

## TESTING OF UNMODIFIED CARBON PASTE ELECTRODES

IVAN ŠVANCARA<sup>a</sup> and KLEMENS SCHACHL<sup>b</sup>

<sup>a</sup>Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, nám. Čs. legií 565, 532 10 Pardubice, <sup>b</sup>Institute of Analytical Chemistry, Karl-Franzen University, Universitätsplatz 1, A-8010 Graz, Austria

Received September 14, 1998

Key words: carbon paste electrodes, testing, characterization

## Contents

1. Introduction
  - 1.1. Why testing of carbon paste electrodes (CPEs)
  - 1.2. Testing of CPEs - historical survey
2. General procedure for the testing of unmodified CPEs
3. Some practical aspects on the preparation of unmodified CPEs
  - 3.1 Carbon paste components and their choice
  - 3.2. Mixing of pastes, their homogenization, and preparation of CPEs
4. Basic characterization of unmodified CPEs
  - 4.1. Physico-chemical properties of carbon pastes
  - 4.2. Basic electrochemical characteristics of carbon pastes
  - 4.3. Model systems for basic characterization of CPEs in voltammetry
5. Special characterization of unmodified CPEs
  - 5.1. Studies on specific interactions with carbon pastes
  - 5.2. Studies on the alteration of the surface characteristics of carbon pastes
  - 5.3. Testing of CPEs in non-aqueous and mixed media
6. Some aspects of simultaneous testing measurements with more CPEs
7. Practical remarks on the testing of CPEs in quantitative analysis
8. Conclusion

## 1. Introduction

Carbon paste electrodes (CPEs) belong to a special group of heterogeneous carbon electrodes<sup>1,3</sup>. CPEs are represented by carbon paste, i.e. a mixture prepared from carbon (graphite) powder and a suitable liquid binder packed into a suitably designed electrode body<sup>4,5</sup>. Due to numerous advantageous properties and characteristics<sup>1,5</sup>, these electrodes are widely used mainly for voltammetric measurements; however, carbon paste-based sensors are also applicable in amperometry, coulometry, and potentiometry. In general, the reason why CPEs

are still popular can be seen mainly in the fact that carbon pastes are easily obtainable at minimal costs and are especially suitable for preparing an electrode material with desired composition, and hence, with pre-determined properties. Electrodes made in this way are usually thought to be used as highly selective sensors for both inorganic and organic electrochemistry<sup>1-5</sup>.

## 1.1. Why testing of carbon paste electrodes

Apparently the most frequently quoted disadvantage of CPEs which limits their applicability in practical analysis is that the success in working with carbon paste-based electrodes depends very significantly upon experimental experience of the user. This, in fact, is valid for any type of solid electrodes<sup>6</sup>, but CPEs are rather an exceptional case. In contrast to commercially available solid electrodes for which basic electrochemical characteristics are comparable for almost all products of renowned manufacturers, each carbon paste represents an individual where the physico-chemical and electrochemical properties may markedly differ from case to case (regardless of the fact whether carbon pastes are hand-made in laboratories or purchased as ready-prepared mixtures<sup>2,4</sup>).

The choice of carbon paste components, their quality and mutual ratio in the mixture as well as the way of preparation of carbon pastes and their optimal homogenization - all these aspects determine the resulting behaviour of a CPE. Practical experience has shown that even the treatment of already prepared CPEs before use may play a very important role<sup>3,5</sup>. Electrochemical properties of various types of CPEs can then be predicted only approximately and their more detailed characterization requires to performing appropriate testing measurements<sup>2,5</sup>.

The testing of CPEs represents an experimental, almost empirical approach which is particularly useful for the characterization of newly prepared carbon pastes. Testing procedures comprise experiments which allow one to define all fundamental physico-chemical and electrochemical properties of carbon pastes. Moreover, procedures chosen for testing measurements should also aid to reveal some specific characteristics of individual types of CPEs<sup>5</sup>. In some aspects, test measurements can be similar or identical to those being recommended for other kinds of electrodes (e.g., voltammetric studies on potential limits and background currents, investigations on the surface characteristics by means of reaction kinetics, reproducibility measurements, etc.<sup>5-7</sup>). Also the reasons and aims for the characterization of an electrode are obviously analogous - finding the electrode of choice for a given purpose or, eventually, to proposing an optimal employment of an electrode accordingly to its parameters confirmed during the testing proper. It is typical for carbon paste-based electrodes that their testing often utilizes special steps and may include even completely unique procedures which - as a whole - are scarcely applicable to other types of electrodes. This can also be documented on a retrospective overview of the develop-

ment of various testing procedures for the characterization of CPEs.

## 1.2. Testing of carbon paste electrodes - historical survey

Adams - the inventor of CPEs<sup>8</sup> - and his research group were the first who published an extensive study on carbon pastes comprising numerous test measurements<sup>9,10</sup>. Their investigations had been focused primarily on the characterization of CPEs with respect to their applicability in anodic<sup>9</sup> and cathodic<sup>10</sup> voltammetry; nevertheless, the authors also suggested the possibilities of the optimization of the carbon paste composition. Testing measurements described in Adams's publications were carried out with carbon pastes prepared from liquid hydrocarbons and several types of spectroscopic graphite powders. Both articles<sup>9,10</sup> firstly offered interpretation of the relations between the electrochemical behaviour of CPEs and the properties of carbon or of the binder, respectively.

A study by Farsang<sup>11</sup> can be regarded as a pioneering attempt to optimize the carbon paste composition via the chemical structure of the binder by observing the behaviour of several CPEs prepared from silicone oils with different molecular weight. Monien et al.<sup>12</sup> published a detailed study in which carbon paste-based electrode had been tested and compared with other carbon electrodes.

Lindquist<sup>13</sup> carried out a systematical comparison of the properties of carbon pastes when investigating mainly the effect of liquid binders with respect to their content in the paste mixture. In this study, selected different types of liquids such as aliphatic and aromatic hydrocarbons, their halogenated derivatives, and silicone oils were always mixed with identical graphite. Testing measurements described by Lindquist were mostly based on the adoption of procedures originally proposed for voltammetric characterization of common solid electrodes.

Söderhjelm<sup>14</sup> devoted his attention to the behaviour of CPEs in dependence of the use of different voltammetric modes (potential ramps). Studies concerning detailed surface characterization of various carbon pastes were published again by Adams' team<sup>15</sup> and later by Urbaniczky and Lindström<sup>16</sup>. The former paper presented so far unknown facts on the surface states at carbon pastes and has also brought some original testing procedures. Finally, Wang et al. published several papers (e.g.<sup>17,18</sup>) in which they summarized the results on the investigation of adsorptive and extractive capabilities of CPEs.

Since that time, the problematics of the testing of carbon paste-based electrodes has not been described in more extent, including recent reviews<sup>1-3,19-21</sup>. Thus, numerous important informations published recently and dealing with the testing of CPEs are scattered in the original papers and may escape one's attention.

