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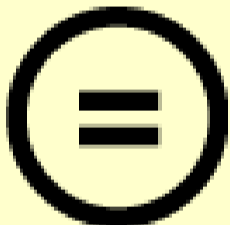
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DEVELOPMENT OF EPOXY-BASED
VOLTAMMETRIC AND ION-SELECTIVE
ELECTRODES

by

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A Doctoral Thesis submitted in partial fulfilment of the
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Tomorrow is today.

Simara (1981).

No research can succeed without freedom and a proper
spiritual and economic environment.

Jaromír Růžička and Elo Hansen in their
book on Flow Injection Analysis (1981).

To Alibert Henriques Carneiro,
my favourite philosopher, best
friend and father.

In place of the term pole, I propose
using that of electrode, ...

Michael Faraday (1834).

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SUMMARY

A highly satisfactory method of preparing graphite-loaded epoxy-based coated wire and disc voltammetric electrodes has been developed. The novel technique of multilayer coating and curing of coated surfaces in the atmosphere above a 40% m/m hydrofluoric acid solution presents many advantages: the possibility of obtaining very thin and smooth layers of loaded-epoxy base has been demonstrated to be of great versatility and convenience for the preparation of electrodes in various shapes and sizes. The technique has been extended to the easy and inexpensive fabrication of other types of voltammetric electrodes, namely coated plastic, coated glass and coated fabric electrodes, and to the preparation of ion-selective electrodes. All the electrode types have been tested and the results compare very favourably with those obtained with commercial electrodes. The behaviour of graphite-loaded epoxy-based electrodes has been examined by linear sweep voltammetry (LSV) and by differential pulse voltammetry (DPV) in various electrolytes. They exhibit very good performance in terms of very low background currents and well-shaped voltammograms.

Three different types of sulphide ion-selective electrode have been prepared and have been evaluated in standard solutions. The construction adopted here could be a viable alternative to existing methods for the fabrication of inexpensive home-made units. Epoxy-based disc electrodes especially constructed for anodic stripping voltammetry have been tested. The results obtained so far have confirmed the possibility of using these graphite-loaded voltammetric electrodes to replace glassy carbon and other expensive commercial electrodes. Loaded and unloaded epoxy bases have been used to reclaim faulty glassy carbon electrodes and, in the case of the

unloaded epoxy base, the isolation of electrode bodies from subsequent contact with electrolyte solutions. The graphite-loaded epoxy base has been used to provide electrical contact as a substitute for the more expensive commercial silver-loaded conductive resin. The construction of micro voltammetric cells for the analysis of small volume samples, and the design of flow-through and tubular electrodes for voltammetric and potentiometric analysis in the flow-injection mode, have been made the basis of preliminary studies. The coating of carbon fibres and wires to prepare microelectrodes has been considered and some initial studies have been made.

The advantages and versatility of the novel coating and hardening technique in terms of thinness and smoothness of layers, the lack of interference usually presented by common hardeners and catalysts and the resistance shown by the hardened surfaces to common reagents and solvents, have been demonstrated. The possibility of polishing and prompt renewal of dirty or damaged surfaces coated by the method presented here has been one of the advantages of the system discussed in the present work.

A simple technique of saturating the surfaces of coated plastic electrodes with graphite powder has been introduced. It has been shown to be of great help in the fabrication of coated plastic electrodes and other systems of comparatively low electrical resistance.

INTRODUCTION

Electrodes and electroanalytical methods

Electroanalytical chemistry originated from electrochemistry, a branch of classical physical chemistry. Its foundations were formulated in the middle of nineteenth century. The basic quantitative relationships of potentiometry and polarography derive from thermodynamics. Furthermore, polarography, and voltammetry in general, is based on studies of diffusion in solution. These qualitative relationships permit the application of electrochemical principles to the identification of chemical species in solution and the interpretation of oxidation-reduction mechanisms. This process of electron-transfer reactions at electrodes constitutes the basis of electroanalytical chemistry.

A combination of thermodynamics and kinetics is essential for the measurement of important parameters related to the mechanism of electron-transfer reactions and the characterization of surface phenomena at the solid-liquid interface. The latter is of great importance for the understanding of catalytic interactions.

The advancement of fundamental theory and the progress in instrumentation as well as the development of new sensors for potentiometric analysis, have resulted in an increasing importance of electroanalytical chemistry. The investigation of inorganic, organic and biochemical systems, the study of metal complex formation and the study of the electrochemical behaviour of organometallic compounds, and other important substances, have been related to the work of the modern electrochemist (1-5). Recently, electroanalytical chemistry has been intensively applied to neurochemistry and to environmental pollution control. The term bioelectrochemistry designates its application to the analysis of biological samples either in

vitro or in vivo (6-10).

The fields of electrochemistry and electroanalysis are completely dependent upon each other and it is not possible to define electroanalytical chemistry simply as an application of electrochemistry as stated by Kolthoff some years ago (11).

Modern electroanalytical chemistry can be regarded as the area of analytical chemistry and electrochemistry in which the electrode is used as a probe, to measure something that directly or indirectly involves the probe but in which the desired information is not concerned with the fundamental operation of the electrode process (12).

The development, study and improvement of electrodes, mainly as selective sensors is the principal objective in the area of electroanalytical research, named voltammetric techniques, coulometry and ion-selective electrodes, including the use of flow-injection analysis and computerized titroprocessors (13).

The electrode as a probe measures what is occurring in the interphase region adjacent to the electrode surface and not the properties of the bulk solution. In any electrochemical experiment it is relevant to consider the transformations that happen in the surroundings of the electrode, regarded as an interphase region that extends out of the electrode into the electrolyte and another interphase region going from the electrode interface inwards. At the electrode interface, a transfer between electronic and ionic conductors takes place.

In principle any electrode is a junction between an ionic conductor and an electronic conductor: it is the interphase region in which currents change from being carried by the movement of ions, in the electrolyte to being carried by the movement of electrons in the electrode itself. The work of electroanalytical chemists is concerned with the operation of inserting electrodes, as probes, into solutions to investigate the properties of

electrolytes.

The electrochemical experiment is better represented by voltammetry, and can be compared with a spectrophotometric equivalent experiment where controlled radiation of determined wavelength is absorbed by an atomic or molecular species, and the response, in the form of a spectrum gives information about the structure and behaviour of the system under investigation (14, 15).

In the voltammetric electroanalytical experiment, the transport of ions and electrons, causes an electrical current to pass through the electrode, and produces a response represented by a current-potential curve. This curve generally can be related to the concentration of the species present in the interphase region of the electrode. Further it serves to give information related to several aspects explaining the structure and kinetics of the electrochemical reactions.

The design of new electrodes with predetermined shape, size and chemical characteristics, to be used in a particular electrochemical cell and determination is the fundamental cause of progress in the electroanalytical chemistry, leading to the development of new methods. It is also responsible for the renaissance and improvement of old techniques.

Electrochemical methods of analysis have been described and discussed, comprehensively either in theory or in their practical aspects by several authors. Reviews and books dealing with the most important techniques have been published. In general terms, the majority of electrochemical techniques can be performed either by controlling the potential applied to the working electrode and measuring the resultant current (potentiostatic mode) or by controlling the current imposed to the stationary working electrode, which becomes polarized, and measuring the variation of potential during the electrolysis (galvanostatic mode, chronopotentiometry and coulometric titrations) (16).

Chronopotentiometry is based on the dependence of the electrode potential on time and the important parameter to be determined is the transition time, τ . At the transition time, the concentration of the ions being reduced at the electrode becomes equal to zero, and the potential of the electrode changes rapidly toward more negative values, until a new cathodic reaction occurs. This could be the reduction of the supporting electrolyte. The chronopotentiometric method is useful as a general analytical tool and in the kinetic studies of electrode processes (17).

All specialized areas in the field of either electrochemistry or electroanalytical chemistry named potentiometry, controlled potential and controlled current methods and conductimetric titrations are centred on the behaviour of electrodes in various media.

Platinum has been one of the most used materials for the construction of electrodes since early work in electroanalysis (18, 19). Platinum and other noble metals have been used frequently in the order Hg, Pt, Au, and less occasionally Pd, Rh, Ir. They are practically inert in respect of chemical reactions with the majority of the electrolytes (20, 21).

Mercury has been chosen for the great majority of experiments for many reasons, mainly because it is a liquid at room temperature which provides several advantages from the electrochemical viewpoint.

Laitinen and Kolthoff (22, 23) pioneered the studies of diffusion conditions at platinum electrodes and introduced the term voltammetry to determine that part of electrochemistry related to the determination and interpretation of current-voltage ($i-V$) curves. In the case of a voltammetric process occurring at a dropping-mercury electrode (DME) this particular case of voltammetry is called polarography as suggested by Heyrovsky (24) who invented the technique.

Voltammetric experiments are conducted in a voltammetric cell provided with a convenient system for deaeration of the electrolyte by purging the

electrolyte solution with nitrogen. This is a practical means of avoiding the presence of oxygen when its absence is convenient or essential for the determination. Modern voltammetric analysis is generally accomplished by a three-electrode system: an indicator or working electrode (WE), a reference electrode (RE) and an auxiliary or counterelectrode (AUX). The working electrode is that electrode whose potential varies with the electromotive force applied to the cell. The resultant current is a function of the process occurring at the working electrode and this in turn is related to the characteristic structure of the particular working electrode. The reference electrode is that whose potential is constant during the experiment and is said to be depolarized.

In modern three-electrode circuits it is ensured that no current flows through the reference electrode. The current flows between the working electrode and the auxiliary electrode which in general is made of platinum foil or wire. The potential of the counterelectrode is not relevant for it serves only to complete the electrical circuit. The potential of the working electrode during the electrolysis is measured in relation to the reference electrode.

The measurement of the current that flows at an electrode as a function of the potential applied to the electrode may be used for qualitative information related to a particular species in solution as well as for quantitative electrochemical analysis (25).

A variety of electrode material has been employed as voltammetric electrodes and their utility is determined mainly by their potential limits considered as its useful potential range and by the size and reproducibility of their currents in the medium used in the experiment.

In the cathodic region, that interval of potential or voltage "window" is determined by the reduction of the supporting electrolyte or reduction of the solvent which in general ends with the evolution of hydrogen. This is

due to the reduction of hydrogen ions present as part of protic solvents. In the anodic (positive side) region the useful potential range or "cutoff" is limited by the oxidation of the supporting electrolyte, oxidation of the solvent or by dissolution of the electrode material to form ions in solution as well as metal oxides, or by the formation of oxygen in water or other solvents which contain oxygen atoms in their structures.

The voltage limits for any electrode varies with the sort of material forming the electrode and with the type of solvent present in the system. The useful potential range for the solid electrodes commonly used has been reported in the literature as determined by many authors (26-29). They belong to an extensive list including noble metal electrodes and electrodes made of inorganic compounds such as oxides, carbides, silicides, and nitrides.

More complex voltammetric electrodes have been produced based on the modification of the surface of solid electrodes via complexation, electrochemical polymerization or adsorption of suitable species. The importance of this new group of "surface modified electrodes" is growing very rapidly (30-32).

Mercury electrodes

Mercury has a melting point as low as -39°C , permitting its use in dropping, streaming or pool configuration which is not possible with solid electrodes. The dropping-mercury electrode (DME) as well as the streaming mercury electrode has the great advantage of providing a continuously renewed surface. This decreases greatly problems related to adsorption of species and impurities from solution and film formation due to the products of electrolysis. Furthermore mercury produces a smooth and continuous surface with a very reproducible surface area and needs no pretreatment or polishing which is necessary with solid electrodes. Finally the high overpotential for hydrogen evolution together with the properties mentioned above make this

material the most useful voltammetric electrode for cathodic processes.

One disadvantage of mercury electrodes is related to the narrow anodic window presented which is limited by the dissolution of the metal around +0.4V versus saturated calomel electrode (SCE). Therefore it is not suitable as an electrode material for most oxidation processes, which includes an important variety of oxidation reactions of organic compounds. For that reason the studies related to anodic voltammetry are better accomplished by solid electrodes, mainly carbon electrodes.

The use of mercury electrodes in electrochemical experiments at high temperatures is not possible owing to the low boiling point of the element (356.6°C). This makes it ineligible for studies in fused salts and corresponding systems at high temperature.

The dropping-mercury electrode (DME) is formed usually by a length of capillary with an inside diameter of about 0.06 to 0.08mm. The top of the capillary is attached to a longer tube containing a column of mercury that is kept in electrical connection with the measuring circuit. During the experiment the tip of the capillary is immersed in the electrolyte under investigation; mercury is able to flow and forms a droplet at the tip that grows until it reaches a determined size which is a function of the geometry of the capillary tip and the interfacial tension between the mercury and the solution. After the natural or forced falling of the first droplet, another starts the cycle by a similar process, growing until it reaches practically the same size within a high degree of reproducibility which it is not possible to obtain with other voltammetric electrodes. In the course of electrochemical determination (a polarographic determination) using this dropping-mercury electrode, the measured current varies during the life of each drop as a function of the increase of the drop area. As subsequent drops pass through the same cycle, following the same process, the average current will be the same from drop to drop.

The continuous expansion and development of polarographic methods of analysis whose renaissance came with the introduction of modern instrumentation capable of carrying out pulse polarography and related techniques (33-35) is largely related to the peculiar and outstanding properties of the dropping-mercury electrode: it does not suffer from the accumulation of solid products, such as adsorbed species, deposited metals, or noble metal oxides; this, coupled with the comparatively small area of the droplet on which the electrochemical reaction occurs, results in an electrolysis free from the accumulation of soluble products and at the same time with a negligible depletion of the bulk solution (36).

Other forms of mercury electrode have been constructed and their potentialities evaluated for some special applications. Among the various types of mercury electrode is the mercury pool electrode (37, 38), which is used either in unstirred or in stirred conditions. Reilley et al (39) applied the mercury pool electrode in a detailed and successful chronopotentiometric experiment in several supporting electrolytes. It has been considered the simplest form of mercury electrode and useful for controlled-potential coulometry, chronopotentiometry and other purposes(40).

The streaming mercury electrode introduced by Heyrovsky and Forejt(41) for use in oscillographic polarography has been considered in respect of its theoretical treatment (42) and has been modified by Lévêque (43) and by Volkov (44) in more or less the same way, using a metal wire or metal plate through which the mercury could flow providing a continuously renewed surface.

