of carbon paste, but without its drawbacks, high-molecular-weight waxes (*e.g.*, refs. 7, 10) or polymers[+]

were used as matrices. In the present work, electrodes prepared from graphite powder. dispersed in silicone rubber, polyvinyl chloride or in a 1:1 mixture of chloroprene rubber and an alkylphenol resin were prepared and tested.

EXPERIMENTAL

The experiments were carried out using carbon paste thin-layer and wall-jet detectors of our own construction, described earlier[1]. However, the construction was somewhat modified to decrease the IR drop between the electrodes (Fig. 1). The glassy carbon disk auxiliary electrode was placed beside the working electrode, and the reference electrode (a silver wire) was immersed in a saturated KCl solution in a compartment opposite the other two electrodes. The reference electrode compartment was closed with porous glass (Code 7930; Corning, NY, U.S.A.).
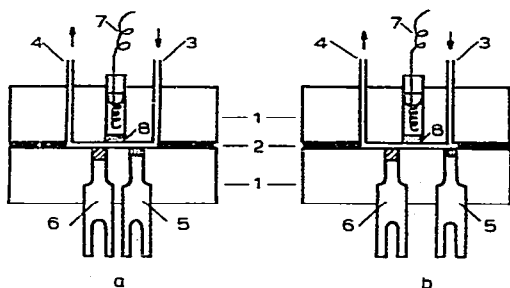

Fig. 1. Thin-layer (a) and wall-jet (b) detectors. 1 = PTFE blocks; 2 = 0.05-mm PTFE spacer; 3 = inlet; 4 = outlet; 5 = carbon paste working electrode; 6 = glassy carbon auxiliary electrode; 7 = silver wire reference electrode; 8 = porous glass.

An LC-XP liiquid chromatograph (Pye Unicam, Cambridge, Great Britain), a PA-3 polarographic analyzer (Laboratorní Přístroje, Prague, Czechoslovakia) and a Varian-Techtron line recorder were used. The samples were injected either directly into the detector through a short stainless-steel capillary, 0.23 mm I.D., or through a Partisil 10 ODS (10 μm) column (250 × 4.6 mm) (Pye Unicam). A 20-μl sampling loop was used.

Adrenaline hydrogen tartrate (MW 333.3; Fluka, Buchs, Switzerland) was employed as the test substance, in a citrate–phosphate aqueous buffer[11] (300 ml 0.1 M citric acid and 160 ml 0.1 M Na_2HPO_4, pH 4.7) as the mobile phase. The buffer was deaerated by purified nitrogen and degassed *in vacuo*. A 10^{-3} M adrenaline stock solution was prepared in the buffer solution and appropriately diluted before use.

The measurements were carried out at laboratory temperature, at a potential of +0.8 V (*versus* saturated calomel electrode, SCE).

Paste preparation

For preparation of the pastes, finely pulverized spectral graphite (Kablo, Topolčany, Czechoslovakia) was used.

(a) *Silicone rubber*. A weighed amount of graphite powder was mixed with a known amount of silicone rubber monomer (Lukopren, Synthesia, Pardubice, Czechoslovakia), an appropriate amount of the polymerization catalyst was added

TABLE I

PROPERTIES OF THE PVC USED

PVC	Molecular weight	Content of initiator residue LiCl (mM/g PVC)	Content of sulphate ash (%)	Viscosity	Specific volume (ml/10³ g)
A	142,500	34.2	0.27	2.222	3900
B	147,000	28.1	0.26	2.278	3900
C	151,000	11.0	0.07	2.341	4300

and the mixture was thoroughly homogenized. A depression over the brass contact in the detector was filled with this mixture and the mixture was allowed to polymerize overnight. The solid electrode formed was then polished with a fine metallographic paper.

(b) *Chloroprene rubber–alkylphenol resin (1:1) (Alkapren)*. The procedure was the same as in (a), but no catalyst was used (the polymerization process is catalyzed by atmospheric moisture). The commercial preparation, Alkapren (Matador, Bratislava, Czechoslovakia), was used.

