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Review

Electrochemical chromatography —packings, hardware and mechanisms of interaction

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ABSTRACT

The purpose of this review is to consider the development of the liquid chromatographic technique wherein the imposition of small electrical potentials are used to induce changes in retention, in order to effect a separation. The term electrochemical chromatography is proposed for this technique in keeping with the existing nomenclature. The available mechanisms of electrochemical control over the chromatographic behaviour are discussed with their dependency upon the type of packing material. Preparation of the stationary phases and column designs are also discussed. Recent progress using conducting polymers, such as polypyrrole, as modifiers for suitable supports is given, with the conclusion that these materials may provide the foundations for the development of electrochemical chromatography into a routine and useful analytical method.

CONTENTS

1. INTRODUCTION

Many separation methods based on heterogeneous phase formations such as adsorption, ion exchange, liquid partitioning, complex formation and size exclusion have been successfully adapted for use in chromatographic procedures after the development of stationary phases with appropriate chemical and physical characteristics. Another method of separation involves electrochemically influencing the interaction between species in solution and a conducting or electro-active surface. Attempts to make use of this capability for the development of electrochemically controlled liquid chromatography were first reported by Fujinaga *et al.* [1] in 1963, and by Blaedel and Strohl [2] and Roe [3] in 1964. Since then, the technique has been contributed to by various research groups as new technology or separation requirements came to light.

The purpose of this review is to consider the development of the technique wherein the imposition of small electrical potentials are used to induce changes in retention with column liquid chromatography. In particular, the characteristics and preparation of stationary phases, that make such a technique possible, will be considered as the recent, explosive advancement of materials science and technology, most notably in the field of conducting polymers, has led to the development of numerous, viable stationary phase materials. The nomenclature and characteristics of the method, the mechanisms of electrochemical control that are available and the hardware design considerations will be discussed leading up to the treatment of the stationary phase material.

2. NOMENCLATURE

The term "electrochemical chromatography" is proposed for this technique, in keeping with the existing nomenclature of the liquid chromatography sub-group of methods. A standard and suitably descriptive name is required, as previous reports use terms that describe their own method adequately, but not others. The distinguishing feature of electrochemical chromatography, as mentioned earlier, is enhancement of separations due to the application of a potential to the column. Thus, the stationary phase material acts as the working electrode in a three-electrode electrochemical cell. Throughout this review, these two terms will be used interchangeably. A counter (or auxiliary) electrode is used in order to complete the electrical circuit. The current flowing between the working and counter electrodes may be measured if desired. A reference electrode is also required to enable precise control of the applied potential. Also, the mobile phase must have a suitable electrolytic strength otherwise a solution resistance will result and control over the applied potential will be lessened.

The manner in which all of the electrochemical and chromatographic requirements are met is discussed in detail in the sections concerning hardware design and the stationary phase material. At this stage, it is more important to give consideration to the manner in which the marriage of electrochemical and chromatographic methods produces a diversely applicable technique, mainly due to the various mechanisms available for electrochemical control over the interactions in liquid chromatography.

3. MECHANISMS OF CONTROL

As in all liquid chromatographic systems, the retention of a particular species will be determined by the distribution coefficient (K_D):

$$K_D = \frac{C_s}{C_m} \tag{1}$$

where C_s is the concentration in the stationary phase and C_m is the concentration in the mobile phase.

K_D can be altered by controlling the properties of three fundamental components of the liquid chromatography system: the stationary phase, the mobile phase and the analyte species. Regulation of each of these components has been used as the mechanism of control to varying degrees. Comparison of the use of each method clearly indicates different stages in the development of electrochemical chromatography.

The earliest examples of electrochemical chromatography used a mechanism that changed the physico-chemical form of the analyte species. The principle of controlled-potential electrolysis producing a quantitative deposition of metals, followed by stepwise dissolution, was utilized. This idea was comparatively old, having been documented previously [4–6] and is still a fundamental procedure used in electroanalytical chemistry today. However, the application of this knowledge towards chromatographic separations was not realized until after the development of large surface-area working electrodes suitable for use in flow-through systems [7–10]. These electrodes were in the form of a column and were able to perform very rapid electrolysis.

In 1965, Blaedel and Strohl [11] investigated some fundamental aspects of the newly developed method and produced a theoretical relationship between chromatographic retention and electrochemical reactions by combining the partition coefficient (K_D) with the Nernst equation.