From a modern approach, the streaming mercury electrode can be considered as a dropping-mercury electrode with short controlled drop time (45) so that theoretically it would be possible to obtain a transition between a DME and a streaming mercury electrode. Practically this has been verified and recent studies have been done with a kind of short controlled

drop time electrodes named the vibrating dropping-mercury electrode (vdme) whose superiority over the DME for some special application has been demonstrated (46). This interesting aspect of rapid (dc) polarography has been the subject of active research (47). Two other types of mercury electrode have gained increasing importance for voltammetric determinations. They are similar to solid electrodes, for their configuration is quite different from that of the DME: the first one in importance and popularity is the so-called hanging-mercury-drop electrode (HMDE), developed by Gerischer (48) and Berzins and Delahay (49), and applied by Ross, De Mars and Shein (50) to the reduction of zinc, cadmium, lead and thallos ions, in voltammetry with continuously varying potential. They have demonstrated that voltammetry at the HMDE is more sensitive and reproducible than conventional polarography. The HMDE has been studied by Kemula and Kublik (51) and new versions have appeared. Commercial apparatus for electroanalysis has included the hanging-mercury-drop electrode, as an essential part of their equipment, for routine analysis. The other "solid" type of mercury electrode, the mercury thin-film electrode (MTFE) is made of a thin film (1 to 100 μ m) of mercury plated on some solid electrode used as the support so that only the thin mercury film is exposed to the electrolyte. Platinum has been used for that purpose since the work of Marple and Rogers (52) who examined the polarography of a variety of compounds on a mercury-plated platinum electrode, including reduction of organic compounds. Carbon electrodes have been preferred for the preparation of MTFE as the carbon surface can be very flat and smooth and does not interact with mercury to form amalgams, as is the case with the metallic electrodes. This prohibits in particular the use of gold as a support for mercury. The great value of the MTFE has been in stripping voltammetry in which technique the mercury film is plated in the course of the procedure (53) usually on the flat surface of either a glassy carbon disc electrode or on another convenient

carbon disc electrodes. These possibilities are described later in the experiments on anodic stripping voltammetry at an epoxy-based graphite-loaded disc electrode prepared as mentioned here (see p128).

Platinum, gold and silver electrodes

Platinum is the noble metal most commonly used as a solid electrode for voltammetry although gold is a better choice for cathodic processes (54). Both metals are easily obtained in a high degree of purity and can readily be machined in a variety of geometric shapes suitable for the construction of electrodes: wires, rods, sheets and woven gauzes. They are resistant to oxidation but are not completely inert.

Platinum has a very small overpotential for hydrogen evolution. On the other hand gold has a comparatively large overpotential, although it is much smaller than that for mercury. Platinum adsorbs hydrogen to a small extent but this is very small compared with for example palladium which dissolves hydrogen into the bulk metal.

Gold is recommended as the best choice for a solid voltammetric electrode intended for cathodic reactions because it does not adsorb appreciable quantities of hydrogen and has a large overpotential for hydrogen evolution. As mentioned above, possibly force of habit has contributed to the extensive use of platinum as an electrode. At high positive potentials all the noble metals are oxidized and a layer of oxide film is formed on their surfaces probably constituting chemisorbed oxygen, but phase oxide can be created and grow under more rigorous conditions of anodization (55). Several authors have studied the problems of oxide formation at the surface of noble metal electrodes. A chronopotentiometric procedure to demonstrate the electrolytic formation of PtO and PtO_2 , on the platinum surface, has been described by Anson and Lingane (56). Rand and Woods have investigated the dissolution of the noble metals and confirmed previous reports that platinum dissolves under anodic conditions even in the absence of complexing acids (57). Palladium and rhodium

also dissolve, more rapidly than platinum and gold. Anson and Lingane (56) have shown that noble metal electrodes formed from gold, platinum, palladium and rhodium dissolve in 1M H_2SO_4 , during experiments with cyclic voltammetry. A consequence of that is the alteration of the surface composition and electrochemical behaviour of solid electrodes made from noble metal alloys (Pt-Rh and Pd-Au).

Platinum and gold when used as working electrodes must be cleaned with chromic acid usually after each determination (58).

The most usual form of platinum electrode is made from a suitable platinum wire sealed in soft glass. Electrical contact is provided by mercury or a soldered copper wire to the platinum. Materials other than glass can be used to support the platinum wire provided that the support can be conveniently isolated from the electrolyte solutions by means of a cement sealant. Gold seals poorly to glass and at the same time it easily amalgamates, and this prevents the use of mercury to complete the electrical connection. A metal contact must be used. A variety of commercial adhesives available nowadays facilitates the problem of constructing a convenient holder for noble metal electrodes. Special configurations for electrodes made from metal powders encapsulated into soft glass has been described by Guilbault and Lubrano (59).

All the noble metals including mercury, are more easily oxidized in the presence of complexing anions like halides and cyanide. They have a narrower usable potential range in the presence of such anions. Gold suffers seriously from that effect as it forms stable tetrachloro and tetracyano complexes of Au(III) and so should not be used in the presence of these complexing agents in which solutions it shows a shorter potential range (17, 60). Silver is used much more in the construction of reference electrodes, for example the silver-silver chloride reference electrode. Silver metal is normally used in the form of wires or foils. It is difficult to seal into glass and it is recommended to seal platinum into glass and spot weld a silver wire to the platinum, as

described by Sawyer et al. (61).

As an indicator electrode, silver has been used amalgamated (62) but even in this case it appeared that the results were not satisfactory. Silver as a voltammetric electrode has not been included by the authors of books on electroanalysis. Plambeck considered the silver electrode as important as the most common noble metal electrode (63) but did not mention any directly application of the use of that metal for voltammetric purposes. Possibly this is due to the fact that silver is not as inert as the other noble metals, and so is less convenient. Alder et al (28) in their comprehensive study on the electrochemical behaviour of various materials have not included silver in the group of materials studied for the construction of voltammetric electrodes. The importance of silver electrodes in voltammetry has not been confirmed by later studies although this material has been studied as early as 1897 when Salomon described current-voltage curves for several electrolytes using the respective metals as stationary working electrodes (64).

Palladium, rhodium and iridium electrodes

Palladium, rhodium and iridium, have been used extensively in voltammetry (12) in spite of several drawbacks: chemisorption of oxygen on rhodium and palladium (55) and adsorption and absorption of hydrogen in large quantity on palladium surfaces(15). This allows the possibility of the construction of a palladium-hydrogen reference electrode (15). However it makes palladium unsuited for use in most voltammetric work. Palladium has a very small overpotential for hydrogen evolution but dissolves under anodic conditions more rapidly than platinum and gold. The same phenomenon occurs with rhodium. These metals can be obtained in the state of great purity, in the form of wire, rod or sheet and normally they have been used constituting alloys with platinum or gold. An alloy of platinum containing 10 % of rhodium has been studied by Alder et al and was shown to behave in the same way as platinum but palladium

electrodes have been demonstrated by those authors to show a much lower anodic range and to present an anomalous value for the Fe(II) oxidation potential. This unusual behaviour of palladium has been attributed to the uneven shape of the electrode whose surface area was reduced by covering most of the surface with Araldite (28). Alder et al (28) have studied the voltammetric behaviour of the iridium electrode and verified that this electrode shows a lower anodic range with rather erratic and poorly-defined oxidation peaks. These findings indicate that palladium, rhodium and iridium cannot be normally considered as an alternative to replace platinum and gold as voltammetric electrodes.

Carbon electrodes

Carbon electrodes made from spectroscopic grade carbon graphite are inert and are useful for electrochemical oxidations or reductions. Nevertheless because of its wide positive potential range electrodes made of this material have been mainly employed for anodic voltammetry, which encompasses the oxidation of a variety of important organic compounds.

Several types of graphite electrode have been prepared and described in the literature and their advantages and disadvantages as well as methods of construction and application have been considered in various books, including chapters on voltammetric techniques at solid electrodes (12, 15, 18, 29).

All the types of graphite electrodes produced so far present many problems concerning their particular structure, porosity, facility of construction and renewing of their active surfaces. The latter constitutes a very especial point to be considered as it is related directly to the reproducibility of measurements performed with any kind of electrode. The capability of renewal of the surface intrinsic to the dropping-mercury electrode is matched by none of the voltammetric electrodes. Several studies have been presented and suggestions have been made to overcome these problems, and to improve the

performance of solid electrodes, especially carbon graphite electrodes, by virtue of their confirmed utility. Among the numerous papers involved with applications of this kind of electrode, many are concerned with the surface pretreatment, and several recommended procedures for obtaining better results and extending the useful range of carbon electrodes, have been mentioned recently in the literature. Even though it appears that the search for a solution concerning the problems of adsorption and film formation will remain for a long time one of the most intriguing tasks for electroanalytical chemists. Studies of limiting currents at carbon rod electrodes were first considered by Wilson and Youtz, in 1923 during their work on the importance of diffusion of species in organic electrochemistry. They investigated fundamental diffusion principles at such electrodes using a cylindrical carbon anode of large area, separated from the cathode, a large hollow carbon cylinder, by a porous cup (65). In 1953-54, Lord and Rogers examined the voltammetric behaviour of carbon rods, as part of their intention to explore new materials for voltammetry other than gold and platinum which have been compared in the same paper (66, 67). In their work they claim that graphite electrodes have been investigated because they offered a rapid means of obtaining a fresh surface. This offered a definite advantage over the platinum electrode.

Carbon graphite for using as an electrode material is usually spectroscopic grade rod or powder and electrical connections are provided by a battery clip, mercury or with the help of any conductive epoxy resin, commonly a commercial silver-loaded epoxy resin. The utility of untreated graphite electrodes is limited by both poor sensitivity and, in some cases, poor reproducibility (67).

Electrodes made of untreated carbon present high background currents. Because carbon electrodes have proved to be the most satisfactory for many applications, many electrodes of this type have been developed after the

discovery that thorough impregnation with wax removes much of the undesired residual currents, lowering the background currents to acceptable values for voltammetric purposes.

Gaylor, Conrad and Landerl (68), described the use of a wax-impregnated graphite rod electrode and stated that absorption of wax into the electrode pores, greatly reduces the high residual currents normally found with the plain graphite rod. They showed at the same time that the sensitivity to small concentrations of voltammetrically active species largely increased and the reproducibility improved. They have applied the wax-impregnated graphite electrode (WIGE) to both oxidation and reduction reactions. In the positive potential region they studied the oxidation of typical organic compounds of the phenolic, amino and diamine types and in the negative potential range they studied the reduction of typical inorganic substances. These authors have shown that the impregnation of the pores of the graphite with a solid wax reduces residual currents to negligible values without affecting faradaic currents to the same extent. The resulting wax-impregnated graphite electrode (WIGE) displays greatly increased sensitivity to low concentrations and highly improved reproducibility. Depending on the type of wax used, the WIGE can be employed for voltammetry in either aqueous or nonaqueous media.

Taking into account the solubility of the wax in the test solution, several types of impregnating agents were considered at that time, including opal, ceresin and castor waxes, and the indicator electrode was prepared by soaking a 0.25-inch graphite rod (spectroscopic grade), in molten opal wax at 100°C for 2h. After ^{being} removed from the melt and allowed to cool the surface of the rod was coated with this sealant. To be used as an electrode the impregnated surface of the rod was cut conveniently, at the lower end, and abraded with a fine abrasive sand paper. This procedure of cutting, and polishing was repeated before each new scan.

Elvin and Krivis, investigated the properties of ceresin-impregnated

graphite rod electrodes for chronopotentiometric determinations (69).

Morris and Schempf (70) developed a new method for the preparation of better impregnated graphite electrodes by evacuating the graphite rod removing the trapped air in it and fully impregnating the pores, using melted wax at 125°C. Later, Elvin and Smith (71) made some improvements in the WIGE and obtained better electrodes using a procedure of prewetting of the electrode surface by a dilute solution of a wetting agent. The performance of the prepared electrode was evaluated in quantitative analysis by cathodic and anodic chronopotentiometric and voltammetric measurements. The results obtained by these authors compared favourably with the results obtained with platinum electrodes.

Another kind of useful graphite electrode, the pyrolytic graphite electrode, has been produced in conditions of high temperature (1900–2500°C) by the decomposition of carbon-containing gases in an inert atmosphere (72). They have been applied to the voltammetry of V_2O_5 in a LiCl-KCl eutectic by Laitinen and Rhodes (73) and applied for the first time in aqueous solutions voltammetry by Miller and Zittel (74, 75). Ionic species having decomposition potentials within the range +1.0V to -0.8V can be determined with this electrode as precisely as with the dropping-mercury electrode, when the DME is applicable. The preparation of pyrolytic graphite electrodes is rather complicated and the technique of its preparation together with the provision of suitable electric contact has been described by the authors mentioned above. Beilby, Brooks, Jr. and Lawrence (76) have made a comparative study of wax-impregnated graphite electrode and pyrolytic graphite electrode, using the techniques of chronopotentiometry and integral chronoamperometry. They studied the ferrocyanide-ferricyanide system: the results obtained with pyrolytic carbon film electrodes compared favourably with similar results obtained with platinum electrodes but at wax-impregnated carbon electrodes they obtained results in disagreement with other workers; they concluded that the reactions

at the latter electrode appears to be more irreversible. The so-called "carbon paste electrode" was proposed by Adams (77, 78) and has been applied to the study of many compounds by Olson and Adams (79, 80) in aqueous medium. Carbon paste electrodes have been prepared for using in nonaqueous media by Covington et al (81) and Mareoux et al (82). Lindquist proposed a new carbon paste electrode holder and a simple method for preparing reproducible electrode surfaces (83). He developed a carbon paste electrode with a wide anodic potential range (84). A new carbon paste electrode developed by Atuma and Lindquist (85) has been applied to the voltammetric determination of tocopherols.

These authors described the method of preparation of this new type of carbon paste electrode made from a suitable amount of ceresin dissolved in n-hexane and mixed with graphite powder. After the evaporation of the solvent silicone oil was added and mixed in order to form a homogeneous paste. The electrode was prepared in the same way as described by Adams (77, 78) by filling the corresponding cavity of the electrode holder (84). After each measurement with the carbon paste electrodes usually a small amount of the paste has to be removed and a fresh amount of the mixture replaces the previous one. This readily guarantees a satisfactory renewed surface. This constitutes a great advantage of carbon paste electrodes. This was confirmed and emphasized by Lindquist during his studies of seven types of carbon paste electrode (86). Recently, Štulík et al (87) examined the properties of carbon paste electrodes when used as voltammetric detectors in high-performance liquid chromatography. They prepared several new solid-matrix carbon paste electrodes, and tested them in thin-layer and wall-jet cells. Pungor and Szepesváry in describing the construction and voltammetric use of silicone rubber-based graphite electrodes reviewed this subject (88). In 1973 Mascini, Pallozi and Liberti (89) described a polythene-graphite electrode for voltammetric use and in 1975 Klatt et al (90) characterized a

graphite-Teflon electrode for voltammetric applications. This electrode had been used previously as the basis of the universal ion-selective electrode described by Růžička et al (91). The general aspects of carbon as an electrode material have been discussed extensively by Randin (92).

Extensive use has been made of electrodes made of glassy carbon (93) and carbon fibres have been used to fabricate miniature electrodes for in vivo biomedical studies (9).

Glassy carbon was prepared by Yamada and Sato (94) in 1962, using a method of controlling the pyrolysis of phenolic resins. They prepared a gas impermeable carbon which they so designated as glassy carbon. This material presented several advantages over other types of carbon including a greater inertness to chemical attack. The physical and chemical properties of glassy carbon and the behaviour of glassy carbon as an electrode for voltammetry has been studied and described by many workers. Zittel and Miller (95) were the first to use a glassy carbon electrode in voltammetry. Gunasingham and Fleet (96) recently made a comparative study of glassy carbon as an electrode material. These authors also investigated the effect of pH on the response of glassy carbon electrodes (97). Dian et al (98) examined the use of glassy carbon electrodes for pulse voltammetric determinations. Amperometric detection, normal and differential pulse techniques have been investigated by Dieker et al (99). Recently new types of carbon electrodes have appeared in the literature: a new pyrolytic carbon film electrode has been prepared for voltammetric study (100) and has been applied for oxidative differential pulse voltammetry of selected organic molecules (101). In these works the author discussed several advantages of the new electrode and drew attention to the many drawbacks presented by glassy carbon which is still preferred for many electroanalytical applications (93). The author claims in this work that the unusual surface of this novel pyrolytic electrode permits determinations at the submicromolar level, as shown in the same communication (101). The

pyrolytic carbon film electrode, produced by deposition of a pyrolytic carbon film on a convenient silica tube at temperatures below 1150°C , has been compared to a highly satisfactory carbon paste electrode whose outstanding behaviour is restricted to use in aqueous solutions (102). The electrochemical properties of activated carbon and carbon black have been examined by Jankowska et al (103) who made a comprehensive potentiometric study of these systems in various conditions of pH, and concentration of solution.