A need for an actual report focused exclusively on the testing of carbon paste-based electrodes initiated the idea to prepare this article. This paper summarizes all important observations, results and conclusions on testing unmodified CPEs omitting some more theoretical aspects described elsewhere<sup>1-3,19</sup>. Informations published hitherto have been updated and complemented by numerous practical notes together with illustrative examples mostly based on the authors' results.

## 2. General procedure for the testing of unmodified carbon paste electrodes

Mixtures containing merely two main components - carbon powder and the liquid binder - are now commonly classified as unmodified carbon pastes. Carbon is usually represented by spectroscopic graphite powders or related materials<sup>1-5</sup> and acts as the electroactive sensing site proper of the paste. In the classical conception, the binder ("pasting liquid") is a lipophilic organic liquid. One can name aliphatic hydrocarbons and their mixtures<sup>1,5</sup> as typical representatives of such substances.

Fig. 1 shows a scheme illustrating a possible way of how to formulate the sequence of individual steps for the testing of carbon pastes. The scheme is structured generally; i.e., it can be adapted for any electrochemical technique. Nevertheless, with respect to typical employment of unmodified CPEs, the arrangement of the entire algorithm has been made mainly for voltammetric measurements.

The scheme in Fig. 1. and its structure represent a combination of previously recommended procedures<sup>9,10,13,15</sup> with experimental approaches of the present authors. This scheme can be further modified according to one's requirements, e.g., by adding new testing procedures for some special advanced studies.

## 3. Some practical aspects on preparation of unmodified carbon paste electrodes

### 3.1. Carbon paste components and their choice

Optimal selection of both carbon powder and pasting liquid can undoubtedly be ranked among the most important factors influencing the resultant behaviour of carbon pastes<sup>1-5</sup>. In order to avoid the choice - and later testing - of evidently unsuitable carbon paste mixtures, it seems to be necessary to point out some basic principles of the preparation of carbon pastes despite the fact that most of them have already been reviewed<sup>1-6,19,20</sup>.

**Choice of Carbon Powder.** At present, various spectroscopic graphites suitable for the preparation of carbon pastes are commercially available. For instance, such products are offered in annual catalogues of Aldrich, Fluka or Riedel-de-Haën (especially the latter has proved to be a very good material for carbon pastes<sup>22</sup>). Other frequently used graphites are "Acheson" and "Graphon"<sup>9,10,15,28,29</sup>, both, however, being marketed mainly in the U.S.A. One of the best carbon powders - according to the authors' experience<sup>5,22,23</sup> - appears to be "RW-B" spectroscopic graphite from Ringsdorf Werke Ltd. (Germany). "CR-2" or "CR-5" graphites (Tesla Lanškroun, Czech Republic<sup>4,5,7,24,25</sup>) and "Sigradur" glassy carbon powders (Maitingen, Germany<sup>7,26</sup>) are also of a very good quality.

The above-mentioned carbon powders (with mesh in  $\mu\text{m}$ ) are characterized by a high uniformity of particle size distribution, high purity, and more or less suppressed sorption capabilities<sup>24,25</sup>. These characteristics are principally important for the preparation of carbon pastes which are to be used in the current measurement-based techniques such as voltammetry,

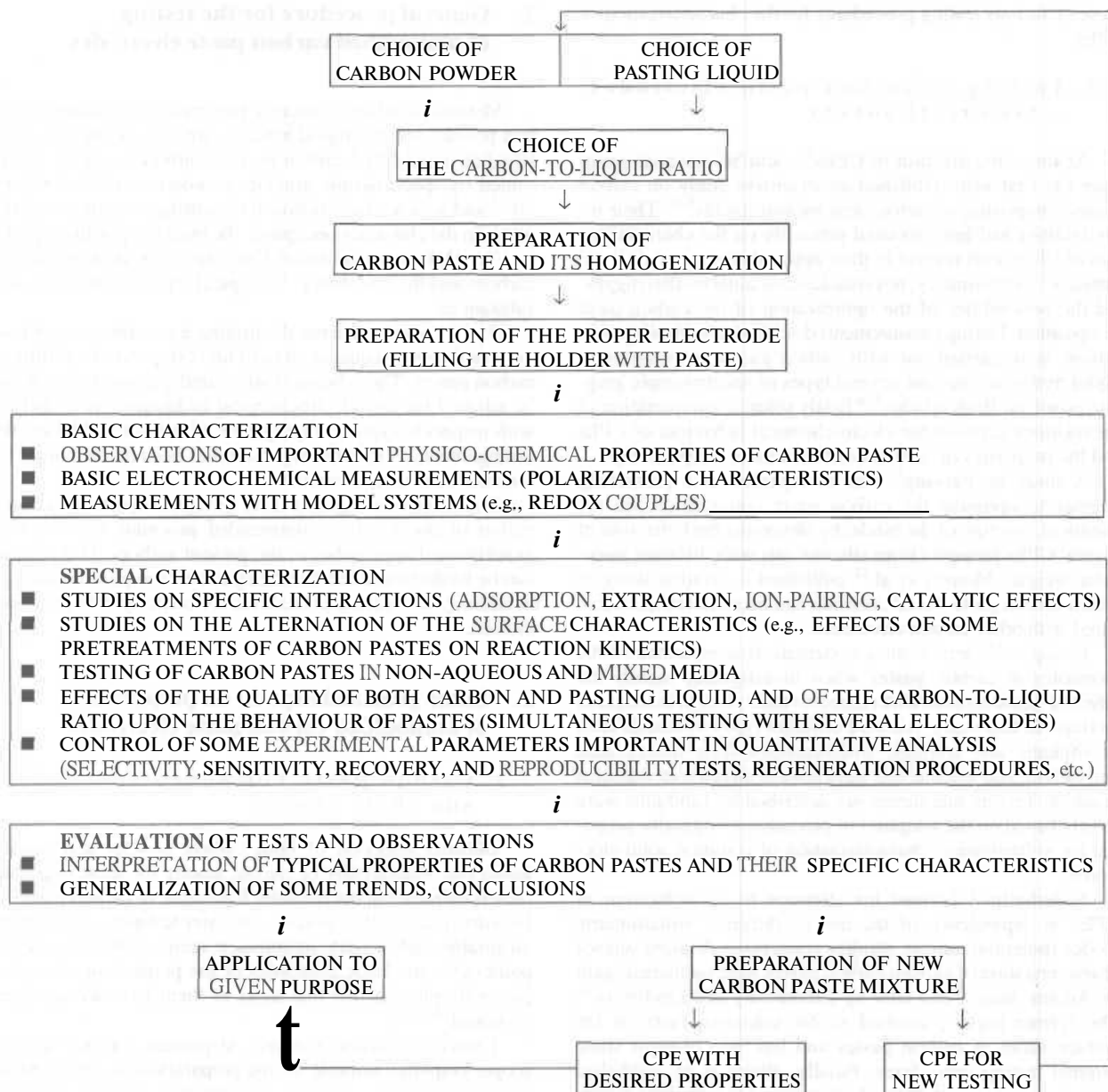


Fig. 1. General scheme for testing of unmodified carbon paste electrodes

coulometry or amperometry. In contrast to this, potentiometric sensors normally do not require the use of graphites with so strictly defined properties. Nevertheless, some carbon materials are inapplicable in potentiometry as well, for example, soot and similar porous powders<sup>5,27</sup>.