(c) *Polyvinyl chloride*. Three kinds of highly pure PVC, A, B and C (provided by the Institute of Macromolecular Chemistry, Prague), were used. All of them were linear, with only one double bond per 1000 units. The purity and porosity of the samples increased from A to C. The properties of these PVC materials are summarized in Table I.

A solution of PVC in tetrahydrofuran (THF) p.a. was prepared by dissolving 0.009–0.010 g PVC in 3 g THF. A weighed amount of pulverized graphite was added. The mixture was thoroughly mixed and excess of solvent was allowed to evaporate (about 1 h at laboratory temperature). When the mixture had become viscous (but not completely dry!), it was placed into the depression in the detector, left to completely solidify (about 1 h) and the solid electrode obtained was polished with a fine metallographic paper.

TABLE II

PARAMETERS OF THE ALKAPREN GRAPHITE PASTE ELECTRODES

Tested with adrenaline. Mobile phase flow-rate: 0.3 ml/min. Potential: +0.8 V (SCE). No drift observed.

Electrode	Detector type	Alkapren:C	Sensitivity (A/mg)	Correlation coeff.	Residual current (A)
1	Thin-layer	1:0.43	2.5×10^{-4}	0.999	4.0×10^{-7}–20×10^{-7}
2	Thin-layer	1:0.56	3.6×10^{-5}	0.998	1.3×10^{-7}–4.5×10^{-7}
3	Thin-layer	1:1.27	1.3×10^{-3}	0.999	1.1×10^{-6}–1.7×10^{-6}
4	Wall-jet	1:0.37	5.9×10^{-5}	0.999	7.5×10^{-7}–13.5×10^{-7}
5	Wall-jet	1:0.56	1.3×10^{-4}	0.999	3.0×10^{-7}–9.5×10^{-7}
6	Wall-jet	1:1.16	2.2×10^{-3}	0.999	2.0×10^{-6}–3.0×10^{-6}
7	Wall-jet	1:1.27	6.5×10^{-4}	0.999	4.3×10^{-7}–8.0×10^{-7}

TABLE III

PARAMETERS OF THE PVC GRAPHITE PASTE ELECTRODES

Conditions as in Table II.

Electrode	Detector type	PVC type	PVC:C	Sensitivity (A/mg)	Correlation coeff.	Residual current (A)	Drift
1	Thin-layer	B	1: 9	8.6×10^{-5}	0.996	2.3×10^{-7}–12.8×10^{-7}	None
2	Thin-layer	B	1:17	1.4×10^{-4}	0.998	6.0×10^{-7}–16.5×10^{-7}	None
3	Thin-layer	B	1:24	1.0×10^{-4}	0.999	6.8×10^{-7}–15.5×10^{-7}	None
4	Thin-layer	C	1:17	2.1×10^{-3}	0.997	2.5×10^{-7}–4.0×10^{-7}	None
5	Wall-jet	A	1: 9	2.2×10^{-5}	0.999	2.8×10^{-7}–11.2×10^{-7}	Small
6	Wall-jet	A	1:10	3.2×10^{-5}	0.985	3.3×10^{-6}–8.5×10^{-7}	Negligible
7	Wall-jet	B	1:17	2.8×10^{-4}	0.999	3.5×10^{-6}–3.8×10^{-6}	None
8	Wall-jet	C	1:17	3.0×10^{-3}	0.999	8.3×10^{-7}–13.3×10^{-7}	None

RESULTS AND DISCUSSION

The paste electrodes were tested under the conditions given in the Experimental section, by monitoring the effect of the graphite-to-matrix weight ratio on the electrode performance. The electrode lifetime, accessible potential range, background current, noise, the detection limit, linear dynamic range, linearity, sensitivity, drift and the measurement reproducibility were determined.