A radiation-cured polymer-impregnated graphite electrode for anodic stripping voltammetry has been prepared from graphite rods impregnated with monomer or monomer-resin mixtures. In spite of the results obtained and the properties associated with this technique it appears extremely complicated (104). An interesting variety of carbon electrode has been described by Yaniv and Ariel (105) consisting of a graphite cloth electrode which has been evaluated for anodic stripping voltammetry. A similar electrode has been applied for the electrolytic recovery and separation of gold from spent electroplating bath solutions (106). Anderson et al described the fabrication and the characterization of a Kel-F - graphite composition electrode for general voltammetric applications (107). This electrode, produced by means of a compressed mixture of the graphite powder and Kel-F polymer powder, has been shown to be of outstanding value due to its resistance against organic solvents and chemicals usually employed in the common voltammetric determinations. Several peculiarities of this so-called Kelgraf electrode have been described by those authors. Kaufman et al developed recently a graphite spray coating technique using a commercially available spray (108) and a colloidal solution of graphite particles dispersed in methyl methacrylate polymer.

This graphite-spray electrode has been applied to the anodic stripping voltammetric determination of bismuth (109). Wang (110) reviewed the use of epoxy-based graphite electrodes and Štulík and Pácaková recently reviewed

electrochemical detection in high-performance liquid chromatography, showing the different types of electrochemical detectors (ECD) which are constructed mainly from carbon graphite electrodes, especially glassy carbon and carbon paste electrodes. Several studies related to the performance of carbon electrodes in terms of surface properties, and other parameters have been made in order to determine the suitability of the known types of electrodes for practical applications and to establish useful correlations in order to highlight the way for new developments. Kinetic studies of the oxygen-peroxide couple on pyrolytic graphite (112), the physicochemical properties of carbon materials (113), the behaviour of carbon electrodes in aqueous and nonaqueous systems (114), the nature of surface compounds and reactions observed (115) and an evaluation of differential pulse voltammetry at carbon electrodes are among those studies (116).

Electrodes based on reticulated vitreous carbon (RVC) are also increasing in importance (117). This recent development of this new form of carbon constitutes a new versatile material which combines the electrochemical properties of a practically non-porous glassy carbon with several interesting hydrodynamic characteristics. Because of this versatility this new carbon electrode has been applied to various electrochemical purposes, including stationary electrodes, tubular and porous electrodes for flow-through systems, stripping analysis and rotating porous carbon disk electrodes (118-122). This material seems to have been developed in 1976 and later applied to non-electrochemical uses. Its main characteristics as an versatile electrochemical carbon electrode have been reviewed by Wang (117). Reticulated vitreous carbon is an open pore material, with a honeycomb (foam) structure, suitable for various applications which have been extensively described. One of the most interesting uses has been the application of this material for the construction of optically transparent vitreous carbon electrodes for spectroelectrochemical study (123). Recently Sleszynsky, Osteryoung and Carter (124) investigated

the electrochemical behaviour of a very small voltammetric electrode made of a small RVC block cut as a disc (6mm internal diameter) and completely isolated from the electrolyte by a non-conductive epoxy resin. The authors reviewed the applications of micro and minielectrodes for in vivo studies and discussed the theoretical basis related to the performance of such micro-electrodes. A general description of the characteristic properties of carbon materials, method of fabrication and applications has been described in a book by Jenkins and Kawamura (125). In a previous article Cahn and Harris, discussed newer forms of carbon and their uses (126).

Ion-selective electrodes

The discovery of the selectivity of a particular glass membrane (127,128) to hydrogen ions in solution can be considered as the starting point for the development of ion-selective electrodes and similar sensors. In their new book published recently, Koryta and Štulík (129) referred to the rapid progress in the whole field of ion-selective electrodes and to the extensive literature that comprises about four thousand references.

The importance of ion-selective electrodes has been confirmed through the publication of several books (129-138). The many features and applications of ion-selective electrodes in the areas of industry, environmental control, *biomedical* ^{analysis} and research has been reviewed by many experts: comprehensive reviews dealing with each particular type of electroanalytical sensor and their uses have appeared in the literature. Bailey (139) reviewed the extensive use of ion-selective electrodes in industry, and discussed the essential aspects of measurement conditions and measurement systems for industrial use. A set of applications for routine analysis of all the ions for which determinations have been made, the types of sensor used and the procedures available were discussed. The principal advantage of the use of ion-selective electrodes in the field of process control seems to be their independence of sample

colour, viscosity or suspended solids; these factors frequently vary from sample to sample in industrial routine analysis and for quality control of food and effluents this results, for example, in more difficult and time-consuming determinations when photometric methods are used. The progress in designing calcium ion-selective electrodes was reviewed by Moody and Thomas (140), and two extensive reviews have been published by Koryta (141, 142) including a list of ca. 1700 references. Following the series of reviews in the journal "Analytical Chemistry", in the section on ion-selective electrodes, Meyerhoff and Fraticelli (143) and Fricke (144) recently completed a list of comprehensive reviews in this field. These reviews encompass the different areas of the field, and mention the work of many researchers giving a total of 1210 references. The review by Meyerhoff and Fraticelli was presented in a classified way, showing the different types of sensors (in a system of separated sections) which are very clear and useful for a search of the literature in each specialized area of the subject. Freiser (145) edited two volumes reviewing the main aspects of ion-selective electrodes: chapters written by experts, include material on the theory of membrane potentials, response times and selectivity coefficients, theoretical and practical aspects of precipitate based ion-selective electrodes, coated wire ion-selective electrodes, ion-selective field effect transistors (ISFETS) and several applications of ion-selective electrodes (ISEs). In his Ph.D. thesis, Yoo (146) reviewed the literature of ion-selective electrodes, its historical development, classification and applications to inorganic and organic analysis. Thomas (147) reviewed some recent improvements in ISEs in his paper presented in a symposium and discussed the improvement in ion-sensors, calibration and mode of use, giving examples on surfactant, calcium, nitrate and chloride to illustrate the progress in ion-selective electrodes. Recent topics were covered, including the grafting of ion-sensors to polymer matrices and the use of bacteria in membranes. In the same article, developments in

microelectrodes with reference to ISFETs, progress in the use of micro-processors and the advantages of the flow-injection systems have also been assessed. The work mentioned 56 references. The interesting area of coated wire electrodes has been reviewed by Cattrall (148) and by Freiser (149) who with his collaborators prepared the first of this then new type of electrode which they designated coated wire electrodes (CWEs) (150, 151). This attractive area of research offers many interesting features among which are low cost and small size. These advantages still encourage active research for the development of new coated wire electrodes with important applications in organic and biomedical analysis (152, 153). The main features of the instrumentation for ion-selective electrodes has been discussed by Burton (154) in a recent review, including prospects of future development. The modern biological and biomedical applications of ion-selective sensors have been reviewed by Thomas (155) and recently by Rechnitz (156). With the purpose of providing a brief introduction to the applications of ion-selective electrodes to bioanalysis, the author of the latter article reviewed the main findings that lead to the development of various types of potentiometric sensor, before discussing the types of bioselective electrodes and future prospects. Rechnitz's article (156) constitutes a very good review on the classification of ion-selective electrodes from the operational point of view with several examples of each type of electrode and its use. The use of ion-selective electrodes in the investigation of biological fluids was treated some years ago by Durst (157) and the introduction of the "universal ion-selective electrode", the so-called Selectrode, has been discussed by Růžička et al (158). The theoretical aspects of membrane phenomena has been comprehensively presented by Lakshminarayanaiah (159).

One of the most progressive areas of ion-selective electrode research is related to applications of these potentiometric devices to enzyme systems. This area of research and application has been reviewed recently by Guilbault

in an excellent and extensive work (160), dealing with the function and selectivity of ion-selective electrodes, their classification, the principles of measurement with enzyme electrodes, their construction and use in the analysis of inorganic ions and organic species. Especial consideration has been given recently to the technique of immobilization of enzymes either by chemical modification of the molecules, introducing insolubilizing groups or physical entrapment of the enzyme in an inert matrix such as starch, polyacrylamide and other kinds of gels and nets (160-162). Immobilized enzymes have been the basis for a porous electrode reactor in a flow-through electrochemical cell (163) and for a chemically modified electrode (164) both constructed with the use of a reticulated vitreous carbon electrode material. Several modifications and new improvements have appeared in the last years leading to new "surface modified electrodes" and to new biosensors. In the latter category, sensors based on the use of bacteria in electrode membranes is becoming of considerable importance (165, 166). Moreover, mitochondria, plant and animal tissue can be used as biocatalysts (166). All this growing possibility of several applications and the prospects of new advancements in the methods of bioanalysis with ion-selective electrodes has been documented in an extensive review by Solsky (167) published recently. Ion-selective electrodes have been classified in respect of several features mainly based on the material of which the sensor matrix was made. The first comprehensive review on the subject is contained in the Proceedings of the First International Symposium on Ion-selective Electrodes (168), now considered as the most important one for subsequent development in this area. Papers from that conference presented a general view on the types of ion-selective electrode. In his review of 1969, the year of the NBS international conference, Covington (169) classified ion-selective electrodes in four categories:

- 1- solid-state electrodes: their membranes consist of single crystals or compact disc of active material.

2- heterogeneous membrane electrodes: the active material is dispersed in an inert binder or matrix.

3- liquid ion-exchanger membrane electrodes: the ion of interest is attached to a large organic molecule which is hydrofobic.

4- glass electrodes: cation selective only.

Another review published by Covington five years later (170) presented a summarized classification of ion-selective electrodes. The main types of sensors were grouped in three sections named glass electrodes, insoluble inorganic salts based electrodes and electrodes based on long-chain ion-exchange materials, such as alkylphosphate salts and the tetralkylammonium salts and complexing agents. Covington described in this paper the principal features of the construction of ISEs and discussed the most important theoretical aspects related with their behaviour. Simon et al (171) reviewed the development of ion-selective electrodes and published an account in 1975 of the earlier developments in the field of neutral ligands for use as ion-exchangers in new ion-selective membrane electrodes and predicted the synthesis of better ligands with higher selectivity. In their communication they classify the main types of electrodes known up to the date in the following categories:

a) solid membranes (fixed ion-exchange sites)

homogeneous: glass membranes and crystal membranes

heterogeneous: crystalline compound in inert binder

b) liquid membranes (mobile ion-exchange sites)

charged ligand and neutral ligand

c) special electrodes

gas sensing electrodes and enzyme substrate electrodes.

In his extensive review on ion-selective electrodes applied to enzyme systems, Guilbault (160) presented a classification of ISEs in four categories, based upon the composition of the membranes of the sensors, with more or less the

same definition of each type:

- 1- glass electrodes
- 2- solid-state electrodes
- 3- liquid ion-exchange electrodes
- 4- special electrodes

Rechnitz (156) in his publication about bioanalysis with potentiometric membrane electrodes gave several examples of the diverse kind of electrodes, corresponding to three main classes:

- a) traditional ion-selective electrodes (glass membrane, liquid ion-exchanger membrane, neutral carrier, crystal membrane and gas sensor)
- b) nontraditional electrodes (ISFETs, coated wires, polymer matrix, microelectrodes and disposable slides)
- c) typical biocatalytic potentiometric electrodes (biosensors formed by couple an ion-selective electrode with a membrane containing an enzyme, mitochondria, bacterial cells, animal or plant tissues).

Rechnitz again repeated the same classification in his didactic article on the subject of ion and bioselective membrane electrodes published recently in the Journal of Chemical Education (166). He considered five broad groups of sensors: glass membrane electrodes, liquid membrane electrodes, crystal membrane electrodes, gas-sensing membrane electrodes and bioselective membrane electrodes. The discussion of CHEMFETs, ISFETs and coated wire electrodes are considered as special topics.

The theoretical aspects of membrane phenomena, origin of membrane potential and the description of the important relationships for the calculation of electrode potentials and selectivity have been the subject of consideration of several authors, each one concerned with his expertise among them. Because of the importance of their particular contribution for the improvement of ion-selective electrodes in general and development of new sensors it is worth mentioning the work done by the pioneers. Eisenman (138) is included

for his work on glass electrodes for cations different from hydrogen and his important work on the development of several theoretical aspects of the field, related to the membrane behaviour. Frant and Ross (172) introduced the first non-glass ion-selective electrode, with their development of the solid-state fluoride electrode, based on a single crystal of lanthanum trifluoride doped with Eu(II) which seems to be still the most sensitive electrode of all, approaching true specificity - Only hydroxyl ions interferes with its response to fluoride. Moody and Thomas for their study on the construction of PVC-based ion-selective membrane electrodes and especially for their comprehensive research work on the development and improvement of calcium electrodes, which work is still being actively undertaken at UWIST in Cardiff, where an important biannual International Symposium on Electroanalysis (137, 140, 147) is held. Simon, Morf and their group pioneered the development of ionophores and provided the leadership for the world research on neutral carriers for ion-selective membrane electrodes (130). Guilbault is included for his work on enzyme electrodes and Janata (173) for his pioneering work on the development of ion-selective field effect transistor (ISFET) together with Huber and their group.

Derived from the pioneering work cited above an enormous interest has grown in research in the still open field of ion-selective electrodes making it almost impossible to evaluate immediately the importance of new developments that certainly will disclose new frontiers and recognize the work of new pioneers among the vast group of workers engaged in this area. It would take as mentioned by Koryta (129) a full book if all the papers published so far, on ion-selective electrodes, were listed and superficially assessed.

Surface modified electrodes

Surface modified electrodes, or better chemically modified electrodes (CMEs), as designated by Moses, Wier and Murray (174), are terms applied to any

electrode having determined molecules deliberately immobilized on their surfaces. They constitute a relatively new area of intensive research work in many laboratories. Platinum, graphite and tin oxide surfaces have been used as supports for the attachment of various compounds which modify their electrochemical behaviour. This research area is growing very fast in assessing the potentialities of chemically modified electrodes (CMEs) for important applications.

The first report on the direct observation of the electrochemical behaviour of such a surface for extended periods, in solutions free from the attached reactants has been communicated by Lane and Hubbard ten years ago (175).

The use of strongly adsorbed species on graphite surfaces was demonstrated by Brown et al (176) in 1976. The adsorption and subsequent electrochemical behaviour of certain reactants such as 9,10-phenanthrenequinone, and $\text{Ru}(\text{NH}_3)_6^{3+}$ were studied by these authors on glassy carbon and pyrolytic graphite electrodes by differential pulse and cyclic voltammetry.