*Choice of pasting liquid.* Apparently most popular are paraffin (mineral) oils such as "Nujol" or "Uvasol"; both being commercially available from Aldrich or Merck, respectively. Various silicone oils and greases are also very suitable and frequently used; as an example, one can introduce "Lukoil" silicone oils from Lučební závody Kolín (Czech Republic). All the above-cited types of organic liquids fulfill the main criteria for carbon paste binders; they are non-conducting, minimally volatile, immiscible with aqueous solutions, and

exhibit a high chemical and electrochemical inertness<sup>1n5</sup>. Other liquids usable for carbon paste mixtures are some organic esters, e.g., tricresyl phosphate<sup>23,26,30</sup>, dioctyl phthalate<sup>25,30</sup> or dinitrophenyloctyl ether<sup>27</sup>. These substances have distinct ion-pairing capabilities which are reflected in rather unusual properties of corresponding carbon pastes.

An organic liquid mechanically binding the carbon particles markedly influences the overall electrochemical behaviour of the paste. First of all, it gives rise to the hydrophobic character of the carbon paste surface, which is - in principle - the main reason for different behaviour of CPEs compared to carbon solid electrodes<sup>1n5</sup>. Previous experience<sup>7,13,15,30</sup> has shown that testing measurements are apparently the most effective tool to reveal and to interpret relatively

complicated relations between the properties of CPEs and individual characteristics of both main carbon paste components.

### 3.2. Mixing of carbon pastes, their homogenisation, and preparation of carbon paste electrodes for measurement

Carbon powder and pasting liquid can simply be mixed and homogenized using a pestle and mortar. In most cases it is sufficient to use an ordinary and cheap porcelain dish<sup>5</sup>. Some sources claim that it is better to choose an agate mortar because of possible contamination of the paste with porcelain particles originating from the rough rubbing wall. This, however, has never been confirmed. Much more important than an equipment used for mixing the carbon pastes is the way of their homogenization<sup>2,5</sup>.

Very intimate homogenization can be achieved by the following procedure<sup>5,7</sup>: Both components are first mixed carefully with a glass rod in mortar and afterwards rubbed by intensive pressing with the pestle. This should be performed for at least few minutes and then, the seemingly compact paste is scrapped off the wall with a spatula and intimately homogenized again. It is recommended to repeat these steps several times in order to obtain a mixture as homogenous as one can get.

The ready-prepared paste is then packed into a hole in the electrode body. Its filling is made in small portions when each of them being pressed intimately before adding the next one. It is not recommended to employ freshly made CPEs immediately, but they should be left unused for a certain time (12–24 hours) to allow their final homogenization to proceed. This process of "self-homogenization" has been confirmed experimentally; freshly homogenized carbon pastes often exhibit a rather unstable behaviour<sup>7</sup>.

The quite complicated task of how to choose a suitable carbon-to-liquid ratio<sup>1,5</sup> can here be reduced to a few statements. For initial studies with carbon pastes made of components recommended in previous paragraphs, mixtures with approx. 1 g carbon powder + 0.2–0.3 ml pasting liquid appear to be optimal with respect to their consistency as well as to their electrochemical behaviour. Incidental corrections of the ratio are evaluable again from testing measurements.

## 4. Basic characterisation of unmodified carbon paste electrodes

### 4.1. Physico-chemical properties of carbon pastes

*Consistency of carbon pastes.* Typical mixtures - as expressed by the term itself - are a paste (plastic) material whose consistency can be compared to peanut butter<sup>28</sup>. Here, it should be mentioned however that some carbon pastes may not be totally compact immediately after their homogenisation in a mortar<sup>30</sup>. The required consistency is achieved later - by pressing such mixtures (originally resembling rather a powdered mass than a paste) into electrode holders. Consistency

of carbon pastes depends mainly on the carbon-to-liquid ratio, but also the components chosen. Although the consistency as such is not directly associated with the resultant electrochemical behaviour of carbon pastes, this physical parameter may indicate some important consequences. For example, too "dry" as well as too "liquid" paste mixtures are with difficulty manipulated with ordinary piston-like holders, and moreover, the surface of such pastes is usually not renewable in reproducible way<sup>2,5,7</sup>.

*Ohmic resistance of carbon pastes.* In contrast to consistency, the ohmic resistance of carbon paste mixtures already has a direct effect in electrochemical measurements depending on the type of technique used. (In voltammetry, it contributes significantly to the signal-to-noise characteristics; carbon pastes with a high ohmic resistance exhibit enhanced background currents. Potentiometric measurements with such sensors often suffer from the signal instability<sup>27</sup>). Ohmic resistance of carbon pastes prepared from insulating binders varies in ohms, maximally in tens of ohms<sup>2,4,5,7</sup>. When assuming that the resistance of the electrode body itself is negligible, undesirably high resistance of CPEs may imply the following: (i) Either graphite or binder is unsuitable and should be replaced by an equivalent. Decision on which component causes too high resistance can be made by comparing paste mixtures tested with those prepared from standardized components<sup>7,30</sup>. (ii) Carbon paste has been homogenized insufficiently; possibly, the filling of the holder with ready-prepared paste has not been done properly. In both cases, it is necessary to prepare the electrode newly and check its resistance again.

*Ageing ("lifetime") of carbon pastes.* Common carbon paste mixtures are usable for several weeks or even months<sup>4,9</sup>. Their ageing depends on more factors; the most frequently quoted being a certain volatility of some pasting liquids<sup>7</sup> and the way of storage of ready-prepared pastes. The ageing of carbon pastes is tested occasionally - in those cases when a CPE exhibits markedly unstable behaviour in time. As an example, special carbon pastes made of organic phosphates can be mentioned. Due to desiccation, these mixtures age more rapidly than ordinary carbon pastes and are applicable for two or three weeks only<sup>24,30</sup>.

### 4.2. Basic electrochemical characteristics of carbon pastes

*Potential range and background currents of carbon pastes.* These characteristics represent probably the most important parameters of CPEs in voltammetry and related techniques, and undoubtedly, they should be tested for each newly prepared carbon paste. It can be briefly stated that the potential range (defined by both anodic and cathodic potential limits) within which CPEs can be operated is determined mainly by the quality of both carbon powder and binder as well as by their mutual ratio. Similar relations can also be written for the characterization of CPEs with respect to the background currents level<sup>1-5</sup>.