For the deposition of metals, according to the following reaction,

$$M^{n+} + ne^- \rightarrow M^0$$
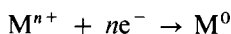
K_D becomes

$$K_D = \frac{[M^0]}{[M^{n+}]} \tag{2}$$

where $[M^0]$ is the concentration of metal deposited on the stationary phase and $[M^{n+}]$ is the concentration of metal ions in solution. The Nernst equation for the same reaction is

$$E = E^0 + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M^0]} \tag{3}$$

where E^0 is the standard reduction potential for the reaction and E is the working electrode potential (corrected for the potential of the reference electrode).

Combining eqns. 2 and 3 gives

$$\log K_D = \frac{n}{0.059} (E^0 - E) \tag{4}$$

Thus, K_D is highly sensitive to changes in E, with each change of $0.059/n$ V producing a ten-fold change in K_D, provided that the efficiency of the column is high enough to allow the partitioning to come to equilibrium.

Given this relationship, it was apparent that use of a constant potential column was restrictive, as metal ions with a standard reduction potential (E^0) more positive than the column potential (E) deposit quantitatively and show a large retention volume. Conversely, metal ions with a standard reduction potential more negative than the column potential pass through rapidly and are eluted together at a low retention volume.

This problem was overcome in various ways by different research groups. A constant potential column could be used with judicious selection of potentials for deposition and stripping [2,3,11], with the actual separation taking place at either stage. Thus, simple mixtures of metal ions could be separated by selectively plating each component at different parts of the column by applying an increasingly negative potential so that less noble metals were deposited towards the end of the column. Then, application of a suitably positive potential oxidized all of the metals, with their order of elution depending upon their position on the column. Alternatively, all of the metal ions could be deposited by applying a very negative potential and then increasingly positive potentials selected for the purpose of stripping the metals in order of increasing nobility. Blaedel and Strohl [2] compared the relative advantages of performing the separation with each approach and observed that complications arose that were dependent upon the characteristic interactions of the components of the mixture. These interactions determined which form of separation was more feasible.

Fujinaga's group had other approaches to this problem. One involved dividing the column up into sections [1] and applying different potentials to each in order to selectively deposit a particular metal, having removed other metals that could deposit at the same potential at an earlier section. Then a positive potential was applied to each section in order to strip off the metals. This idea was extended further by the use of a long column electrode through which a gradient potential could be applied [12–16]. This resulted in considerable improvement in the separation performance. The rate of change with time of the potential magnitude and the potential gradient could be programmed in order to devise the separation of complex mixtures, as the rate of electrolysis is controlled not only by the equilibrium potential, but also by the rate of change of the potential. The theory concerning the mechanism of electrolysis with a solution flowing through a porous electrode [17,18] has been developed since the 1960s and this has enabled more efficient column design to be made [16].

Readers interested in more detailed information regarding separation of metals in this manner are directed to a comprehensive review by Fujinaga and Kihara [16] that discusses the electrolytic, chromatographic and instrumental aspects of electro-chemical chromatography as well as related applications of column working electrodes

including concentration of metals, smoothing of oxidation states, elucidation of reaction mechanisms on electrode substrates and coulometric analysis.

All of the studies described so far have involved inorganic species, usually heavy metals, as the electrochemical chromatography began as a form of thin-layer electrochemistry on a large scale. However, it is possible to adsorb organic compounds from a solution flowing through a porous column electrode with application of a potential as well [19]. This principle of electrosorption has been applied to the separation of various species in chromatographic processes [20–22]. It was observed that the retention of the organic species varied with the applied potential. Thus, with the proper choice of potential, any number of components of a mixture could be quantitatively adsorbed. Selective desorption may then be achieved via stepwise potential variation in a procedure very like that followed for the electrodeposition and stripping of metals, except that the analyte species have not changed chemical form. Therefore, this process involves employment of electrochemical control over components other than the analyte itself as the mechanism for achieving separation.

Antrim and Yacynych [22] discussed the mechanism in detail and attributed it to the process of electrosorption predominantly, but noted that there was a secondary effect that was dependent upon the type of electrolyte used in the mobile phase. From an electrochemist's point of view, electrosorption involves subtle changes in the stationary phase, with a change in potential that are manifested in the form of a charge. This induces a change in the magnitude of the attraction between the substrate and the species in solution that may cause adsorption or desorption to occur. The interaction can be represented by the following equilibrium

$$A(sol) + S^{E_1} \rightleftharpoons [S^{E_2} \cdot A(sub)] \qquad \qquad (5)$$
$$\Delta E$$

where $A(sol)$ is the analyte species in the solution phase, $A(sub)$ is the analyte species adsorbed to the substrate, S^E is the substrate phase at potential E and ΔE is the change in potential from E_1 to E_2.