Miller et al (177) introduced a new approach for preparing modified surface electrodes based on the adsorption of polymers. Their proposed technique of chemically binding organic or organometallic compounds to the surface of conductors was expected to produce chemically modified electrodes showing great specificity in terms of electrode reactions. The adsorption of modifiers like amines and other more complex molecules onto convenient surfaces, mainly carbon graphite, platinum and tin oxide films, confer to these surfaces new chemical properties. In those authors' work several interesting points have been discussed: the characterization of the polymer film formation, mechanism of the reactions that caused the surface alteration and the indication of appropriated physical methods for the investigation of CMEs produced.

Several reviews on this subject have appeared in the literature. Among them, Heineman and Kissinger (178) published a review in 1978. Snell et al (179) published a comprehensive review in 1979. Dantartas, Evans and Kuwana

in their article about a novel technique for obtaining CMEs via cyanuric chloride, have reviewed the aspects of the research in this area (180).

Recently, Murray (181) who with his team introduced the most common approach for the preparation of modified surface electrodes, has written an extensive review updating the developments in all aspects of this very excited area of investigation. The review contains 363 references.

Several groups have been worked intensively presenting many different ways to prepare chemically modified electrodes and trying to take advantage of the increasing volume of data related to the experience obtained so far.

Murray's team (174) have introduced the most common technique, based on the sililation of the surface hydroxyl groups to form rugged surfaces with $\text{O}-\text{Si}-\text{C}-\text{R}$ linkages. Kuwana's group have been engaged with the investigation of electron transport components to rapidly exchange electrons with electrode surfaces.

A novel and extremely interesting family of chemically modified electrodes has been created by Santhanam et al (182) with the adsorption of enzymes on a mercury electrode placed on the top of a thermistor for monitoring the temperature changes associated with the enzyme action on the substrate.

Among the analytical applications of chemically modified electrodes should be mentioned the catalysis and inhibition of electrochemical reactions, improvement of photoelectrodes, electrochemical synthesis, study of immobilized molecules related to structural orientation and electron transfer (179). Lane and Hubbard (183) have described the use of a chemically modified electrodes obtained by iodide adsorption, in the selective determinations of catecholamines.

In the last few years there has been an explosion of research activiti in the area of chemically modified electrodes: Heineman, Wieck and Yacynych were the first to use a polymer film chemically modified electrode as a potentiometric sensor (184). They showed that a poly(1,2-di-aminobenzene) coated

platinum electrode exhibits a near Nernstian response to changes in pH. These authors have stated a prediction that polymer adsorbed (coating) modified electrodes conveniently designed would function in the same way as the so-called Freiser's coated wire electrodes.

Ianniello and Yacynych (185) presented a chemically modified electrode fabricated on the basis of an immobilized enzyme by covalent attachment of L-aminoacid oxidase (E.C. 1432) to a graphite rod, via cyanuric chloride linkage. The electrode potential varied logarithmically with the concentration of L-phenylalanine, L-methionine and L-leucine. These authors discussed the mechanism of potential response. Ravichandran and Baldwin (186) prepared a CME on a carbon paste support as a catalytic voltammetric sensor by the incorporation of the appropriate quantities of N,N,N',N' - tetramethyl -p-phenylenediamine (TMPD) directly into the paste mixture. This CME was able to catalyse the electrochemical oxidation of ascorbic acid and distinguish its wave from another wave characteristic of nicotinamide adenine dinucleotide (NADH). This behaviour has been studied by cyclic voltammetry.

Minh-Chan-Pham et al (187) prepared an electroactive polymer film obtained by electropolymerization of 5-hydroxy-1,4-naphthoquinone onto graphite. They also showed that the electroactive films made of naphthoquinone polymer have a long life time and can be prepared in a wide variety of films with different thicknesses. Minh-Chan-Phan et al. have reviewed this subject and published 25 references.

A recent paper reported by Gorton et al (188) presented a detailed discussion of the properties of some electrodes modified by adsorption of phenoxazinium salt, medola blue, on their surface. They reviewed the area and pointed out the importance of modified electrodes for the oxidation of nicotinamide coenzymes (NADH and NADPH) of great value for biotechnology and analytical purposes.

In his recent article Bard (189) has reviewed the main features of the

study of chemically modified electrodes (CMEs). The author discussed the technique of preparation and the objective of the intensive investigations in this area. He stated finally that CMEs have not been applied yet to real analytical problems but many promising possibilities are predicted.

Electrodes under controlled hydrodynamic conditions

The advantages of the hydrodynamic approach to potentiometric and voltammetric detection are well known. This technique involves the moving of the electrode past the solution or vice-versa. The resultant increase in the mass transport increases the current and usually increases the sensitivity. This does not mean necessarily that there is an increase in the signal-to-noise ratio. Hydrodynamic electrodes, best represented by the rotating platinum microelectrodes or by rotating disc electrodes, exhibit a current-potential behaviour similar to that of the dropping-mercury electrode (DME): they present the characteristic limiting current curve when the current is limited by mass transport to the electrode and it can be shown that the current is proportional to the concentration of electroactive species in solution.

The vibrating mercury electrode - a dropping-mercury electrode mounted in a particular way can produce a drop time of the order of milliseconds. The advantages of such a system was discussed above (see mercury electrodes).

The rotating platinum microelectrodes have been prepared in several configurations and have been extensively used for electroanalytical determinations and for theoretical studies of diffusion currents. In general they consist of a platinum wire sealed into a soft glass support and connected electrically through a mercury contact. Their construction, applications and their theoretical implications are discussed by Sawyer (15) and by Laitinen and Kolthoff (19, 22).

Among the most useful hydrodynamic electrodes the rotating disc electrode

(RDE) and the rotating ring-disc electrode (RRDE) are considered to be of even greater importance. They have been preferentially used by many researchers for both theoretical and practical applications. In the case of the ring-disc electrode its advantage is related to the possibility of determination of the nature of the products generated at the disc. Usually the ring, which surrounds the disc at a close distance permits the detection of the products of oxidation or reduction at the central disc, the ring and the disc working at different potentials (190). These electrodes are commercially available although they can be "home-made" provided that a careful and precise machining can be afforded.

Rotating disc electrodes can be classified as amperometric detectors because they are normally operated at constant potential and used as sensors for measuring currents (12). In this electrode the current is limited by convection as well as by diffusion unlike most other amperometric devices. The mass transport to such a disc electrode at certain conditions is due only to convection and diffusion and the equation for the reduction current limited by mass transfer to a rotating disc electrode is the well known Levich's equation (191):

$$I_{\text{lim}} = - zFAcD^{2/3} \omega^{1/2} / 1.61 \nu^{1/6}$$

where ω is the angular velocity of rotation of the disc and ν is the kinematic viscosity of the solution. This is identical to the Nernst diffusion-layer equation for the limiting current when $\delta = 1.61D^{1/3} \nu^{1/6} \omega^{1/2}$.

From the equation above it is seen that the thickness of the diffusion layer increases with the viscosity of the solution and decreases with increasing speed of rotation of the electrode. The steady state achieved by this electrode is dependent upon the bulk concentration of the electroactive species and the rate of rotation of the disc. The shape of the waves obtained

for reversible charge transfer only is identical to the shape of a classical polarographic wave. Because of its characteristics rotating disc electrodes can be strongly recommended for practical analytical determinations in spite of the difficulties involved with its fabrication. RDEs have been used frequently especially for stripping voltammetry (see electrodes for stripping analysis on p.38) on the other hand, the rotating ring-disc electrode introduced by Frumkin and Nekrasov (192, 193) in 1959 is most useful for detection of intermediate species formed during electrode process as discussed above.

Instead of moving the electrode past the solution, the sample solution can be flowed past a stationary electrode which works as an electrochemical detector (ECD). There has been increasing interest in recent years on the need for continuous flow analysis in several important areas such as process control, environmental protection, biomedical screening, and especially on detectors for high performance liquid chromatography (HPLC).

The use of voltammetric techniques in a continuous or automated monitoring flow mode is treated in a broad area of electroanalytical chemistry defined by the term hydrodynamic voltammetry (HDV). In the case of amperometric detection the term hydrodynamic amperometry applies but it seems that the former is generalized (194). Tubular, planar, wall-jet and rotating-disc configurations comprise the main types of electrodes used in continuous monitoring HDV. The tubular platinum electrode (195) was one of the first attempts to produce electrodes for using in continuous flowing streams. This tubular platinum electrode (TPE) was developed and applied by Blaedel et al (196) to the enzymatic determination of glucose. These authors have presented a theoretical discussion on the electrochemical behaviour of the tubular platinum electrodes on the basis of hydrodynamic principles discussed previously by Levich (191). Sharma and Dutt (197) prepared the first graphite tubular electrode and described the theoretical foundations of its behaviour during their study of the chemisorption of oxygen on the electrode surface.

Masson et al (198) have reviewed the literature on the tubular electrodes (TEs) and has presented a new tubular graphite electrode (TGE) similar to that published by Sharma et al (197). These tubular electrodes have been applied to many practical situations, such as the determinations of pharmaceuticals using a flow-rate of 10 ml min^{-1} provided by a gravity feeding system with a constant head (199). This electrode was constructed from a 1.2 cm length of graphite rod with 1 mm internal diameter. They used $2 \times 10^{-4} \text{ M}$ solutions and a $0.1 \text{ M H}_2\text{SO}_4$ supporting electrolyte. Sharma et al. have applied the same TGE to the determination of the diffusion coefficients of 59 aromatic amino and phenolic compounds (200). The diffusion coefficients (D) were determined on the basis of the following expression

$$I_{\text{diff}} = (5.24 \times 10^5) \eta C X^{2/3} D^{2/3} V_f^{1/3}$$

where X is the length of electrode (cm), V_f is the volumetric flow-rate (ml s^{-1}) and C is the concentration of electroactive material (mol ml^{-1}). η and D have their usual significance. Comprehensive reviews have appeared in the literature on the subject, dealing with the theoretical and practical aspects of hydrodynamic voltammetry and presenting the current innovations in terms of electrodes and cells. Pungor et al (201) reviewed the subject of hydrodynamic voltammetry as a whole. Pungor et al (202) published a review on automated methods of analysis and Štulík and Pacáková recently reviewed the matter of electrochemical detectors (203). Fleet and Little discussed the fundamental problems regarding electrochemical detector design and examined various alternatives including the dropping-mercury electrode, and tubular carbon electrode. These authors have proposed a new wall-jet type cell for electrochemical detection in flow streams (204). Recently, Gunasingham and Fleet (205) have discussed the anomalous behaviour of the wall-jet electrode at small inlet-separations and derived equation for the boundary-layer and

for the diffusion layer thickness. They also introduced a variation of the wall-jet cell using a modified ring-disc approach. Kissinger (206) reviewed the main features associated with amperometric and coulometric detectors for HPLC. The author has discussed the principles, limitations and applications of these detectors. Other interesting reviews on the theory, applications and characteristics of electrochemical detectors are published by Rucki (207), by Hanekamy et al (208) and by Brunt (209). The latter author described in his work the general properties of the different systems used as electrochemical detectors and the basic principles of voltammetry. Amperometric, coulometric and potentiometric detectors have been discussed by Brunt who also presented a list of commercially available devices.

A few modifications of the usual flow systems have appeared envisaging the increase of the sensitivity and the selectivity of detectors. Other approaches have been published dealing with the problem of background currents and alternatives for the detection of the signals have been proposed. Fenn et al have determined catecholamines in blood plasma using single and twin electrode thin-layer electrochemistry (210). Schieffer, introduced a dual coulometric-amperometric cell for increasing the selectivity of ECD in HPLC (211). Blaedel and Wang have used an electrochemical flow detector with two carbon electrodes in a thin-layer configuration. They claimed that the elimination of the usual reference electrode results in minimal potential drop (IR) and simplifies the design of the cell which can detect concentrations at the nanomolar level, by using the sensitive pulsed-flow technique (212). Wang has reviewed the potentialities of hydrodynamic modulated voltammetry (HMV) (213) and has shown that this new approach for highly efficient background correction is a feasible alternative to other procedures reported using twin electrodes or even several electrodes to obtain a voltammogram (214) increasing the sensitivity and decreasing the detection limit (215). This new approach is based on the modulation of the convection rate of the solution at

a solid electrode surface. It is expected that flow-detectors operating on the basis of hydrodynamic modulated voltammetry (HMV) will find considerable application in liquid chromatography due to the enhancement of sensitivity and expansion of the useful potential range of the detector. In this work Wang has produced a table summarizing the characteristics and applications of the diverse approaches adopted in the HMV mode whose publications appeared within the last decade. Many variations of the work published so far include the use of chemically modified electrodes for this purpose.

Electrodes for stripping analysis

Anodic stripping voltammetry (ASV) has become increasingly important as a popular technique for detecting trace metals. The monitoring of heavy metals is fundamental for environmental pollution control, as heavy metals are one class of contaminants capable of accumulating and of producing undesirable effects. In general they are not biodegradable and its control at very low concentrations has become vital for the preservation of nature. On the other hand it is well known that the lack of certain trace metals can drastically affect the health of human beings as they are essential for life in general. Anodic stripping voltammetry is one technique that cannot be considered as a novelty (53) but has been continuously used, modified and improved by the appearance of new instruments and techniques such as, for example, its application with flow-injection systems (216-218). The popularity and preference for this technique for trace metal determination is justifiable as it is a simple technique, and is precise, accurate, sensitive and economical. It is very useful for the identification of metal species present in solutions and their distribution. This subject known as speciation, is the subject of intense research nowadays (219). Analysis using anodic stripping voltammetry is carried out in two main steps, the plating or deposition step and the stripping or redissolution step. In the first step the metals are concentrated by electrochemical reduction on the surface of a convenient

electrode of a small surface area. In the second step reoxidation (stripping) of the metal deposited takes place. The result when linear sweep or differential pulse studies is carried out is a peak-shaped current-potential curve. Each metal has a characteristic peak potential which serves to identify it and the peak height is a measure of its concentration in solution. In general the deposition step is carried out on a very thin film of mercury, previously deposited onto the working electrode surface -sometimes simultaneously with the reduction of the heavy metals to be determined (220).

The increasing importance of the ASV techniques is shown by the large number of publications describing the results of investigations and routine analyses besides the various modifications to the technique. These advancements have been aimed at the improvement of the accuracy and sensitivity of the determination, and other special purposes. Copeland and Skogerboe (221) reviewed the subject of anodic stripping voltammetry listing 56 references and describing the fundamentals, the instrumentation and the procedures for practical applications.

The historical development has been reviewed by Ellis (222) who also included the theoretical principles, several applications and a discussion of the instrumentation used. Wang (53) reviewed the uses of ASV in water analysis, in speciation and in other determinations, giving useful details from the technical point of view, for the electrochemists engaged with environmental surveillance of heavy metal contaminants. This author pointed out the convenience of ASV in measuring simultaneously several elements at very low concentrations (sub-ppb levels) at relatively low cost. Moreover the simplicity of anodic stripping voltammetry apparently requires little expertise and any analyses by this technique can be completed in a few minutes, when the necessary conditions have been previously established and controlled, as for instance to eliminate the effect of interferences. Recently, Vire et al reviewed the subject as applied to determinations of trace metals in biological

media and foodstuffs (223). In their comprehensive and illustrative work these authors looked at the fundamental principles and conditions for successful determinations and gave several detailed procedures for food analysis including many descriptive tables.