Typical potential range of common CPEs depends, naturally, upon the type of medium in which measurements are to be performed. In acidic solutions, the potential range varies between -1.0 V and +1.5 V vs Ag/AgCl, in neutral media between -1.3 V and +1.4 V, and finally, in alkaline electrolytes

between  $-1.2$  V and  $+1.2$  V (Ref.<sup>7,9,10,13</sup>). In special cases, both anodic and cathodic limits can be further extended<sup>22,24,30</sup>. The level of background currents cannot be exactly defined; it strongly depends on the composition of carbon paste as well as upon the type of measurement. For instance, in stripping voltammetry, carbon pastes containing Nujol or silicone oil exhibit background currents of about  $10$ – $500$  nA (Ref.<sup>6,7</sup>) whereas the background of tricresyl phosphate-based CPE may exceed the level of  $\mu$ A due to unique interactions of the binder<sup>25–32</sup>. In such a case, it is necessary to consider the overall signal-to-noise characteristics.

In order to demonstrate the elements of the strategy for testing of CPEs with respect to their potential limits and background currents level, one can present the results and conclusions of recent studies on various carbon pastes as possible supports for mercury films<sup>7,24,31</sup>. The aim was to find such a carbon paste which could be polarizable as negatively as possible, i.e., with sufficiently high hydrogen overpotential. (This is required for every electrode support in order to be plated with an optimally generated mercury film<sup>31</sup>). Studies<sup>7,24</sup> included the testing of numerous carbon pastes prepared from different graphite powders and pasting liquids. Comparison of individual carbon paste mixtures via their cathodic potential limits and background currents level is shown in Table I. The results summarized in the table show that, in this case, the choice of pasting liquid plays a more important role than the quality of carbon powder used. Whereas the exchange of the binder in the paste results in a negative shift of cathodic limit by about  $0.35$  V, the use of different carbon powder has led only to a slight change in cathodic polarisability (by ca  $0.1$  V). Higher background currents of CPEs with lower overpotential then correspond to the fact that their signal has been affected by a residual current of starting hydrogen release. The lowest

Table I

Cathodic potential limits and background currents level for five different carbon paste electrodes<sup>7,24</sup>

Type of CPE <sup>a</sup>	Cathodic potential limit <sup>b</sup> $E_{Cl}$ [V] vs Ag/AgCl	Background current level <sup>c</sup> $I_R$ [ $\mu$ A]
RW-B/Nj	$-1.25$	$0.30$
RW-B/SO	$-1.15$	$0.50$
RW-B/TCP	$-1.50$	$0.20$
Sig.K/TCP	$-1.40$	$0.20$
Sig.G/TCP	$-1.50$	$0.10$

Measurements were performed in DPV mode using  $0.1$  M-ammonia buffer as test electrolyte. <sup>a</sup>All carbon pastes were prepared at identical carbon-to-pasting liquid ratio ( $0.5$  g vs  $0.2$  ml) from the following components: RW-B spectroscopic graphite powder; Sig. G or K, resp. glassy carbon powder; Nujol oil (Nj); Lukool silicone oil (SO); tricresyl phosphate (TCP). <sup>b</sup>Potential limits were evaluated as the current measured in the supporting electrolyte which exceeded an arbitrary value of  $1$   $\mu$ A (Ref.<sup>6</sup>). <sup>c</sup>Background currents level was defined as the mean residual current signal registered in blank electrolyte within the potential range of interest (from  $E_{cl}$  to  $0.0$  V vs Ag/AgCl)

background observed for the Sig.G/TCP electrode can be attributed to a unique structure of "Sigradur G" powder; the particles of this carbon material have specially pretreated surface with minimized sorption capabilities<sup>7,26</sup>. (Especially the sorption of electroactive impurities onto carbon particles is often responsible for markedly increased background currents of some carbon pastes<sup>5</sup>).

Carbon pastes listed in Table I were tested as mercury film supports for anodic stripping voltammetry of Zn(II). Fig. 2 makes a comparison of the responses for Zn at all five CPEs. Voltammograms shown in Fig. 2 confirm why both RW-B/TCP and Sig.G/TCP electrodes have been selected as the most suitable mercury film supports<sup>7,24</sup>. Thanks to favourable polarisation characteristics, stripping peaks of Zn obtained with these CPEs are the highest ones and only minimally affected by the background.

During the testing of CPEs in cathodic voltammetry, one will apparently register relatively high background currents appearing within a range from  $-0.5$  to  $-1.0$  V vs Ag/AgCl. This undesirable plateau-like response corresponding to the

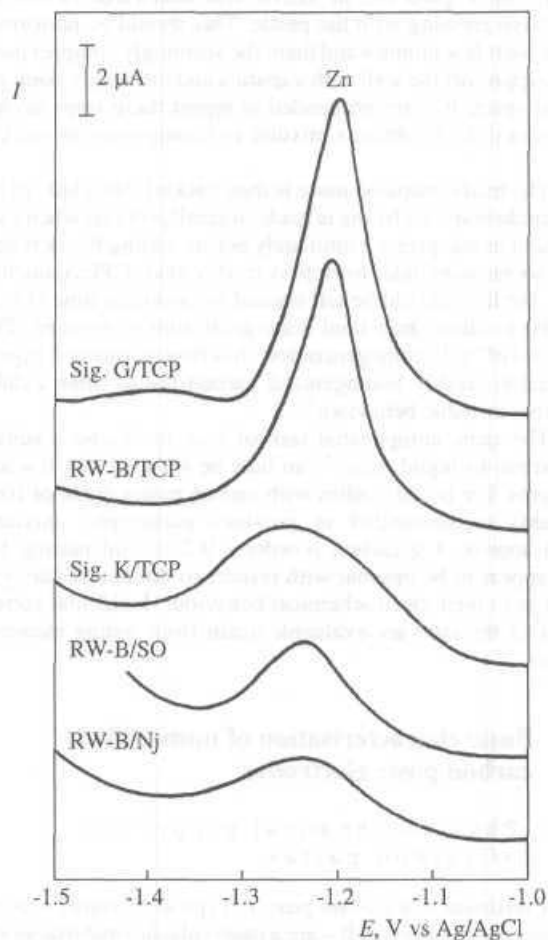


Fig. 2. Anodic stripping voltammograms of Zn at five different carbon paste electrodes<sup>7,24</sup>. Experimental conditions: DPASV,  $0.1$  M- $\text{NH}_4\text{Cl}$  +  $0.1$  M- $\text{NH}_3$  +  $1 \times 10^{-5}$  M- $\text{Hg}^{2+}$  +  $1 \times 10^{-6}$  M- $\text{Zn}^{2+}$ . Accumulation time:  $80$  s, accumulation potential ( $\equiv$  initial potential):  $-1.5$  V, final potential:  $+0.5$  V. (Denotation used for individual carbon pastes is identical to that given in Table I)



two-step reduction of oxygen (contained in the paste) cannot normally be eliminated<sup>2,4,5</sup>. Although recent test measurements<sup>32</sup> have revealed that the use of some carbon powders of extremely high purity in combination with a suitable binder may result in substantial lowering the unwanted oxygen signal<sup>7,26,30</sup>, carbon pastes as such seem to be not very suitable for cathodic reductions at potentials more negative than -0.5 V. According to some reports<sup>10,28</sup>, however, the cathodic base-line deformed in this potential interval is also usable since any reduction signal of interest can be measured and evaluated as a peak superimposed upon the flat response of oxygen.