However, Antrim and Yacynych noted that the supporting electrolyte (mobile phase) type had a significant effect on the retention of organic species also and concluded that this resulted from a change in the composition of the electrical double layer (the interface between the stationary and mobile phases) with a change in potential. This was explained by a change in the orientation of the mobile phase, at the stationary phase, that affected the partitioning of the analyte species. Thus, a fairly insignificant change in the supporting electrolyte, from a conductivity viewpoint, was found to have dramatic effects on chromatographic behaviour in such systems. Therefore, the mechanism of control may be described as being due to subtle, electrochemically induced changes at the interface between the stationary and mobile phases. This covers both the electrosorption and reorientation effects described above.

In some cases, the imposition of an electric potential can actually change the bulk chemical composition of the mobile phase by oxidizing or reducing components. An example of where this has been used as the basis for controlling a separation was reported by Hern and Strohl in 1978 [23]. A column of graphite particles with adsorbed organic complexing agents was used to separate metals that had differing stability

constants at different pH values. The electrochemical properties of graphite are such that H^+ ions are efficiently produced by anodic currents (positive potentials) in the following reaction

$$2H_2O \rightarrow 4H^+ + O_2 + 4e \tag{6}$$

Thus, metals that were chelated to the organics could be released by electrochemically changing the pH of the mobile phase. One limitation of this form of control is that some of the ions' maximum chelate formation occurs at about the same pH.

In 1986, Ghatak-Roy and Martin [24] described a new stationary phase material that was an electro-active copolymer. Previously they had described these as ionomers; polymers that contain both electro-active and ion-exchange functionalities [25]. The copolymer described is made from maleic anhydride (the ion-exchange functionality) and vinylferrocene (the electro-active functionality). The ion-exchange characteristics of the polymer are controlled by application of a potential. In the reduced form (neutral ferrocene), cations from the mobile phase are incorporated into the film to charge compensate for the negative carboxyl groups. When the ferrocene groups are electrochemically oxidized, the positive sites formed can function as the counterion and the mobile cations are expelled. Thus the polymer can no longer behave as an cation-exchanger.

This is an example of electrochemically changing the chemical nature of the stationary phase and thus its chromatographic behaviour, in order to effect a separation. This is potentially the most powerful tool available to electrochemical chromatography as, in other chromatographic techniques, changing the stationary phase entails changing the column which is only used as a last resort.

This concept of using electro-active polymers, as stationary phase material in electrochemical chromatography, was developed further in 1989 by Ge and Wallace [26,27], who used a conducting polypyrrole-modified packing. Conducting polymers such as polypyrrole have been synthesized electrochemically and chemically [28]. As the polymer is positively charged in its oxidized form, a counter-anion is incorporated during preparation. An important characteristic of conducting polymers is their electro-active nature, as depicted in the following reaction

$$PP^+C^- + e^- \rightleftharpoons PP^0 + C^- \tag{7}$$

where PP^+ is the oxidized, charged form of polypyrrole, PP^0 is the reduced, neutral form of polypyrrole, C^- is the counter-anion and e^- is the electron transferred in the process.