Although the principles of anodic stripping voltammetry were discussed as long ago as 1931 by Zbinden (224), the progress of the technique from his first determination of copper at a platinum electrode to the present stage took a considerable time and a great amount of effort. Only after the familiarization with the use of mercury electrodes, mainly the hanging-mercury-drop electrode (HMDE) and the mercury-thin-film electrode (MTFE) between 1950 and 1960 (48-52) did the ASV technique gain its present popularity. Brainina (225) published an extensive review about fundamentals of stripping voltammetry. This author gave an account of the theoretical background involved with the redissolution of metals and discussed his published work. Brainina mainly used a film of metal or insoluble compound directly deposited onto a solid electrode. Only in a few cases did they employ the plating step of mercury as it has been considered later. In some investigations Brainina used an epoxy-impregnated graphite electrode, and either the hanging-mercury-drop electrode or the mercury-thin-film electrode but the new era for ASV and correlated techniques seems to have gained rapid progress after the use of the "composite graphite-mercury electrode of Matson et al (226) and following the work of Florence and other investigators. Florence (220) was the first to suggest the preparation of mercury thin films for ASV using glassy carbon electrodes plated with a very thin film of mercury (0.001 to 0.01 m) in situ. This was accomplished by add^{ing} mercury(II) nitrate to the sample solution and simultaneously depositing the mercury film at the same potential used for the plating of the heavy metals being determined. In this way the trace metals deposited could be stripped off the mercury film surface and the electrode renewed for subsequent analyses simply by wiping the previous mercury film off

with a tissue. This step of constant renewing of the mercury film in between scans is no longer normally adopted as it seems that the thin mercury film can be used for several subsequent analyses. (216). Batley and Florence made a comparative study of the use of the HMDE and the MTFE for ASV applied to the analysis of typical environmental samples. They recently published their report about the comparison between linear scan and differential pulse technique for anodic stripping voltammetry at mercury-thin-films electrode (227).

A drawback of the technique of very thin film plated in situ is confirmed by Florence as being the poor sensitivity for the determination of zinc a fact attested by Kemula and Galus in an earlier work but not satisfactorily explained at the time (228). Batley and Florence (229) assessed the various problems related to the sensitivity of lead and cadmium in respect to mercury film thickness and discussed their observations. It has been demonstrated by Štulíková (230) that mercury thin films are formed by a series of droplets leaving some empty spaces on the glassy carbon electrode surface which are preferential sites for the deposition of either cadmium or lead. The latter used to be deposited on glassy carbon itself and this accounts for the increasing in sensitivity for lead with an increase in the mercury film thickness. On the other hand the difficulty resulting from the poor resolution for copper and zinc with the impossibility to determine zinc on a thin mercury film surface have been assessed recently and found to be related with the formation of intermetallic compounds.

The determination of metals able to form intermetallic compounds by the small difference between their deposition potentials can be accomplished either by the use of HMDE in place of MTFE or by employing a metallic species that could favorably combine with one of the two elements to be determined. Another possibility is reported to be the use of different deposition potentials (53).

The analytical applications of the ASV technique was limited to a few cases up to 1970. The suggestion of Matson et al (226) for the use of a

wax-impregnated graphite electrode with a thin film of mercury as the substrate for the metal deposition introduced an electrode with a high surface-to-volume ratio. This offered a large preconcentration advantage which increased the sensitivity and reproducibility of the stripping step itself. The extensive study of Florence (220) on the use of glassy carbon coated with a thin film of mercury deposited in situ was followed by the improvement of the technique by the use of differential pulse voltammetry (DPVASV) in substitution of linear scan stripping techniques. The advantages of DPASV over LSASV was demonstrated by several authors and was confirmed by Copeland et al (231). These workers stated that differential pulse anodic stripping voltammetry increases the sensitivity by factors varying from 4 to 20 or more compared with linear scan adopted earlier. Using DPASV these authors have performed a thorough investigation to define the optimum conditions for many practical applications of stripping voltammetry to the analysis of different sample types, including the determination of cadmium and lead in natural water, blood, blood plasma and urine, using a few microliters of the samples. Batley and Florence (232) examined the effect of dissolved organics on the stripping voltammetry of sea water, and more interesting applications appeared in the literature after the seventies, making it a very difficult task to list all of them. Deanhardt et al (233) determined lead and cadmium in pottery by ASV as an inexpensive alternative to the use of atomic absorption by the United States Food and Drug Administration (FDA) and to introduce the technique in the undergraduate program. Vydra and Nghi (234) studied the ASV of metals in nonaqueous media in depth in comparison with the work of previous authors. They extracted lead with ditizone using a substitution reaction with Hg-salt and this was followed by the raising of the conductivity of nonaqueous media by adding the alcoholic solution of suitable salt and the normal procedure for ASV similar to that in aqueous media. The evaluation of a coulometric procedure at thin-film-mercury electrodes using a microcell with rotating

mercury-covered glassy carbon electrode has been carried out by Eggli(235, 236). The author claimed the advantage of the exhaustive preelectrolysis of the sample solution over the common voltammetric technique using partial deposition of the sample. The coulometric stripping technique has been used before employing different solid electrodes such as platinum, mercury-pool and carbon paste, as mentioned by Eggli (235) but this was the first time that a rigorous evaluation of the method using coulometric determination has been carried out for the determination of cadmium and lead. The expressions for the calculation of the detection limit of anodic stripping coulometry has been derived and discussed by Eggli (236). An important application of DPASV for the determination of copper and lead in EDTA extracts of soils has been done by Edmonds et al (237) using a mercury-film glassy carbon electrode, and the simultaneous estimation of lead and tin in fruit juices and soft drinks have been accomplished by potentiometric stripping analysis (PSA), using methanol as supporting electrolyte at pH 1 to provide the resolution of the lead and tin signals that otherwise overlap (238). This is a new facet of the stripping technique recently reviewed by Jagner (239).

Anodic stripping voltammetry with flow-injection systems is growing in importance. Wang et al and Blaedel et al , published the results of ASV with flow-injection analysis (FIA) either at a glassy carbon disc electrode in a wall-jet cell(216) or using a reticulated vitreous carbon-mercury electrode (121). Recently Wang and Dewald introduced the new approach called subtractive anodic stripping voltammetry with flow-injection analysis (240). This new approach eliminates the signal due to the background using a common flow-injection system and appears to be quite attractive and useful as it permits the determination of 24 samples per hour using 200ml sample volume at ppb levels. This subtractive mode provides a way for the correction of both Faradaic and non-Faradaic background current contributions and shortens the deposition time: the author claimed that $6 \times 10^{-9} \text{ M}$ (0.14ng) of cadmium can

be determined with a minimum deposition time. An interesting feature of the new approach seems to be that it is unnecessary to deaerate the sample and electrolyte as the background signal is subtracted from the sample signal in the same electrolyte solution, provided that the necessary conditions are observed as discussed by Wang and Dewald (240). Another system for ASV with FIA was mentioned by Schulze and Frenzel (241) who used a thin-layer cell for potentiometric stripping analysis at a glassy carbon electrode covered with a mercury film. Damokos and Laszlo (242) reviewed the main aspects of instrumentation for chronopotentiometric stripping analysis or simply potentiometric stripping analysis (PSA) the newest approach to the stripping technique, describing the relevant points of this technique and giving indications of the analytical procedures.

A more significant communication by Tanaka and Yoshida (243) gave a new anodic stripping voltammetric method for the determination of cysteine at a copper amalgam electrode. Cysteine was deposited at -0.06V versus SCE and accumulated as the cupric complex on the surface of the electrode. The change of the potential to $+0.06\text{V}$ vs. SCE produced a characteristic anodic peak whose height was proportional to the concentration of cysteine. A hanging-mercury-drop electrode (HMDE) amalgamated with copper was used and its behaviour is discussed. The methods for the determination of cysteine have been reviewed and the biological importance of this compound has been emphasized. Among these methods it is interesting to note the possibility of using cathodic stripping voltammetry (CSV) at a copper amalgam electrode (243). These results confirm the importance of stripping analysis as a powerful technique for environmental protection and quality control.

The search for new electrodes

From the considerations presented so far on the methodology of electro-analytical chemistry and the types of electrochemical sensors, it seems

practically impossible to include all the details related to a special technique and cite all kinds of electrodes. This would involve too extensive a report.

The main features of most relevant approach for characterizing an ionic species in solution and to determine its concentration were reported above. Nevertheless certain steps in this development and in particular the development of certain types of electrodes were not discussed and they have to be considered as some of these are potentially very useful.

Recently the problems concerning film formation and adsorption of ionic species on voltammetric electrodes became a subject of major importance. These electrodes are termed chemically modified electrodes. These devices are made by intentionally attaching new groups or compounds to the surface of simple electrodes mainly graphite and platinum electrodes. Special attention has been paid to chemically modified electrodes for the analysis of coenzymes such as NADH.

New materials for using as electrodes need to be investigated together with the complete investigation of certain electrodes not used previously such as those made from chromium and its alloys (28). The search for new forms of carbon graphite electrodes and new impregnated graphite electrodes, especially for use in nonaqueous media and for high temperature electroanalysis, should have priority as it is known that many problems related to the reproducibility of electrode surfaces still remain without a real solution. Recently Rusling reported on the reactivity of polished glassy carbon electrodes for which the surfaces cannot be considered completely inert (244).

The search for a solid pH electrode is also growing in importance, due to the need for miniature and rugged electrodes for use in biological studies and soil analysis (245). Neutral carriers (246) were made the basis of a new liquid-liquid membrane hydrogen ion-selective electrode and palladium-

palladium oxide pH electrodes were prepared by Grubb and King (247).

An active area of research started to be opened up with the work of Johansson et al (248) This group has been investigating the properties of synthetic zeolites as sensors for the construction of ion-selective electrodes.

Membrane separation in flow-injection analysis for gas diffusion has been thoroughly investigated by Van der Linden (249). Membrane-covered rotating-disc electrodes have been studied by Gough and Leyboldt (250) This appears to be an area of investigation in both voltammetry and potentiometry.

A new generation of ion-selective electrodes was presented by Ebdon et al (251). These authors prepared ISEs based on sensor groups covalently cross-linked onto a polymer matrix. They claimed several advantages for these new type of ion-selective electrodes, mainly longer life-time and robustness.

Antibody electrodes constitutes a new area of development (252), and a tissue based membrane electrode for the determination of glutamine in cerebrospinal fluid was reported by Arnold and Rechnitz (253). Rechnitz and his group have been developing bioselective probes on the basis of living bacterial cells and intact tissue cells, an area of intense research at the present.

Ion-selective field effect transistors (ISFETs) comprise another area of research work in continuous development, led by Janata's team (173).

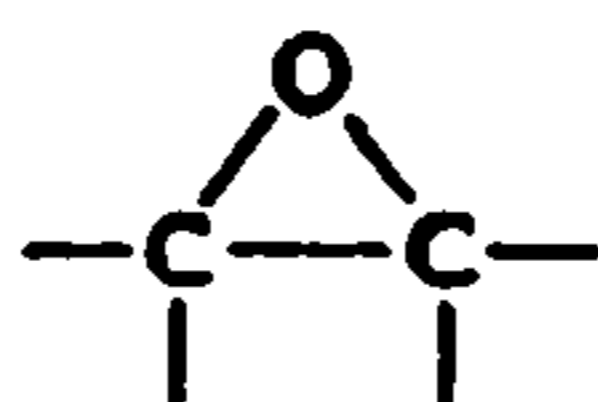
The most promising area for great discoveries is expected to be the study of natural membranes (254) as well as its artificial models in the form of bilayer lipid membranes (BLM), probably associated with ISFETs (255) or in the form of the interface between two imiscible electrolyte solutions (ITIES) described by Koryta (254) and by Lamb et al (256) as liquid membranes.

The use of epoxy resins in the preparation of voltammetric and ion-selective electrodes has been reported in the literature and will be discussed later. On the basis of the characteristics of the epoxide compounds and taking into account the results presented so far by a few authors it is

possible to predict that this area of research deserves more exploration.

Properties and uses of epoxy resins

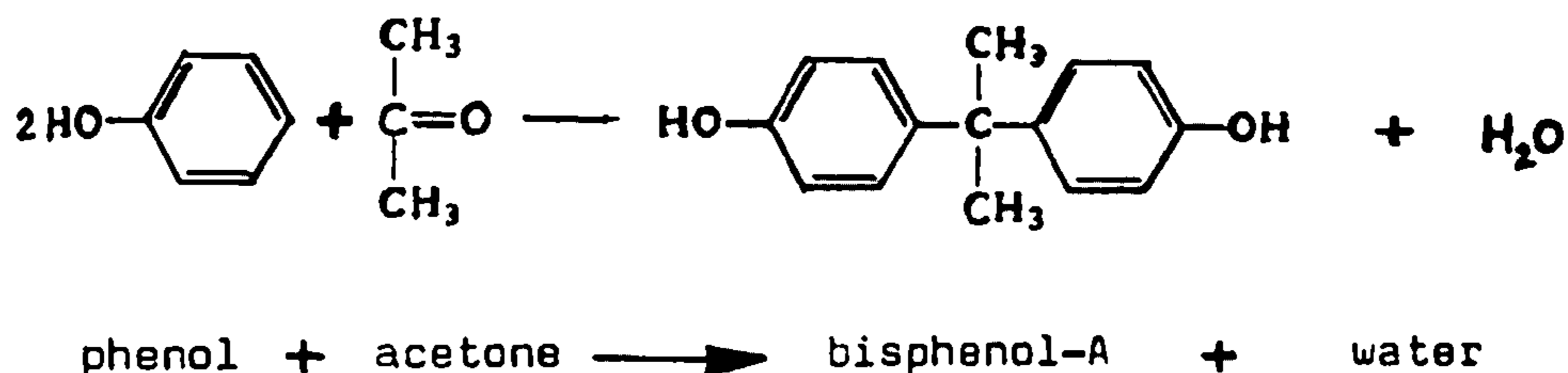
Epoxy resins are characterized by the existence of at least two epoxide groups per molecule. The epoxide group or epoxide ring has the following structure:



epoxide or glycidyl ether

This is the so-called epoxide or glycidyl ether. It is also called the epoxy, oxirane or ethoxylene group.