The silicone rubber electrodes were insensitive and were not further studied. All the other electrodes tested exhibited a low regular noise amounting to 1×10^{-9}– 2×10^{-9} A (peak-to-peak). The accessible potential range is wide, namely, from -1.1 to $+1.2$ V (SCE). The lifetime of the electrodes is 4–5 weeks. It follows from Tables II and III that the electrodes exhibit a good linearity and virtually no signal drift. The optimal graphite-to-matrix weight ratio is 1.1:1 for Alkapren and 17:1 for PVC. Among the PVC samples, that with the highest purity, molecular weight and porosity (the highest specific volume) yielded the best electrode. The linear dynamic range is more than three orders of concentration. The detection limit is of the order of 0.1 ng, the typical peak height relative standard deviations being 1% (>600 ng adrenaline), 3% (100–600 ng), 5% (10–100 ng) and 10% (<10 ng) for the Alkapren paste; the corresponding values for the PVC paste are somewhat higher.

There is very little difference between the performance of the thin-layer and wall-jet detectors. The wall-jet system is somewhat more sensitive, but exhibits a higher residual current.

The pastes require polishing once a day before starting measurements; during measurement the sensitivity very slowly decreases (the peak height decreases by 4.8% in 4 h). As seen in Fig. 2, the Alkapren paste attains maximum sensitivity immediately, then the sensitivity decreases and remains constant. The sensitivity of the PVC paste first increases, reaches a maximum and then slowly decreases. Both pastes require about 1 h for signal stabilization at the beginning of measurement.
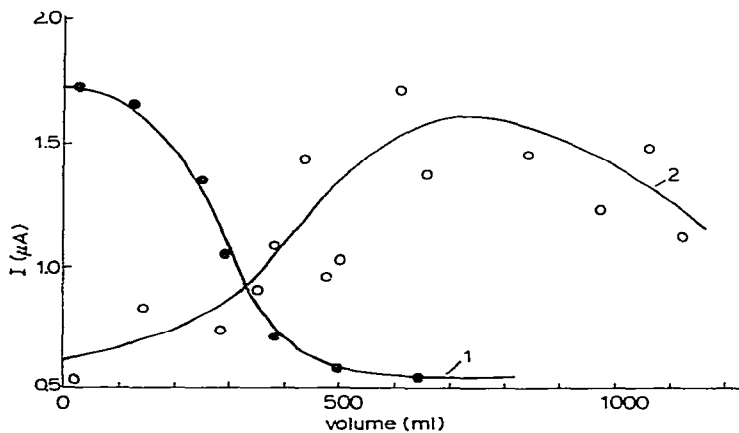

Fig. 2. The dependence of the sensitivity of the Alkapren (1) and PVC (2) paste electrodes on the volume of the mobile phase passed. Sample: 3.3 μg adrenaline in a citrate–phosphate buffer. Potential: $+0.8$ V. Flow-rate: 0.3 ml/min. The measurements were carried out over the whole lifetime of the electrodes. Between measurements, the electrodes were stored dry in the air.

Unpolished pastes have about 60% lower sensitivity and a high residual current; similar properties indicate the end of the electrode life.

The above results show that the electrodes with Alkapren and PVC matrices have virtually the same properties. However, Alkapren electrodes are easier to prepare and polish, although the polymerization requires longer than solvent evaporation in PVC electrodes. The electrodes obtained are sufficiently mechanically strong, and can readily be polished and replaced. However, the optimal weight ratio of graphite and matrix must be strictly observed, as electrodes with a higher graphite content have a tendency to peel on polishing and exhibit high residual current and noise, whereas those with a higher matrix content have a low sensitivity.

Comparison with literature data on detectors having various carbon electrodes (*e.g.*, refs. 1, 3, 4, 12–15) indicates that the present electrodes retain the advantages of classical pastes and, in addition, are sufficiently mechanically strong, resistant to many organic solvents and have a substantially longer lifetime.

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