For electrochemical chromatography, the application of a potential to the stationary phase can modify the chromatographic behaviour. This behaviour is illustrated in Fig. 1, which shows that separation of caffeine and theophylline on a conducting polymer column was possible only with application of a potential [27]. The chromatographic properties of the conducting polymer can also be altered by changing the incorporated counterion [29].
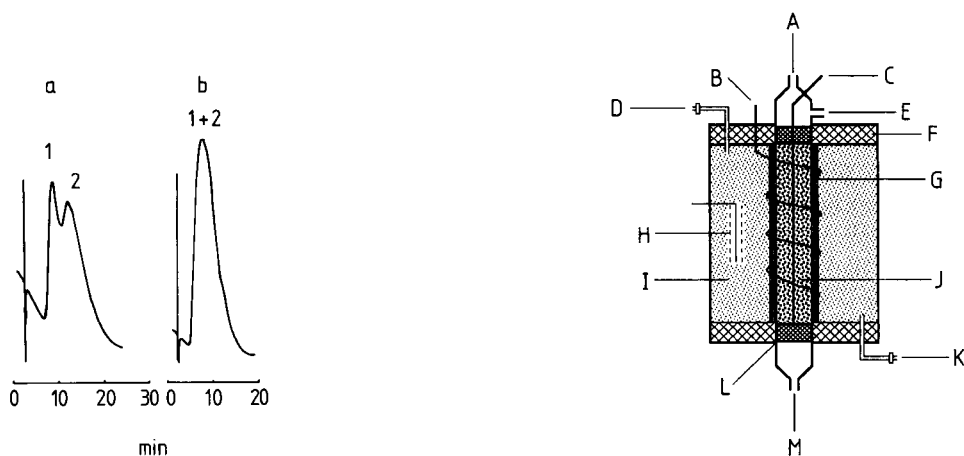
Fig. 1. Effect of an applied potential on the separation of caffeine and theophylline. Column: 100 mm × 5 mm I.D. packed with polypyrrole–dodecylsulphate on 5–40 μm RVC particles. Eluent: 10% acetonitrile in 0.02 M acetate buffer (pH = 4.5) at a flow-rate of 1.0 ml/min. Sample: 1 = 50 ppm theophylline; 2 = 50 ppm caffeine. (a) −0.20 V $vs.$ Ag/AgCl applied to the column; (b) no applied potential.

Fig. 2. General column construction. A = Mobile phase inlet; B = counter electrode; C = contact for working electrode; D = electrolyte solution inlet; E = sample injection port; F = inert seal; G = porous, insulating column or membrane; H = reference electrode; I = electrolyte solution compartment; J = working electrode (stationary phase); K = electrolyte solution outlet; L = porous glass material or packing; M = mobile phase outlet.

4. HARDWARE CONSIDERATIONS

4.1. Column design and construction

The column design must meet all the criteria of a normal liquid chromatography system. However, the incorporation of additional components (the counter and reference electrodes, electrical contacts for each electrode and electrically insulating membranes between the electrodes) imposes some new requirements and complicates the column construction. For much of the earliest work with electrochemical chromatography, column designs of a similar type were used that were suitable for low-pressure liquid chromatography only. The differences were mainly in the materials and geometric arrangements of each of the electrodes and also in the nature of the membranes that insulated them. The application governed the makeup of the stationary and mobile phases. A general column construction is shown in Fig. 2, with the main features highlighted. The most important are further described below.

4.1.1. Counter (auxiliary) electrode. In most cases this was an inert metal (platinum or silver) wrapped around the porous column. An important feature was that the electrode should have as large a surface area as possible, in order to minimize the current density, so that unwanted products were not generated and also, so that reactions at the working electrode were not limited by the size of the counter electrode.

4.1.2. Contact for stationary phase. This was usually a graphite rod or platinum wire running down the middle of the column. As all columns have a certain resistance

from end to end, due to their large size, it was important that this was minimized [10]. The arrangement described sufficiently achieves this.

4.1.3. Porous column support or insulating membrane. This was normally made out of porous glass in order to provide the necessary ionic bridge between the working and counter electrodes, as the very high dependence of the partition ratio upon the electrode potential (eqn. 4) requires that iR drops (where i is current and R is resistance) be kept to a minimum. However, problems may arise due to loss of the analyte species from the column, contamination caused by entrance of the electrolyte solution and also contamination due to reaction products generated at the counter electrode. These may be overcome by using ion-exchange membranes to minimize contamination and losses at the working electrode [24]. However, this may compromise control over the working electrode potential.

4.1.4. Reference electrode. This was not of great significance other than that it should enable precise control over the column potential. Silver or AgCl-coated silver wires performed adequately.

A major development in electrochemical chromatography was the designing of a high-pressure column that enabled high-performance liquid chromatography (HPLC) to be performed [22,23]. However, the column efficiency was still quite poor with the height equivalent to a theoretical plate (HETP) about 4–20 plates/metre. This was an area in which further work was required and was consequently undertaken in these laboratories.

A column that can resist very high pressures has been developed [26,27]. The column design is shown in Fig. 3. Electrical contact is made to the stationary phase (6) via a tantalum wire (11). A filter paper membrane (4) prevents the stationary phase from contacting the counter electrode (5) which is a strip of carbon foil wrapped around the packing bed. The reference electrode is set at the outlet of the column. A flexible-wall column suitable for use with the RCM-100 cartridge holder (Waters) is employed. Advantages of the column are that the dead volume is minimized due to hydraulic compression of the flexible column wall and that a high pressure can be applied onto the column. Both of these factors are important for attaining efficient HPLC. The HETP of this column has been measured at greater than 1000 plates/metre [30], which is an improvement, but is still much lower than values attained with other modern HPLC methods.