Most commercial types of epoxy resin are derived from bisphenol-A. The "A" come from the origin of the bis-phenol, produced by the reaction of phenol and acetone :



The simplest bisphenol-A epoxide molecule is generally obtained by the reaction of epichlorohydrin with bisphenol-A resulting in an epoxy terminated molecule with two epoxide groups:

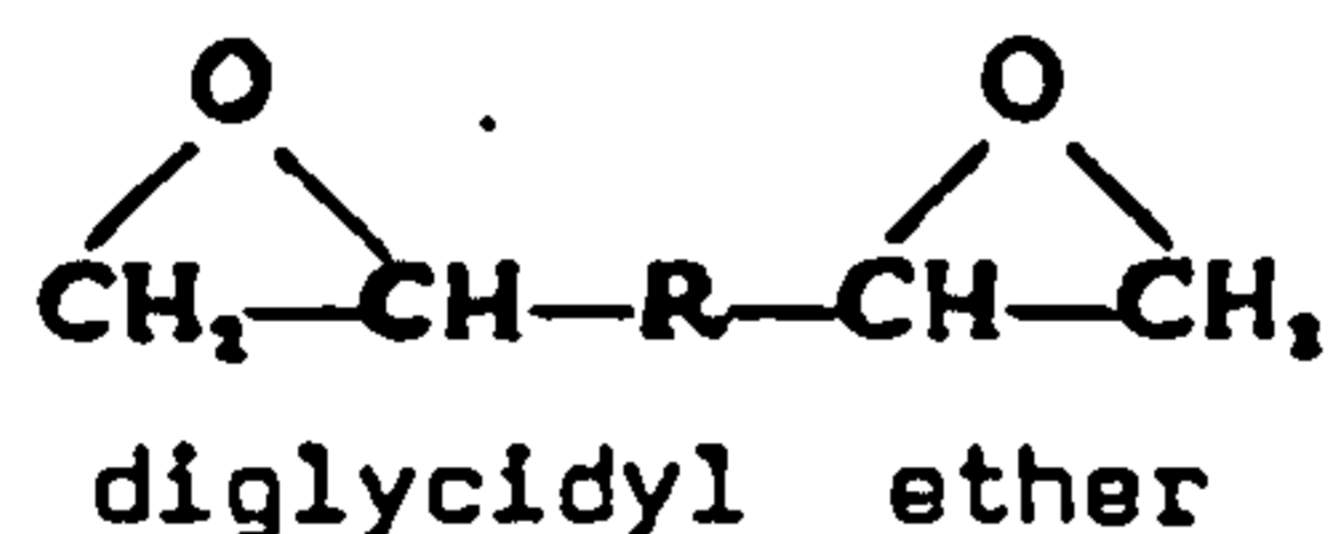
laboratory.

Reactivity of epoxide compounds is expressed as equivalent weight defined as molecular weight per reactive group. For instance, the diglycidyl ether of bisphenol-A, the simplest epoxy molecule has a molecular weight of 340. As it contains two epoxide groups per molecule the equivalent weight is 170. The equivalent weight of the resin should be balanced with the equivalent weight of the hardener, when a determined system is formulated.

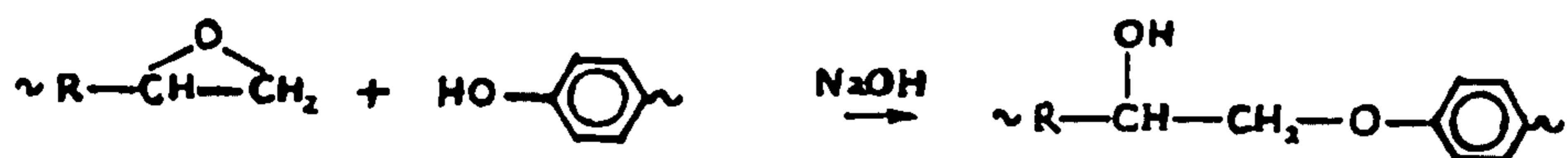
Usually the commercial liquid glycidyl ether resins have average molecular weights within the range 300-400 and they are known to be composed largely of diglycidyl ether.

By reducing the amount of excess epichlorohydrin and reacting under more strongly alkaline conditions to favour the reaction of epoxide groups with bisphenol-A higher molecular weight products may be obtained.

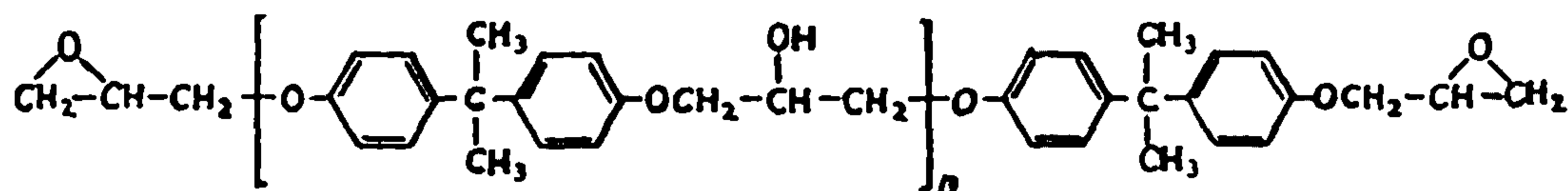
Representing the diglycidyl ether by



and considering its reaction with other hydroxyl groups this mechanism may be represented by



Most commercial resins are partially polymerized to viscous liquids or solids in their uncured stage with average molecular weights lower than 4,000. The general form of an epoxy resin can be represented by



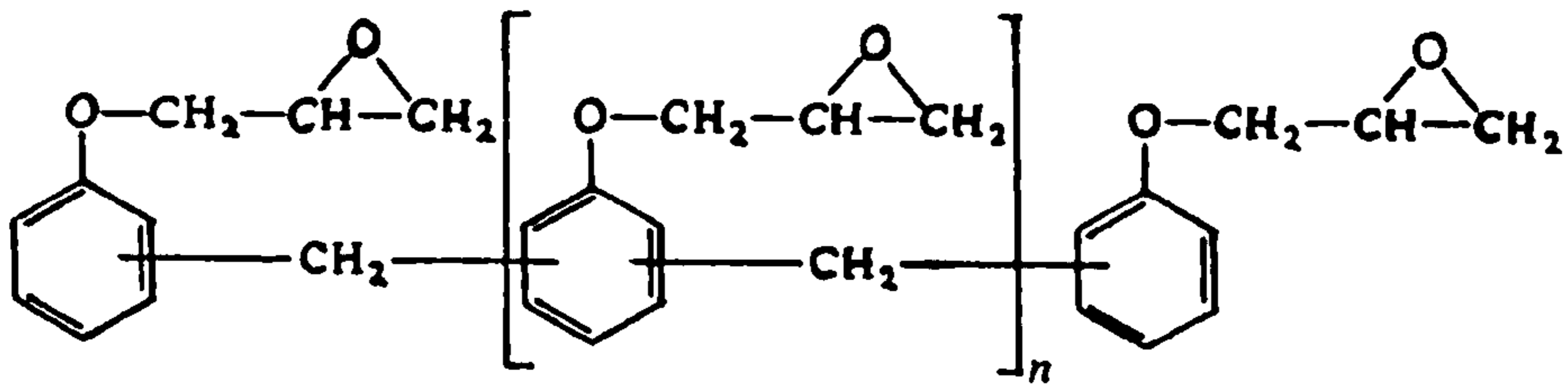
epoxy resin

When $n=0$, the product is the diglycidyl ether and the molecular weight is 340. When $n=10$ the molecular weight is ca. 3,000. The liquid types have $n=0$ to approximately $n=0.3$.

The liquid resins are available from specialized firms and are recommended for casting, laminating, adhesives and coatings (263, 264).

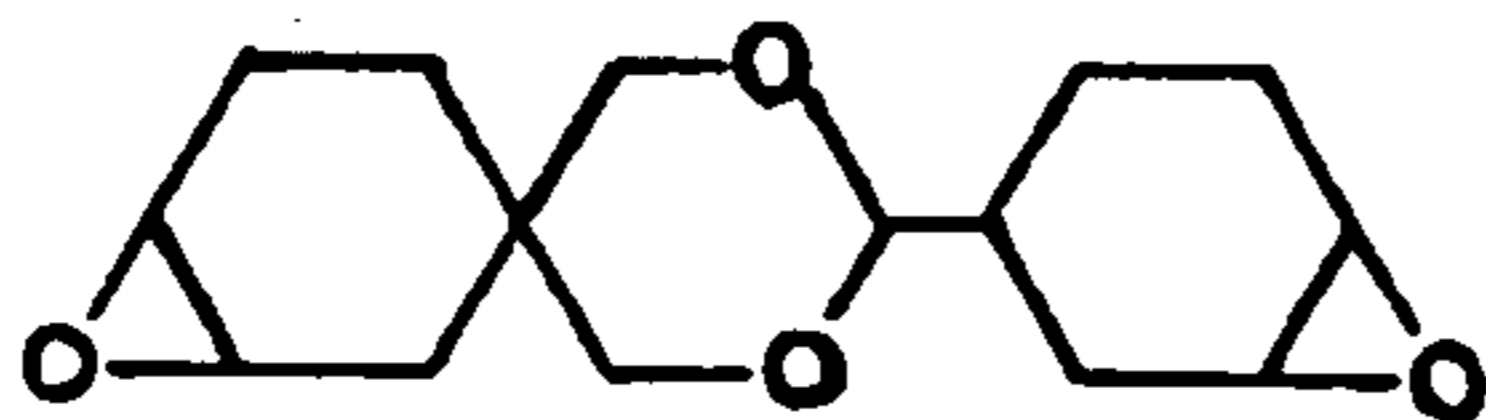
Bisphenol-A resins with several repeating units are solids at ambient temperature. They have a characteristic melting point from 60 to 160°C and equivalent weights within the range 380-6,000 (263, 264). Solid epoxy resins are specially used in molding powders and coatings. Several chemical and physical properties are enhanced in the solid epoxides as lower shrinkage, increased toughness and mechanical properties of cured systems.

Resins with a large number of rings in the structure are available for use in high temperature conditions. For instance the trade mark Novolac epoxy which has an increased ring structure and functionality has improved temperature stability:



epoxy - Novolac resin

Another interesting category of epoxy resins formed by the cycloaliphatic epoxies, with saturated rings in their structures, are normally cured with anhydrides resulting in thermally stable systems capable to support temperatures up to 370°C:



cycloaliphatic epoxide

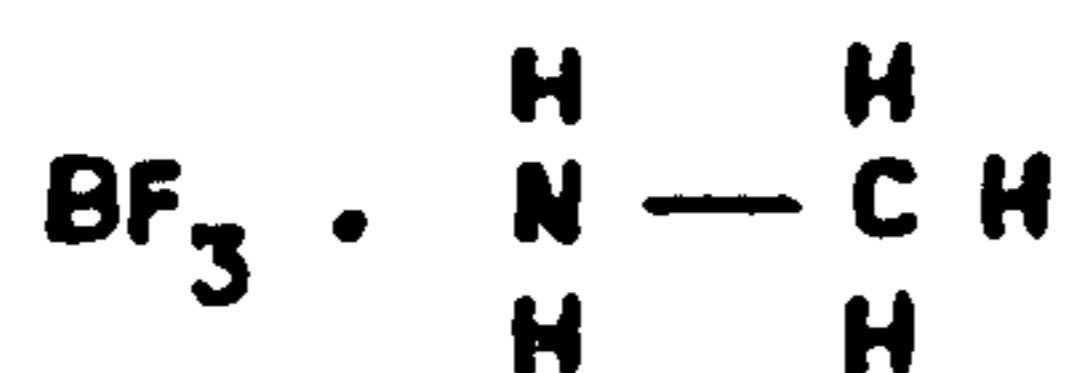
The conversion of epoxy resins from its original form as a liquid or solid into a three-dimensional network held together by covalent bonds in the form of a cross-linked polymer is called curing or hardening. This is attained by the use of a curing agent or hardener. Curing agents in general belong to two types, named catalytic and polyfunctional. The reaction that causes the cross-linking between the resin molecules is achieved via the epoxide groups or through the hydroxyl groups.

In curing by catalytic polymerization the hardener, considered as the catalyst, initiates the resin homopolymerization. Normally the catalysts are used in very small amounts. On the other hand polyfunctional curing agents are used in approximately stoichiometric amounts and integrate the reactions

working as comonomers in the polymerization, causing the formation of a three-dimensional network where the curing agent links the epoxy molecules together. In some cases the curing of an epoxy system may involve both catalyst and polyfunctional cross-linking agent.

There are a very large number of hardeners for the polymerization of epoxy resins. Among them the most common used include, primary, secondary and tertiary amines, boron trifluoride-amine complexes, anhydrides, carboxylic acids, mercaptans (thiols) and several modifications of these curing agents in order to obtain a particular cured epoxy system with previous determined properties. The study of the curing mechanisms has been considered by many investigators and are extensively treated in the mentioned references. They are listed by their commercial names in the catalogues of the companies that offer a variety of formulations recommended for each particular use. Some examples of the curing mechanisms of epoxy compounds with amines are shown in Table 1.

Primary amines are more reactive than secondary and tertiary amines. The linear primary amines normally react at room temperature but aromatic primary amines require heat curing. Tertiary amines act as catalysts initiating homopolymerization. In practice polyfunctional primary amines are mostly used eg. diethylene triamine (DETA). Fig.1 shows a cured epoxy resin with the use of DETA as a curing agent. A common catalyst used is the amine complex of boron trifluoride, mainly that with monoethylamine:

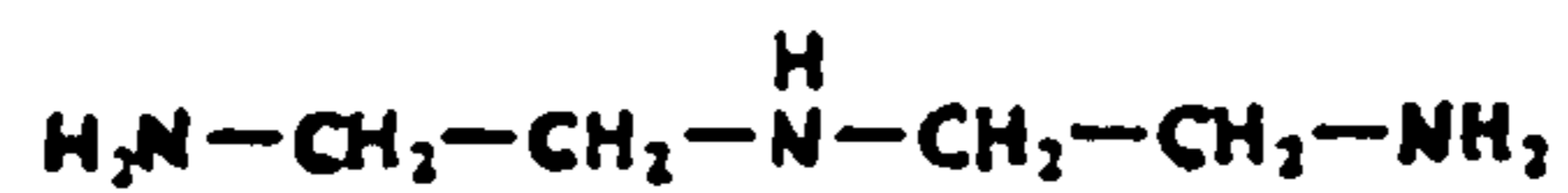


This complex is stable at room temperature and dissociates into BF_3 and $\text{NH}_2 - \text{CH}_2 - \text{CH}_3$ when heated so that at higher temperatures the active catalyst BF_3 functions as a Lewis acid and reacts very rapidly with the epoxy resin promoting its curing via a similar mechanism to that for the tertiary amine.