#### 4.3. Model systems for basic characterisation of carbon paste electrodes in voltammetry

There have been proposed numerous model systems such as selected inorganic redox couples and organic compounds that, under specific reaction conditions, are electrochemically transformable into exactly defined products. Authors who were using selected model systems for the testing of CPEs<sup>9,11-13</sup> had often exploited their knowledge and experience from the electrochemistry with solid electrodes. The most suitable models for the testing of CPEs are apparently the following systems.

$[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ . This redox couple represents a typical reversible system. It can be studied in 1 M-KCl when recommended concentration of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  varies in an interval from  $10^{-4}$  to  $10^{-3} \text{ mol.l}^{-1}$  (Ref.<sup>7,9,13</sup>). By using conventional cyclic voltammetry, the potential difference,  $\Delta E_p$ , between anodic and cathodic peaks should be about 0.059 V. Markedly higher values indicate irreversible behaviour, which - in the case of carbon pastes - is mostly caused by the effect of the pasting liquid<sup>21</sup>. This phenomenon can be eliminated by lowering the quantity of binder in the paste; but, sometimes, it is necessary to replace apparently unsuitable pasting liquid by a new one<sup>5</sup>.

$\text{Ag}^+/\text{Ag}^0$ . Studies of this system recommended by Farsang<sup>11</sup> and Monien et al.<sup>12</sup> may provide information similar to that described in the previous paragraph. Cyclic voltammetry of the  $\text{Ag}^+/\text{Ag}^0$  redox pair usually performed in nitrate or acetate solutions. Some measurements with the  $\text{Ag}^+$  ion seem to be quite useful for testing CPEs in anodic stripping voltammetry<sup>23</sup>.

*Quinone/hydroquinone ( $Q/\text{H}_2Q$ )*. This redox pair is classified as "quasi-reversible" system whose reaction kinetics depends on the type of electrode used. (At CPEs, the  $Q/\text{H}_2Q$  system usually exhibits irreversible behaviour<sup>6,13</sup>). Its cyclic voltammograms are recorded in buffered media<sup>6,13</sup> covering an interval of pH 2-10; recommended test concentration of  $\text{H}_2Q$  being again  $1-10 \times 10^{-4} \text{ mol.l}^{-1}$ .

Using model systems, CPEs can advantageously be studied parallelly with some standard electrodes (e.g. Pt-disk or glassy carbon<sup>12,24,33</sup>), which allows a direct observation of incidental differences in the behaviour of CPEs and their solid counterparts. This approach is not always necessary as voltammetric experiments with common solid electrodes are extensively described in the literature (Ref.<sup>6</sup> and refs. therein), including data about all herein-discussed model systems.

## 5. Special characterisation of unmodified carbon paste electrodes

### 5.1. Studies on specific interactions with carbon pastes

Carbon paste as a unique ensemble of highly conducting centres (hydrophilic carbon particles) and insulating regions (lipophilic molecules of pasting liquid) is characterized by numerous specific interactions with the analyte<sup>26</sup>.

*Investigations on adsorptive capabilities of carbon pastes.* Detailed studies which describe the behaviour of carbon pastes with respect to adsorption processes have been published quite rarely. For instance, Lindquist<sup>13</sup> recommends to test the adsorption onto CPEs using cyclic voltammetry of phenol in buffered solutions at pH 2-10. Only a few sources (e.g.<sup>19</sup>) quote that the hydrophobic layer of pasting liquid at the carbon paste surface may promote the adsorption of some lipophilic molecules. However, in accordance with the very recent results and observations, it seems that such a kind of interaction is rather an ion-pairing than an adsorption<sup>32</sup>.

*Investigations on extraction onto carbon pastes.* Contradictorily to the somewhat unclear character of adsorption processes at CPEs, possibilities of the extraction onto carbon pastes have been clearly confirmed<sup>2,17,18,25,30</sup>. Extraction onto carbon pastes is enabled by the pasting liquid; the higher being the solubility of a substance in the binder the more effective extraction can be achieved<sup>18,25</sup>. In stripping voltammetry, accumulations via extraction belong to the most selective preconcentration mechanisms for a number of analytes<sup>2,17,30</sup>; therefore, the testing of various CPEs on their extractive capabilities is carried out relatively often. As inorganic species suitable for extraction tests with CPEs, either the  $\text{I}_2/2 \text{I}^-$  redox couple<sup>1,25,32</sup> or the  $\text{AuCl}_4^-$  anion<sup>30,34</sup> can be recommended. The effectiveness of extraction of iodine onto CPEs is well observable with the aid of repetitive cyclic voltammetry with  $5 \times 10^{-4} \text{ M-KI}$  in 0.1 M-KCl (Ref.<sup>11,25</sup>) when the peaks corresponding to the reaction  $\text{I}_2 + 2 \text{e}^- \rightarrow 2 \text{I}^-$  gradually increase. The extraction of tetrachloroaurate can be studied in 0.1 M-HCl containing  $1 \times 10^{-6} \text{ M-AuCl}_4^-$  which is accumulated at +0.8 V vs  $\text{Ag}/\text{AgCl}$  and then reduced cathodically<sup>30</sup>. Voltammetric signals of extracted species can be easily recognized as very broad peaks, which is depicted in Fig. 3. The characteristic reduction responses of  $\text{I}_2$  and Au are compared here with the sharp cathodic peak of Ni, representing a signal typical for accumulation via adsorption<sup>4,35</sup>. In this voltammogram, one can also notice a flat reduction response of oxygen contained in the paste.

Extraction studies were also performed with various organic compounds and pharmaceuticals (Ref.<sup>17,18</sup> and refs. therein) when individual measurements had to be complemented with corresponding optimization of pH value in order to aim the most effective extraction of molecules by suppressing their incidental protonation<sup>18</sup>.