4.2. Electrochemical hardware

The potential of the stationary phase may be controlled using a simple
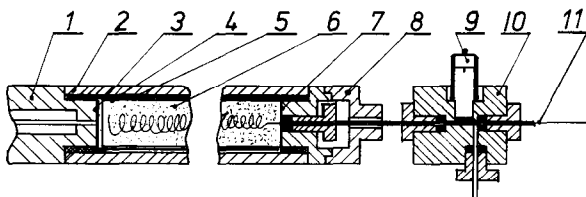

Fig. 3. HPLC column suitable for electrochemical chromatography. 1 = Stainless-steel fitting; 2 = PTFE column tube; 3 = frit; 4 = membrane; 5 = counter electrode (carbon foil); 6 = stationary phase; 7 = frit; 8 = fitting; 9 = reference electrode; 10 = PTFE fitting; 11 = tantalum coil (contact for stationary phase). Reprinted with permission from ref. 26. © 1989 American Chemical Society.

potentiostat. Commercially available electrochemical instrumentation is adequate for constant potential columns. For more complicated arrangements, involving different potential sections or gradient potentials, more specialized equipment may be necessary, as described by Fujinaga and Kihara [16].

5. STATIONARY PHASE MATERIAL

The stationary phase material must satisfy the requirements for conventional liquid chromatography; it should be chemically inert, mechanically strong, have a high surface-to-volume ratio and dimensionally thin phases. Usually porous, evenly sized particles are preferable. In addition, the stationary phase must fulfil the electro-chemical requirements of possessing good electrical conductivity and be stable over a wide potential range. However, if the stationary phase undergoes an electron transfer reaction that changes its chemical form, but does not decompose it, then an attractive means of affecting chromatographic retention is provided.

In the early stages of electrochemical chromatography, metal [1,3,10–12] and carbon [2,13] packings were employed. The mechanism of control was based on an electrochemical reaction of the analytes (M_1, *i.e.*, mechanism 1). The stationary phase acted only as an electrolytic reactor and the chromatographic selectivity was dependent upon the E^0 of the analytes. The applications using this mechanism were limited to species that underwent reversible electrochemical reactions.

Another mechanism involved using chemically modified graphite packings and affecting retention by changing the mobile phase composition, electrochemically, in such a way that the analytes would interact differently with the chemical modifiers. Thus, the chromatographic selectivity was influenced by an electrochemical reaction with the mobile phase (M_2). This mechanism is also quite limited, as evidenced by the few applications for which it has been used.

Modified packings [21,22], as well as graphite packings [20], have been used to employ a more useful mechanism in which a change at the interface of the stationary and mobile phases could be induced electrochemically (M_3). This has allowed the separation of organic species using electrochemical chromatography. Thus, as new stationary phases have been adopted, the number of mechanisms available to electrochemically influence the retention has increased.

More recently, electro-active polymers have been used as stationary phases, in which the chromatographic behaviour could be varied by electrochemically changing the chemical nature of the packing material. Thus, a new mechanism involving electrochemical control over the nature of the stationary phase has been realized (M_4).

The other improvement that has been made in the development of stationary phases for electrochemical chromatography has been in the size of the support particles used. This has parallelled developments in other types of liquid chromato-graphy, with the stationary phases used becoming smaller in recent years, thus enabling more efficient chromatography to be performed. Therefore, improvements in both the selectivity and efficiency of the stationary phases have been made since the concept was first described. The development of each mechanism, as described above, and the decrease in the size of the packing materials over the years is summarized in Table 1. Currently, work in these laboratories is being undertaken using even smaller particles (< 10 μm) in order to further improve the efficiency of electrochemical chromatography.

TABLE I

SOME STATIONARY PHASES USED IN ELECTROCHEMICAL CHROMATOGRAPHY

Stationary phase	Size (μm)	Separation mechanism	Ref.
Silver grains	850–1770	M_1	1
Graphite grains	74–150	M_1	2
Amalgamated nickel particles	100	M_1	3
Mercury-coated platinum	380–1780	M_1	11
Graphite particles	105–147	M_3	20
Trimethylchlorosilane on carbon	105–147	M_3	22
Ion-exchanger modified graphite	105–150	M_2	23
Electro-active copolymer on carbon	40	M_4	24
Polypyrrole on RVC[a]	<40	M_3	
		M_4	26, 27

[a] RVC = Reticulated vitreous carbon.