Table 1. Mechanism of curing of epoxy resins with amines

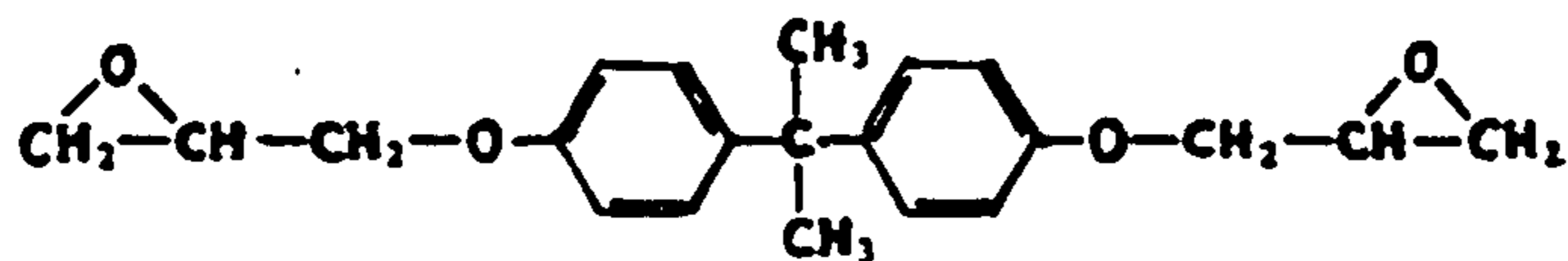
<u>amine</u>	<u>epoxy</u>	<u>product</u>
$R'-NH_2$ primary	$ \begin{array}{c} O \\ \diagup \quad \diagdown \\ R-C \quad CH_2 \\ \\ H \end{array} $	$ \begin{array}{c} OH^* \quad \quad \quad OH^* \\ \quad \quad \quad \\ R-C \quad H \quad CH_2-C-R \\ \quad \quad \\ H \quad H \quad N-R' \end{array} $
$ \begin{array}{c} R' \\ \diagdown \\ NH \\ \diagup \\ R' \end{array} $ secondary	$ \begin{array}{c} O \\ \diagup \quad \diagdown \\ R-C \quad CH_2 \\ \\ H \end{array} $	$ \begin{array}{c} OH^* \\ \\ R-C \quad H \quad N \begin{array}{l} / R' \\ \backslash R' \end{array} \\ \quad \\ H \quad H \end{array} $
$>N-$ terciary	$ \begin{array}{c} O \\ \diagup \quad \diagdown \\ R-C \quad CH_2 \\ \\ H \end{array} $	$ \begin{array}{c} H \\ \\ HO-C-R \\ \\ CH_2 \\ \\ O \\ \\ R-C \quad H \quad O-CH \\ \quad \quad \\ H \quad H_1 \quad R \\ \quad \quad \quad \vdots \\ \quad \quad \quad CH_2 \end{array} $

* Reactive sites for the continuation of crosslinking



Diethylene triamine (DETA)

+



Bisphenol-A epoxy resin

↓

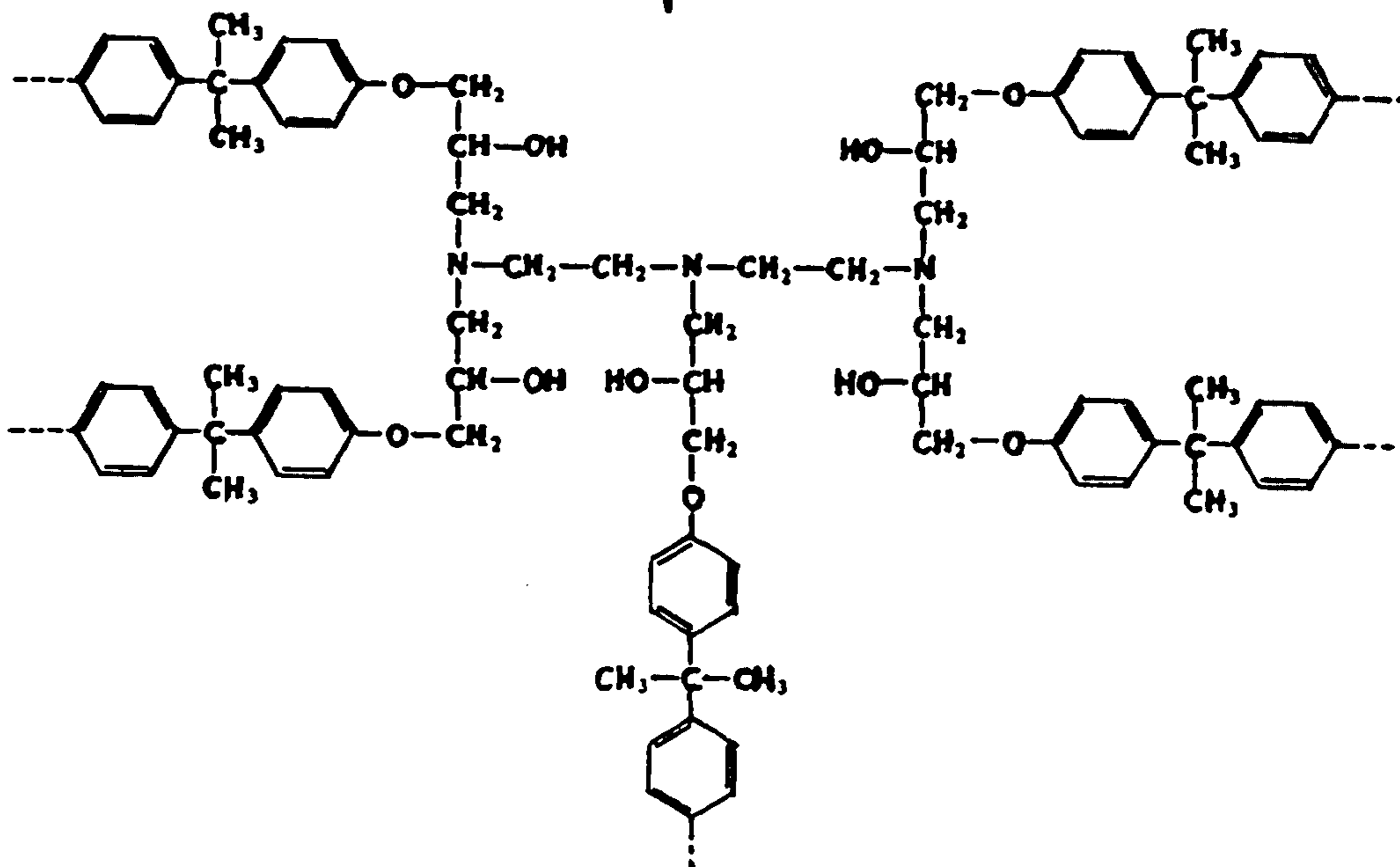


Fig.1 Aliphatic Amine Cured Epoxy Resin

The mechanism of curing with boron trifluoride complexes, aldehydes and mercaptans are more difficult to interpret and have been presented in the literature (257). Usually the presence of hydroxyl groups is essential and in the cases of aldehydes and mercaptans the polymerization reaction generally is initiated by amines as accelerators.

Several modifiers have been added to the epoxy resins. They have been used for various reasons, mainly to decrease the shrinkage of cured systems, to decrease the viscosity of the resins and to impart more flexibility to the product. Among them the diluents, the fillers and the plasticizers play an important role as is obvious from the great variety of commercial products whose formulation for specific applications are marketed under trade names and kept undisclosed.

In the case of epoxy resins the use of glycidyl ethers as reactive diluents for viscosity reduction is very common. These solvents like for example butylglycidyl ether, contain an epoxy group as part of the molecule which will constitute a reactive site during the polymerization process. Decylglycidyl ether and cresylglycidyl ether are most used due to their lower vapour pressure. They have been marketed and used in epoxy formulations produced by specialized companies. The fillers mostly common used include silica, talc, aluminum powder, besides graphite or silver powder in the conductive resins. These fillers modify the mechanical properties of the cured resins and lower the cost. The most common plasticizers used with epoxy resins comprise dibutylphthalate, *n*-octylphthalate and flexible epoxy resins derived from aliphatic polyols or long chain acids. The use of amidoamines as the curing agent and polysulphides in the epoxy composition also promote the flexibility of the cured products. All these flexibilizers, in the form of special curing agents, plasticizers, diluents or polysulphides increase the distance between cross-links giving more flexible products.

Several modifications of epoxy resins can be carried out with synthetic

polymers as for instance in the preparation of the epoxy Novolac systems, the composition of which includes the phenolic-formaldehyde resins. The result of the reaction of these resins with epichlorohydrin produces the solid Novolac epoxy resins, of great utility as a high temperature resistant product. Another important association results from the nylon-epoxy films containing 30-50% of epoxy together with nylon of the type Zytel 61. These nylon-epoxy films have been shown to present outstanding adhesive properties and are normally used in the aircraft industry. It seems that an almost endless list of different products can be obtained from epoxy resins combined in addition to the main recommended systems. These have a great variety of properties and this justifies the still increasingly research work in this area. These resins have been exploited in numerous ways and have been extensively applied to practical problems.

The use of epoxy resins in the preparation of membranes for electrochemical use is clearly a minor application. Progress, however, seems to be slow in spite of the published work in the literature. Those publications have been produced at a comparatively slow rate compared with other common approaches for the preparation of membranes and almost nothing has been reported in terms of the addition of modifiers, as part of epoxy-based electrochemical sensors.

Epoxy-based graphite voltammetric electrodes

Epoxy resins have been used as an impregnating material for the fabrication of graphite voltammetric electrodes. Brainina et al (225,265,266) seem to be the first to use epoxy-impregnated spectrographic graphite rod as a voltammetric electrode. Epoxy-based microelectrodes made with glass capillary tubes of tip diameters ca. 75-200 μ m were prepared by Conti et al (10) and by Cheng et al (267) for in vivo studies. These authors employed Nujol as a nonreactive diluent and plasticizer. The electrodes so prepared

with tri-ethylenetetramine as the hardener cured in 24-48h (10). Sykut et al have developed a new type of epoxy-impregnated graphite electrode (EIGE). They used a spectrographic carbon rod impregnated with epoxy resin and hexahydrophthalic anhydride as a curing agent, heated at 343-353K, under vacuum, for a period of 1.5h. After finishing the impregnation step the resulting impregnated graphite rod was covered by a new layer of epoxy resin as an isolation layer which was allowed 12h at 393K and 6h at 423K for complete curing (268). These electrodes were used mainly for ASV determinations. Swofford, Jr. et al constructed a rotating carbon-epoxy electrode for current-voltage investigations (269). From their studies they assumed that under appropriate conditions the bonds formed in the polymerizations of the resin could be attacked and thus introduce anomalous electrode behaviour. They recommended caution about using the electrode in highly oxidizing or reducing media and pointed out that the electrodes used became poisoned at potentials greater than +0.80V. Furthermore they used a complicated procedure for the preparation of the electrodes involving centrifugation and a curing time of 36-48h. The electrical contact with the carbon disc was made using mercury. Anderson and Tallman (270) described a graphite-epoxy (graphoxy) electrode as a viable alternative to other working electrodes currently used in anodic stripping voltammetry (ASV). They claimed that the electrode is easy and inexpensive to make, is easily polished and durable. They used centrifugation to eliminate the air bubbles entrapped in the epoxy base employed for the construction of the electrode. The system used required 5h for hardening. Moreover problems with background currents possibly due to excess of hardener on the electrode surface (107) limited the use of the electrode to ASV. Wang (110) reviewed the use of epoxy-based graphite electrodes and indicated that these had been used previously mainly for ASV as large and irreproducible background currents limited their application in other voltammetric techniques. This author described a method of constructing

minielectrodes based on commercial graphite epoxy mixture which requires 4h for hardening. Falat and Cheng (271) reported on the use of an electrochemical pretreatment of a graphite-epoxy microelectrode and its successful application for the voltammetric differentiation of ascorbic acid and dopamine. It was similar to the electrode produced previously by Cheng et al (267) cured at 150°C for several hours and presenting typical resistance of 200ohm. They applied the conditioned electrode for in vivo experiments. Recently, McLean has reviewed the application of carbon electrodes for liquid chromatography detection (272). He examined various types of electrodes made of carbon black in a matrix of polythene or polypropylene and also investigated the properties of electrodes containing various types of impregnating materials commonly used including oils, monomers and resins, in place of the polymers mentioned. He found that epoxy resin did not produce useful results in the considered conditions and none of the impregnating materials studied were successful as they failed to provide the desired combination of low background noise and solvent resistance. Because of that this author preferred to consider the polymeric matrices as more important for the preparation of electrodes for electrochemical detection in liquid chromatography.

Epoxy-based ion-selective electrodes

Epoxy resins have also been used in the fabrication of ion-selective electrodes. Hirata and Date (273) appear to be the first to use epoxy resin as an inert matrix for the preparation of an ion-selective electrode. They prepared copper(I) sulphide-impregnated membrane using 10-70% of the epoxy resin as the binder and have studied the behaviour of the membranes in solutions of copper sulphate, copper nitrate and potassium chloride. They showed that the epoxy-impregnated membranes responded to anions and the slopes were almost independently of the fraction of epoxy resin within the range they have used. They prepared epoxy-impregnated membranes with silver chloride

and barium sulphate which also responded to anions. A membrane prepared with copper(I) sulphide containing up to 10% of the resin was prepared by mixing the appropriate amount of the sulphide with the resin and pressing the mixture in a form of a disc. The obtained pressed membrane was sealed onto the end of a plastic tube and an internal solution (10^{-3} M copper sulphate) used. A SCE as the internal reference electrode completed the design. The electrode was shown to respond to Cu(II) when less than 2% of epoxy resin was used but the response was not Nernstian. After preparation the membranes were soaked in a 10^{-2} M solution of copper(II) sulphate for more than five days. Coetzee and Basson developed a new type of epoxy-impregnated ion-selective membrane electrode (274). They used a 50% m/m of commercial resin marketed under the name Araldite mixed with a thallium(I)-heteropolyacid salt to prepare the base of the membrane. Usually the mixture of 0.5g of Araldite and 0.5g of the salt was spread on a filter paper and left for curing after which a 2.5cm diameter disc was cut and equilibrated in 0.1M thallium nitrate solution for 6 days. This membrane was used to prepare the electrode with 0.1M thallium nitrate as internal reference solution. The electrodes were used as described by the authors mainly for potentiometric titrations. They reported a longer response time than that obtained with commercial available electrodes. Moreover the electrode behaviour was not Nernstian but they could determine thallium up to 10^{-4} M although this electrode showed poor selectivity for thallium in ^{the} presence of monovalent cations. They discussed the behaviour of this new kind of membrane in nonaqueous solutions in respect to pH, claiming that the membranes lasted for about 5 months. Yamazato et al(275) powdered epoxy resin as the binder for the preparation of a mercuric-ion-selective electrode without an inner reference electrode. They used mercury(II) sulphide and mercury(II) selenide as sensors mixed with the resin and connected directly to the electrical lead. They reported that very good mechanical properties were provided by the epoxy resin and observed linear relationships

between the electrode potentials and the logarithmic concentration of mercuric ion up to 10^{-5} M for HgS and up to 10^{-8} M for HgSe. Silver ions and halogen ions showed strong interference owing to the formation of Hg(II) complexes (275). Zhukov et al (276) prepared a pressed disc with solid powders of 325 mesh, containing 7% of epoxide resin ED-6 by weight mixed with Cu_2HgI_4 as the sensor for copper ions. The system was hardened by polyethylene-polyamine used in 10% of the weight of the resin. To obtain the disc for the preparation of the electrode the mixture was pressed for 4h under 150Kgcm^{-2} at 90°C . The membrane showed a high sensitivity toward copper ions and the response was linear up to 5×10^{-6} M Cu^{2+} . Only silver and ions of the type I^- , CNS^- etc. which formed weakly dissociated complexes or sparingly soluble compounds with Cu^{2+} and Hg^{2+} interfered significantly.

Tungstoarsenates were used as sensors for cesium and thallium(I) ions in an epoxy base made of Araldite (277). The corresponding membranes were equilibrated in 0.1M cesium chloride solution or thallium(I) nitrate solution for 6 days. The values of the membrane potentials were much smaller than the expected Nernstian values and the authors assumed the hypothesis of incomplete permselectivity of the membrane as the factor responsible for that behaviour, based on the work of Moody and Thomas (278). In spite of the deviations observed from Nernstian behaviour they found the membranes suitable for determination of cesium or thallium(I) concentrations as low as 10^{-4} M. Membranes prepared with rubidium 12-tungstoarsenate in Araldite were used for the preparation of an ion-selective electrode for silver which did not suffer from interference by Hg^{2+} and S^{2-} ions (279). The membranes were equilibrated in 0.1M silver nitrate solution for three to four days in order to display a stable potential. The response of the membrane, when the authors followed the technique introduced by Coetzee and Basson (274), did not show Nernstian behaviour presenting a slope of 34mV per decade but they obtained

a linear plot in the concentration range of 10^{-1} to 10^{-4} M. This membrane showed a short response time of 30-40s compared to 2-3min of a similar membrane based on heteropolyacid salts in Araldite (277, 279). The best pH range was considered to be between 4 and 6 as above pH 6 the depolymerization of the heteropolyacid salt occur. These membranes usually last for 1-2 months. The silver selective membrane described above has been shown to be very selective for Ag^+ ions.