*Studies on ion-pairing and catalytic effects at carbon pastes.* Recent studies have shown that above-discussed extraction of iodine and tetrachloroaurate may be accompanied by ion-pairing processes<sup>25,30,32</sup>. Iodine undergoing extraction is formed by electrolytic oxidation of iodide in the pre-accumulated  $\{\text{Q}^+, \text{I}^-\}$  ion-associate whereas tetrachloroaurate is extractable directly as the  $\{\text{Q}^+, \text{AuCl}_4^-\}$  ion-pair<sup>30</sup>. Their effective

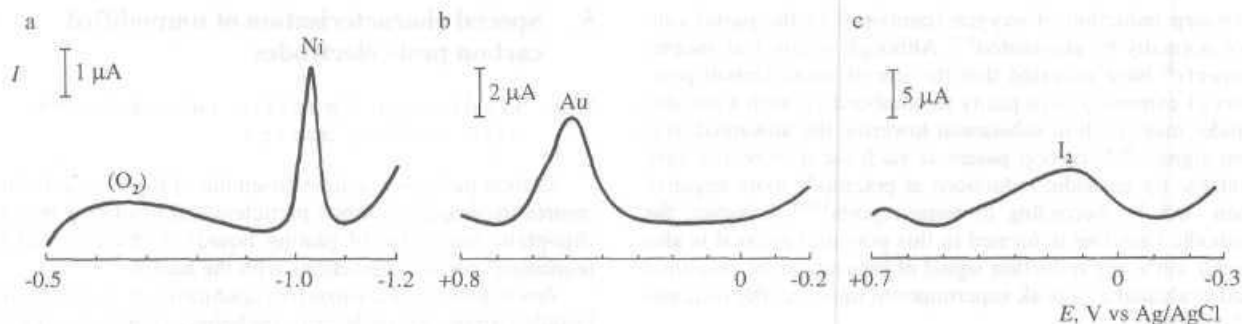


Fig. 3. Cathodic stripping voltammograms of  $I_2$ , Au, and Ni at carbon paste electrodes<sup>25,30,34,35</sup>. Experimental conditions: a) C/TCP, DPCSV, 0.1 M-KCl + 0.1 M-HCl +  $1 \times 10^{-6}$  M-I<sup>-</sup>. Accumulation time: 60 s, accumulation potential ( $\equiv$  initial potential): +0.7 V, final potential: -0.4 V. b) C/TCP, DPCSV, 0.1 M-HCl +  $1 \times 10^{-6}$  M-Au<sup>III</sup>. Accumulation time: 30 s, accumulation potential: +0.8 V, final potential: -0.5 V. c) C/SO, DPCSV, 0.1 M-NH<sub>4</sub>Cl + 0.007 M-triethanolamine +  $1 \times 10^{-4}$  M-dimethylglyoxime +  $3 \times 10^{-7}$  M-Ni<sup>2+</sup>. Accumulation time: 40 s, accumulation potential: -0.1 V, final potential: -1.3 V

preconcentration is best performable at special CPEs, permitting such an ion-pairing via positively charged ions at their surface, which is the case of protonated tricesyl phosphate-based carbon paste<sup>30,34</sup>. Otherwise, the formation of ion-pairs at unmodified carbon pastes with common binders is not very typical. The same can be stated even with respect to catalytic effects. Both ion-pairing and catalytic phenomena are a domain of chemically and biologically modified carbon pastes<sup>1-3,19,20</sup>.

## 5.2. Studies on the alteration of the surface characteristics of carbon pastes

As already mentioned carbon pastes prepared from lipophilic pasting liquids exhibit markedly hydrophobic character of their surface, including the so-called dry mixtures with a relatively low content of the binding component<sup>2,5</sup>. This hydrophobicity then results in moderately reversible or even totally irreversible behaviour of numerous compounds and redox couples at CPEs whereas the same substances measured at ordinary solid electrodes may exhibit a fair reversibility<sup>15,36</sup>. In voltammetric applications, moderated reversibility (or irreversibility, resp.) is, of course, undesirable since the signals of interest are considerably shifted towards the corresponding potential limit and therefore obscured or completely overlapped by higher background currents<sup>7,15</sup>. Besides possible change of the pasting liquid and its content in the paste, the degree of hydrophobicity of CPEs can be lowered by partial or complete removing of the surface layer of binder; e.g., by short-time exposing the carbon paste surface to extreme potentials. Under these conditions, the surface of carbon particles is transformed - depending on the potential polarity - into hydrophilic functional groups such as  $-C=O$ ,  $-C-O^-$  or  $-C=OH^+$  that are able to repel the lipophilic liquid layer<sup>15,23</sup>.

The effect of this surface alteration which is also known as electrolytic activation (or anodic and cathodic polarization, respectively) can advantageously be investigated using comparative measurements with activated and unactivated CPEs. One can recommend cyclic voltammetry of either hydrazinium ion or ascorbic acid; both representing typical irreversible systems with reaction kinetics "sensitive" to surface states at a CPE (Ref.<sup>7,36</sup>). Fig. 4 shows voltammograms obtained by analysing  $5 \times 10^{-4}$  M-N<sub>2</sub>H<sub>5</sub><sup>+</sup>Cl in phosphate buffer. As

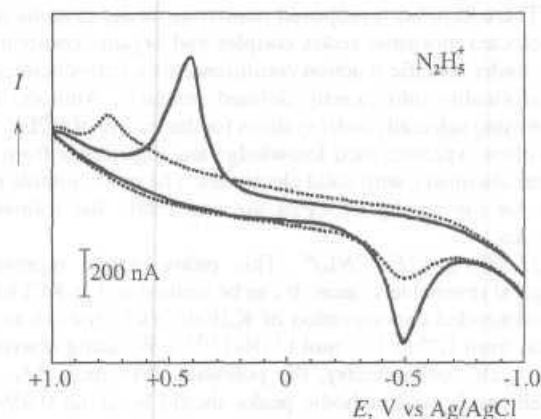


Fig. 4. Cyclic voltammograms of  $N_2H_5^+$  ion - effect of anodic activation upon reaction kinetics at a carbon paste electrode<sup>7</sup>. Experimental conditions: C/SO, CV, 0.1 M-phosphate buffer (pH 7) +  $5 \times 10^{-4}$  M-N<sub>2</sub>H<sub>5</sub><sup>+</sup>. Potential sequence: -1.0 V  $\rightarrow$  +1.0 V  $\rightarrow$  -1.0 V, scan rate: 20 mV.s<sup>-1</sup>. Dotted line: unactivated surface, full line: activated carbon paste surface (at +1.75 V for 5 min)

can be seen, anodic activation of the carbon paste surface has resulted in a shift of the anodic peak (about 0.3 V) towards the potential region with lower background; the signal-to-noise characteristics are thereby significantly improved.

Measurements similar to those shown in Fig. 4 should always include an optimisation study on the activation procedure. Unappropriately chosen parameters, mainly very high activation potential or its application for longer time may already cause too "drastical" changes at the carbon paste electrode surface accompanied by increased residual currents. Then, the originally expected positive effect of the activation procedure is practically negated.

## 5.3. Testing of carbon paste electrodes in non-aqueous and mixed media

In purely non-aqueous solution, CPEs are almost inapplicable because of disintegration of the paste<sup>1</sup>. However, some carbon pastes with strongly lipophilic binder are usable in selected mixed media in which numerous organic substances are also sufficiently soluble<sup>10,37</sup>.