It should be noted that even though only one type of mechanism has been used predominantly, each of the previously described mechanisms may also be available. Thus, the trend in stationary phases of going from normal electrode materials to modified materials to electro-active materials has increased the scope of application and also the number of mechanisms of control available.

5.1. Preparation of stationary phases

Some unmodified stationary phases, such as graphite particles, are commercially available. Similarly, the use of metal substrates involved little preparation, other than formation of an amalgam with mercury in some instances. As the packing materials became more advanced, their preparation was more complex. The carbonaceous and other commercially available materials that were used as the stationary phases were now acting as supports for chemical modifiers. These modifiers were deposited in a number of ways, according to their nature. The modified packings used could be prepared in essentially three ways: by chemisorption, chemical bonding or polymerization.

Graphite particles were modified with complexing agents containing sulphonic acid groups using an *in-situ* chemisorption process [23]. These modifiers were not electro-active, at the potentials applied, and their interaction with the analyte species was dependent upon the pH of the mobile phase.

Other non-electro-active modifiers were coated onto conducting support-material after a chemical-grafting (silanization) procedure [21,22]. This could only be carried out *ex situ* and therefore, as the modifier was non-conducting, the thickness of the coating was critical if the packing was to maintain its conductive properties. The column was then prepared using slurry packing in ethanol at 2000 p.s.i. This packing method may also have served to maintain the electrical contacts between the support particles by forcing them to pack more compactly.

The next stage was to use electro-active modifying agents. The vinyl ferrocene–maleic anhydride copolymer was electro-active but non-conducting [24]. Therefore, it had to be deposited *in situ*, using chemisorption, after the carbon support particles had
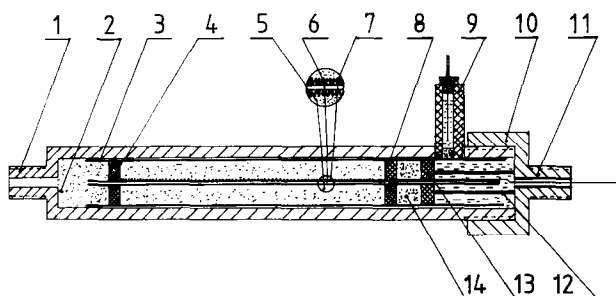
Fig. 4. Construction of a cell for electropolymerization of polymers onto conducting particles. 1 = Stainless-steel body; 2,14 = glass wool; 3 = microporous film; 4,8,13 = silicon rubber; 5 = conductive particles; 6 = PTFE tube with pores; 7 = tantalum wire coil; 9 = reference electrodes; 10 = stainless-steel cap; 11 = insulating material; 12 = plastic tubing. Reprinted with permission from ref. 29. © 1989 American Chemical Society.

already been dry-packed and electrical contact made between them. The copolymer was prepared and then dissolved in benzene, with the support particles coated by percolating this solution through the packed column.

Finally, the use of coatings that were both electro-active and conductive was established [26,27]. These conducting polymers could be deposited onto conductive supports by electropolymerization or even onto non-conducting materials, such as silica gel, using a chemical polymerization process. As the prepared particles are still conducting they may then be slurry-packed under high pressures.

In these laboratories, use of a number of new conducting materials has been experimented with as supports, e.g., carbon fibre and RVC. From these, stationary phases may then be prepared in two manners. Either, the polymer is firstly electrodeposited onto the support and this is then comminuted, sieved and slurry-packed, or the support is comminuted and sieved, before deposition of the polymer in a specially designed cell, as shown in Fig. 4.

Currently, work is being carried out in order to optimize the preparation stage so that more efficient columns can be produced. The use of non-conducting silica gel as a support, after chemical polymerization, has struck difficulties due to the low conductivity of the resultant packing. This causes a very high potential within the column and this problem may prove difficult to overcome.

The main challenge still confronting developers of electrochemical chromatography is to improve the efficiency of the columns. Use of conducting polymers has several advantages in terms of the mechanism of electrochemical control available to the user and thus, in the degree of selectivity that may be achieved. They also have a high degree of flexibility in the chemical properties that may be produced during preparation. Therefore, research into the development of suitable stationary phase materials for electrochemical chromatography, in these laboratories, will favour use of conducting polymers. The ultimate goal is to produce a technique that has its own analytical niche within the powerful group of liquid chromatographic methods.

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