The stability of CPEs in mixed electrolytes can be studied via the shape and character of the voltammetric base-line<sup>37,38</sup>. Obviously, an organic solvent in the electrolyte is miscible with the pasting liquid and its thin film (approx. 1  $\mu\text{m}$  (Ref.<sup>26</sup>)) covering carbon particles may be dissolved, i.e., removed. As a result, bare carbon particles at the carbon paste surface exhibit very high background currents<sup>15</sup> deforming the whole base-line. Recent test measurements<sup>37</sup> have confirmed that the stability of a CPE depends on the degree of mutual miscibility between the organic solvent and the binder in the paste as well as upon the content of the solvent in mixed medium. This is well illustrated in Fig. 5. The base-line of Nujol oil-based CPE is much more deformed compared to that obtained with C/SO carbon paste made of silicone oil. Increased background currents of the C/Nj electrode are indicated by the parabolic character of the corresponding curves in Fig. 5. In addition, the base-line of the C/Nj in methanolic solutions suffers from a very broad peak overlapping practically the whole anodic range. This signal, observed also in other mixed media such as 1 M- $\text{H}_2\text{SO}_4$  with 50 % dimethylformamide, dimethylsulfoxide or acetonitrile<sup>38</sup> has been identified as an extraction peak, implying a relatively high miscibility of Nujol with organic solvent. On the basis of these observations, it seems that the C/Nj and related CPEs are totally inapplicable in mixed media with common organic solvents<sup>37,38</sup>. Compared to this, the C/SO electrode has exhibited a far better resistivity against all the aforementioned organic solvents. Good stability of the C/SO electrode can be explained by minimal miscibility of highly viscous silicone oil with organic solvents tested<sup>37,38</sup>.

## 6. Some aspects of simultaneous test measurements with more carbon pastes

In order to characterize newly proposed carbon paste mixtures, it is advantageous to perform initial testing measurements simultaneously with several CPEs. In this way, one can

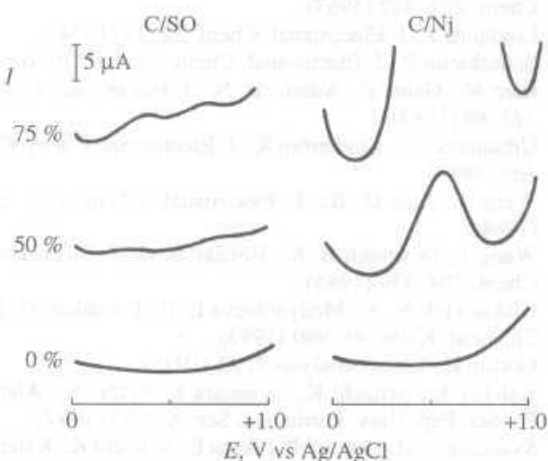


Fig. 5. Behaviour of different carbon paste electrodes in methanolic solutions<sup>37</sup>. Experimental conditions: DC-V, 2 M- $\text{H}_2\text{SO}_4$  + X % of methanol (w/w, percentage values given in Figure). Initial potential: 0.0 V, final potential: +1.0 V, scan rate: 20  $\text{mV}\cdot\text{s}^{-1}$ . (Denotation used for carbon pastes is analogous to that given in Table I)

conveniently compare the behaviour of various carbon pastes differing, e.g., in the carbon-to-pasting liquid ratio. It is advised to supplement such a set of CPEs with some other carbon pastes made of commonly recommended materials (e.g. commercially available spectroscopic graphites in combination with Nujol or Uvasol oil<sup>7,13</sup>). A parallel testing of more carbon pastes which are usually prepared at the same time is also more effective with respect to their special characterization and may simply allow the observation of ageing effects<sup>7,30</sup>.

Successful simultaneous testing of carbon pastes requires the employment of identical construction type of electrode holder for each CPE. Also, the proper preparation of individual carbon pastes and their filling into the holders should be made in the same manner. Otherwise, there is a risk that the results and observations from test measurements would be influenced by some undesirable factors (e.g., marked variability in ohmic resistance, different surface geometry or the effect of pressure upon the self-homogenisation process in various construction types of piston-like holders).

## 7. Practical remarks on the testing of carbon paste electrodes in quantitative analysis

Specific behaviour of electrode materials based on carbon paste should also be considered in quantitative analysis. Special attention shall be paid to the following aspects.

**Quality of the carbon paste surface and its control.** The success of quantitative voltammetric analysis with CPEs considerably depends upon the quality of the carbon paste surface layer which is reflected mainly in reproducibility of the signal. At CPEs, measurements are reproducible with a relative error of about  $\pm 5\%$ , but in some cases, this value may be even worse<sup>2,4,5,31</sup>. Heterogeneous and relatively rough surface of carbon pastes requires an adequate treatment<sup>1,5,26</sup>. Well-defined surface can be obtained either by appropriate mechanical renewal or using a suitable chemical reagent.

**Mechanical surface renewal of CPEs.** Quick and very effective renewal by simple removal of the used carbon paste layer is appreciated as one of the most valuable characteristics of CPEs<sup>1-5,19,20</sup>. Proper technique of mechanical surface renewal must be tested individually, best on reproducibility measurements under optimal experimental conditions for a given type of quantitative analysis. Previous experience with renewal techniques<sup>5,7,28</sup> confirms that the smoother surface the more reproducible results are attained. Especially smooth carbon paste surface can be achieved by careful wiping the surface layer with a wet filterpaper<sup>1-5</sup>. Some authors<sup>18,39</sup> use special polishing of the carbon paste surface by intensive circling with the electrode at a suitable pad. In accordance with some recent results<sup>38</sup>, both these procedures lead to comparable results and, therefore, the latter approach appears to be rather unpractical and time-consuming in situations when the surface layer of the paste has to be renewed after each measurement (e.g., in stripping voltammetry with extractive preconcentration onto carbon pastes<sup>18,25,30</sup>). The significance of mechanical renewal of CPEs in quantitative analysis can be documented on the fact that some measurements at CPEs with optimally prepared surface are reproducible within  $\pm 3\%$ , which is a value fully comparable with common solid electrodes<sup>7,12</sup>.



Table II

Carbon paste components and their mutual ratio in relation with typical physico-chemical and electrochemical characteristics of CPEs

Characteristics (phenomenon, parameter)	Carbon powder <sup>a</sup>	Pasting liquid <sup>a</sup>	Carbon-to-liquid ratio <sup>b</sup>
Consistency	+	++	→
Ageing (lifetime)	—	++	←
Potential range	++	++	↔
Background currents level	++	++	←
Reaction kinetics	+	++	→
Adsorption capabilities	++	?	←
Extraction capabilities	—	++	→
Ion-pairing	?	++	→
Effect of oxygen	++	+	↔
Stability in mixed media	—	++	↔
Analytical parameters (selectivity, sensitivity, recovery rate, reproducibility, etc.)	++	++	↔

<sup>a</sup> ++ ... Significant effect; + ... little effect; — ... with no effect; ? ... questionable effect; <sup>b</sup> → (←) ... effect is more (less) pronounced with increased content of liquid; ↔ ... dependence upon the ratio cannot be defined unambiguously

*Regeneration and conditioning of carbon pastes.* In the case of unmodified CPEs, procedures based on chemical regeneration of the carbon paste surface are not frequently used<sup>3</sup>. They have a rather limited effectiveness; nevertheless, it may result in better reproducibility and recovery rate in practical determinations. For example, the recovery of stripping voltammetric determination of mercury at trace level can be improved if the surface of carbon paste electrode support is first conditioned in a solution of 0.1 M-HNO<sub>3</sub> before being plated *in situ* with a gold film<sup>22</sup>. Carbon pastes treated in this way do not need then to be renewed mechanically and the same surface can e.g. be used for a set of 15 replicate measurements with a reproducibility of  $\pm 2\%$  (Ref.<sup>22,31</sup>). Some other regeneration procedures based on the use of solutions with special chemical reagents such as surfactants<sup>40</sup> already represent a specific way of carbon paste modification, which is a topic beyond the scope of this review.

*Storage of carbon paste electrodes.* It is recommended to place unemployed CPE(s) in a beaker with distilled water where the electrode tip filled with the paste is completely dipped down to the waterline<sup>4,5,10</sup>. Such a storage prevents mainly the desiccation of carbon pastes. CPEs stored in distilled water exhibit a very stable behaviour, only it is necessary to remove a small portion of the paste before the electrode surface is smoothed and used for further measurements. (Some previous investigations indicate that the outer layer of carbon paste exposed for longer time to the aqueous phase may be saturated with water<sup>15,38</sup>. So the debased carbon paste exhibiting enormously high background currents must be removed. The amount which is to be cut off can be ascertained simply: the paste is consecutively removed till the background drops

to a normal level; e.g., below 100 nA for silicone oil-based CPEs (Ref.<sup>7</sup>)).

Some other aspects dealing with practical applications of CPEs are already closely associated with individual methods and can be found in the corresponding original literature (Ref.<sup>1-5,19,21,28</sup> and refs therein)

## 8. Conclusion

Individual relations, dependences, and trends discussed in previous paragraphs are comprehensively surveyed in Table II.

*Financial supports of the Grant Agency of the Czech Republic (projects No. 203/98/P086 and 203/99/0044) are gratefully acknowledged.*

## REFERENCES

- Kalcher K.: *Electroanalysis* 2, 419 (1990).
- Kalcher K., Kauffmann J.-M., Wang J., Švancara I., Vytřas K., Neuhold C., Yang Z.: *Electroanalysis* 7, 5 (1995).
- Kalcher K., Cai X., Kölbl G., Švancara I., Vytřas K.: *Sb. Ved. Pr., Vys. Sk. Chemickotechnol., Pardubice* 57, 5 (1995).
- Švancara I., Vytřas K., Renger F., Smyth M. R.: *Sb. Ved. Pr., Vys. Sk. Chemickotechnol., Pardubice* 56, 21 (1992/93).
- Švancara I., Vytřas K.: *Chem. Listy* 88, 138 (1994).
- Adams R. N.: *Electrochemistry at Solid Electrodes*. M. Dekker, New York 1969.
- Hvízdalová M.: *MSc Thesis*. University of Pardubice, Pardubice 1994.
- Adams R. N.: *Anal. Chem.* 30, 1576 (1958).
- Olson C., Adams R. N.: *Anal. Chim. Acta* 22, 582 (1960).
- Olson C., Adams R. N.: *Anal. Chim. Acta* 29, 358 (1963).
- Farsang Gy.: *Acta Chim. Hung.* 45, 163 (1965).
- Monien H., Specker H., Zinke K.: *Fresenius Z. Anal. Chem.* 225, 342 (1967).
- Lindquist J.: *J. Electroanal. Chem.* 52, 37 (1974).
- Söderhjelm P.: *J. Electroanal. Chem.* 71, 109 (1976).
- Rice M., Galus Z., Adams R. N.: *J. Electroanal. Chem.* 143, 89 (1983).
- Urbaniczky C., Lindström K.: *J. Electroanal. Chem.* 176, 169 (1984).
- Wang J., Luo D. B.: *J. Electroanal. Chem.* 179, 251 (1984).
- Wang J., Desmukh B. K., Bonakdar M.: *J. Electroanal. Chem.* 194, 339 (1985).
- Ulakhovich N. A., Medyantseva E. P., Budnikov G. K.: *Zh. Anal. Khim.* 48, 980 (1993).
- Gorton L.: *Electroanalysis* 7, 23 (1995).
- Kalcher K., Schachl K., Švancara I., Vytřas K., Alemu H.: *Sci. Pap. Univ. Pardubice, Ser. A* 3, 57 (1997).
- Švancara I., Matoušek M., Sikora E., Schachl K., Kalcher K., Vytřas K.: *Electroanalysis* 9, 827 (1997).
- Švancara I., Kalcher K., Diewald W., Vytřas K.: *Electroanalysis* 8, 336 (1996).
- Švancara I., Pravda M., Hvizdalová M., Vytřas K., Kalcher K.: *Electroanalysis* 6, 663 (1994).

25. Švancara I., Konvalina J., Schachl K., Kalcher K., Vytřas K.: *Electroanalysis* in press.
26. Švancara I., Hvízdalová M., Vytřas K., Kalcher K., Novotný R.: *Electroanalysis* 8, 61 (1996).
27. Ježková J.: *MSc. Thesis*. University of Pardubice, Pardubice 1994.
28. Adams R. N.: *Rev. Polarog. (Jpn)* 11, 71 (1963).
29. Beilby A. L., Mather B. R.: *Anal. Chem.* 37, 766 (1965).
30. Švancara I., Vytřas K.: *Anal. Chim. Acta* 273, 195 (1993).
31. Švancara I., Vytřas K., Kalcher K.: *Sci. Pap. Univ. Pardubice, Ser. A3*, 207 (1997).
32. Čermáková I.: *MSc Thesis*. University of Pardubice, Pardubice 1998.
33. Galus Z., Adams R. N.: *J. Phys. Chem.* 67, 866 (1963).
34. Vytřas K., Švancara I., Renger F., Srey M., Vaňková R., Hvízdalová M.: *Collect. Czech. Chem. Commun.* 58, 2039 (1993).
35. Švancara I.: *MSc. Thesis*. University of Chemical Technology, Pardubice 1988.
36. Ravinchandran K., Baldwin R.P.: *Anal. Chem.* 56, 1744 (1984).
37. Švancara I., Vytřas K., Renger F., Smyth M. R.: *Electrochim. Acta* 37, 1355 (1992).
38. Švancara I.: unpublished results.
39. Navrátilová Z., Kula P.: *Electroanalysis* 4, 683 (1992).
40. Švancara I., Čermáková I., Vytřas K., Kalcher K.: *Electroanalysis*, submitted.

**I. Švancara<sup>a</sup> and K. Schachl<sup>b</sup>** (*<sup>a</sup>Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Pardubice, <sup>b</sup>Institute of Analytical Chemistry, Karl-Franzen University, Graz, Austria*): **The Testing of Unmodified Carbon Paste Electrodes**

The review (40 references) deals with the testing of unmodified carbon paste electrodes emphasizing mainly practical aspects of the preparation and the overall characterization of carbon pastes with the aid of specially designed measurements and experimental procedures.