Jain et al (280) prepared a thallium(I) selective solid heterogeneous membrane electrode from a 60:40 mixture of thallium(I) molybdoarsenate and Araldite. They reviewed previous work on the use of heteropolyacid salts in epoxy resin as the basis for ion-selective electrodes. They found that the molybdoarsenate-Araldite membrane was selective for thallium(I) ions with Nernstian response of potentials in the range 10^{-1} to 10^{-3} M but that it could be used for determination of thallium(I) down to 10^{-5} M. The response was independent of pH over the range 4 to 6 and the slope of the log-concentration versus potential plot was improved in 10 and 25% acetone-water mixtures. The preparation of the membrane was cumbersome and the time for equilibration of the discs cut from the master membrane was one week before the disc was sealed on the electrode body. An epoxy-based ion-selective electrode with solid internal contact was prepared by Yoshihiro et al (281). They prepared a disc electrode from a mixture containing 55% of cerium(IV) oxide and 45% rapid Araldite adhesive in weight. The appropriate amount of the mixture was coated on the copper plate of the electrode body as described by these workers. The resultant electrode was selective for trivalent rare earths with a slope of 58mV and less selective for bivalent and quadrivalent cations.

As described previously in the section about the search for new electrodes, zeolites embedded in low viscosity epoxy resin have been used for the preparation of ion-selective electrodes (248). In these preparations Johansson and co-workers adopted a different system based on a preliminary

fabrication of a pressed pellet to be impregnated with the selected resin. They prepared the electrodes by polishing both sides of the prepared discs and sealing these membranes onto the electrode body, after convenient equilibration. As employed by these authors it seems that the epoxy resin is only working as an impregnating material. Lal et al (282) developed a novel nitrate-selective electrode based on precipitated nitron nitrate in a matrix of 50% m/m epoxy resin Araldite as the binder. These authors reviewed the development of nitrate-selective electrodes discussing the principal disadvantages of the previous methods for the analysis of nitrate and indicating the problems presented by the nitrate ISEs produced so far. The method of preparation of the sensor and the fabrication of the membrane were described. The electrode prepared on the basis of a procedure used first by Coetzee (274) and later by other researchers (277, 279, 280) showed a series of advantages: linear response to nitrate concentrations down to 10^{-4} M with a slope of 50mV per decade change in nitrate concentration, and the possibility to determine nitrate up to 10^{-5} M with a calibration curve. The slope was constant within a period of six weeks. After this time it decreased but a linear response remained constant even after six months. They observed linearity of response down to 10^{-4} M, using a 40% aqueous ethanol medium with a slope of 49mV. The response time was 1min and the potential response of the electrode was independent of the pH in the range 2 to 8.5. Several anions showed no interference to the response but iodide interfered seriously. The authors did not suggest an explanation for the iodide interference. The selectivity coefficients for NO_2^- , Cl^- and Br^- are of the order of 10^{-1} and Co^{2+} , Cu^{2+} and Al^{3+} were shown not to interfere. This electrode was used successfully for the direct determination of nitrate in soil extracts. The results of these determinations compared favourably with a spectrophotometric method.

Thind et al (283) reviewed the development of lead-selective electrodes

and described the preparation of a non-sulphide based ion-selective electrode for the estimation of lead within the range 10^{-1} to 10^{-4} M Pb(II) with a slope of 22mV per decade of concentration. Lead(II) antimonate was the basis for the membrane containing 25% m/m of the salt in a matrix of Araldite. Saraswat^{et al}(284) described the preparation of an epoxy-based ion-selective electrode sensitive to the complex cation $[\text{Co}(\text{en})_3]^{3+}$ where en=ethylenediamine. They used a chromium ferrocyanide gel saturated with the mentioned cation as the sensor in a membrane prepared similarly to other epoxy-based electrodes described earlier (280). They reported good selectivity of this membrane electrode toward $[\text{Co}(\text{en})_3]^{3+}$ ions as a series of cations tested have shown no interference in the potential response of the electrode fabricated with 20% m/m of Araldite as the binder. They claimed that the electrode can be used for a period of two to three months for measuring the mentioned cations in the range 10^{-1} to 10^{-4} M in a pH interval of 3.5 to 6.5 and no drift in potential is observed during this time. Another electrode of this type was prepared by Jain et al (285) using copper hexacyanoferrate(III) as a sensor for thallium(I) ions. It was demonstrated that this electrode is better than the thallium(I) selective electrodes prepared so far. These authors reviewed the development of ion-selective electrodes based on inorganic ion exchangers as the sensor material.

Ishiwada et al (286) reported on the different types of miniaturized polymer membrane electrodes (PMEs) for chloride ions using epoxy resin as the binder. The best electrodes were said to be obtained using the system formed by a copper wire coated with three successive layers of silver paste of epoxy matrix type, silver chloride and epoxy matrix incorporating 45% m/m of an ion exchanger solution. They found that the most appropriate ion-exchanger solution was 1-decanol containing 0.4% m/m of trioctylmethylammonium chloride. Srivastava et al recently reviewed the preparation of cation-selective electrodes based on heteropolyacid salts as sensors and

reported on the preparation of a new probe in this series, selective for rubidium ions (287). The membranes for electrode construction were prepared as described previously by Coetzee (274) containing 0.6g of titanium tungsto-arsenate and 0.4g of Araldite. A comprehensive study of the performance of this electrode was presented including a study of the selectivity of the membrane for Rb^+ over other cations.

An interesting report on Araldite-based membrane electrodes was published by Agrawal and Abe who recently described a new nitrate ISE based on crystalline antimonite(V) acid incorporated in epoxy resin (288). During their studies on the performance of the electrode prepared by mixing 0.7g of the acid with 0.3g of Araldite they made important observations on the behaviour of the membrane: some membranes constructed with Araldite only, containing no sensor, responded to nitrate and the potentials showed almost linear relationships with the concentration of nitrate ions. Nevertheless steady potentials were obtained only with the presence of the mentioned sensor in the membrane when its concentration were greater than 50%. As they used a standard type of Araldite said to be a polyamide-type epoxy polymer it appears that the interference of nitrate ions with the pure membrane perhaps is related to the structure of the polymer itself. The authors assume that the functional group $=\overset{+}{\text{N}}=$ may remain in the polymer after polymerization and can behave as an anion exchanger. They suggested that the response on this membrane may be due to the anion-exchange contribution of the polymer and in this case the crystalline antimonite(V) "sensor" (C-SbA) acts as an electro-conductive material. Nevertheless no further proof was presented for this assumption and they applied the electrode for nitrate determinations in the range of 10^{-1} to 10^{-5} M with a near Nernstian behaviour. Stable potentials were attained within 10-30s and remained unchanged for ca. 2min. They used the electrode in solutions containing 10% and 25% of ethanol and of acetone. With 10% of nonaqueous solvent the response was similar to that

in aqueous medium. They claimed that one advantage of the system is that no leakage of ion-exchange material occurs. This leakage constitutes a drawback of commercial units and epoxy-based electrodes containing liquid ion-exchangers (289).

Basis and intentions of the present work

The study of new possibilities for the preparation of voltammetric and potentiometric epoxy-based electrodes was made the basis of the present research. The intentions were to provide a new methodology for the construction of reliable and reproducible detectors.

The search for a new technique of curing the epoxy base used and to modify the cured product conveniently, was considered of vital importance in the planned studies. These studies were to consider the construction of voltammetric and potentiometric sensors to be used in the stationary mode and in the controlled hydrodynamic conditions in the form of flow-through cells of several different geometries, namely tubular, conical and porous electrodes as well as thin layer cells. It was also decided to apply the electrodes and cells of various configurations to common electrochemical determinations performed normally with the well known commercial versions of these electrodes.

PRELIMINARY EXPERIMENTAL WORK

Chemical treatment of loaded-graphite-Araldite electrodes

An epoxy base made of Araldite (Rapid Araldite) including the hardener containing 50% m/m of spectrographic graphite powder was prepared and used in the fabrication of graphite voltammetric electrodes. These electrodes were constructed by inserting a small amount of the mixture into a plastic tube 6cm long provided with a copper wire 1cm thick as the electrical conductor. An approximately 1cm length of this paste was pushed inside the electrode body and left for 30min for complete hardening. Then the surfaces of the electrodes were polished with fine abrasive paper, washed with distilled water and dried with a tissue. Linear sweep voltammetry (LSV) was used for testing these electrodes in comparison with the response of a glassy carbon electrode under the same conditions. The performances of three electrodes were examined and the results obtained are shown in Fig. 2.

Sunset Yellow (20ppm) in pH 2 Britton-Robinson solutions was used as the test solution, and was scanned at 10mVs^{-1} and $0.2\mu\text{Amm}^{-1}$ between 0.8V and 1.12V. Electrode No.I was previously treated with distilled water at 90°C for a period of 30min, rinsed with distilled water and dried with a tissue. Electrode No.II was left in 96% ethanol for 30min, washed with water and dried. The third electrode tested underwent no treatment except polishing. As can be seen from the diagram the electrodes did not behave well for no characteristic peaks appeared similar to those obtained with the glassy carbon (electrode No.IV) and it was assumed on the basis of the previous reports that this bad performance was due simply to high background currents. Later it was found that adsorption, film formation and leakage caused by a poor seal contributed to this imperfect behaviour. In some cases attempts were made to improve the performance of the graphite-Araldite surfaces by cleaning or modifying them

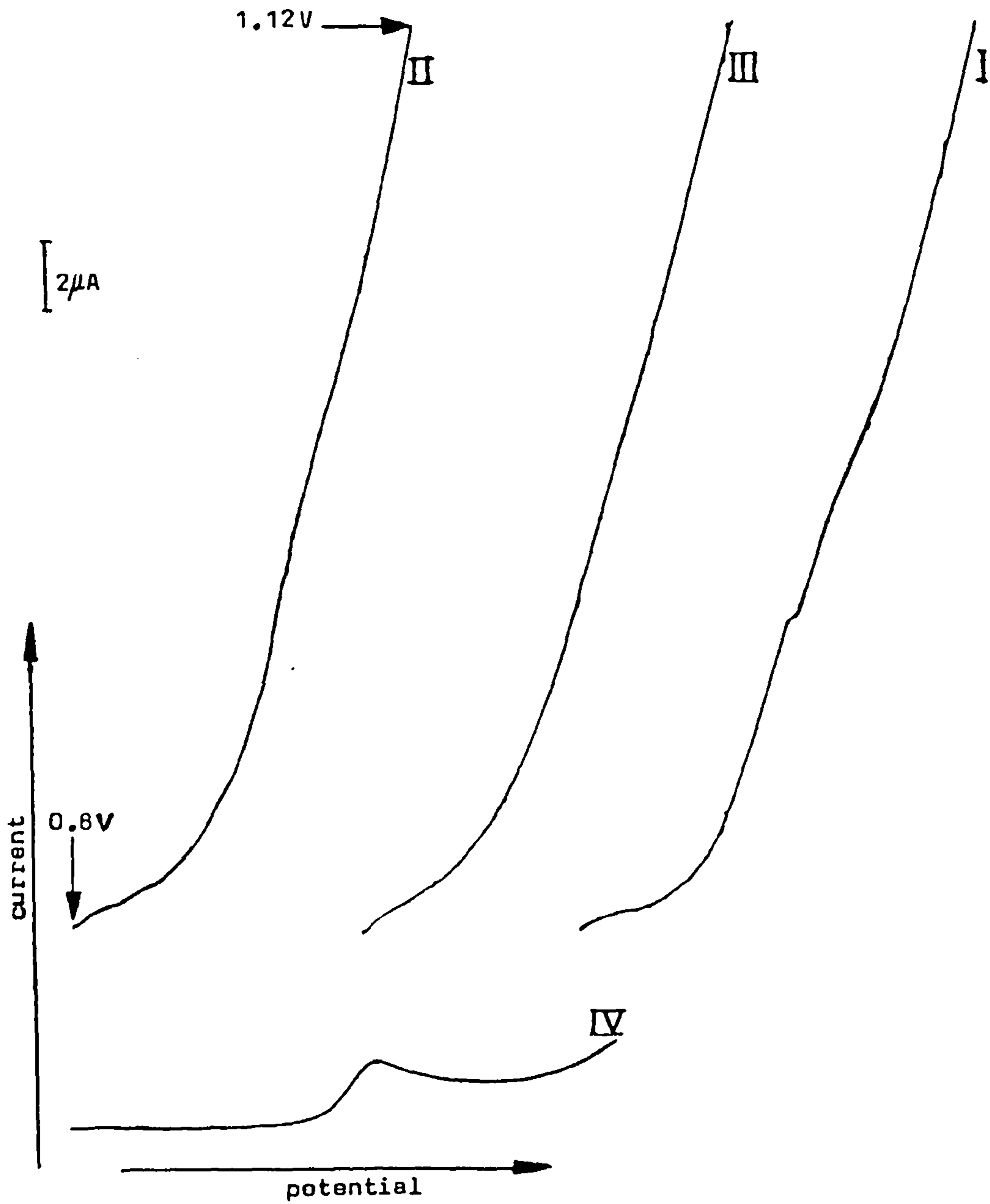


Fig. 2 LSV of 20ppm Sunset Yellow in pH 2 at Loaded-graphite-Araldite Electrodes (I,II and III) Compared with Glassy Carbon Electrode (IV).

with concentrated acids and other chemicals.

Among the chemicals selected to treat the electrode surfaces it was observed that concentrated sulfuric acid immediately carbonized the epoxy adhesive. A typical polymerization reaction was initiated with the hardener when these ingredients were tested separately. On the other hand concentrated phosphoric acid slowly polymerized the adhesive component producing a purple colour on heating. Both concentrated acids imparted a yellowish colour to the cured epoxy resin and the system became brown and brittle being finally destroyed. The action of hydrochloric acid was less vigorous as this reagent (12M) caused a slow polymerization of both adhesive and hardener when treated separately and had no effect on the cured product. Other chemicals, namely sodium hydroxide, ammonia and organic solvents were tested without causing any significant change on either the epoxy adhesive or the curing agents. The most impressive change of physical properties was observed during the interaction of 40% m/m hydrofluoric acid solution with the components of the epoxy resin mixture under investigation. When both the epoxy adhesive and the hardener of the Rapid Araldite were brought into contact with a drop of the reagent mentioned above chemical reaction occurred and a new system was formed with properties characteristic of a polymerized material. Hydrofluoric acid (40% m/m) was therefore used to treat the surface of the graphite-loaded Araldite-based electrodes in order to eliminate or to change the behaviour of the electroactive groups remaining on their surfaces.

White spots were observed after treatment of the electrodes for a period of 30min by dipping them into the HF solution in a plastic beaker. Then the electrodes were washed thoroughly with distilled water and were tested in the same Sunset Yellow solutions as were used previously. They showed significant improvements in performance as depicted in Fig. 3. The scans for three electrodes treated in this way with 40% m/m hydrofluoric acid show some indications of the characteristic waves of the food colouring which were not

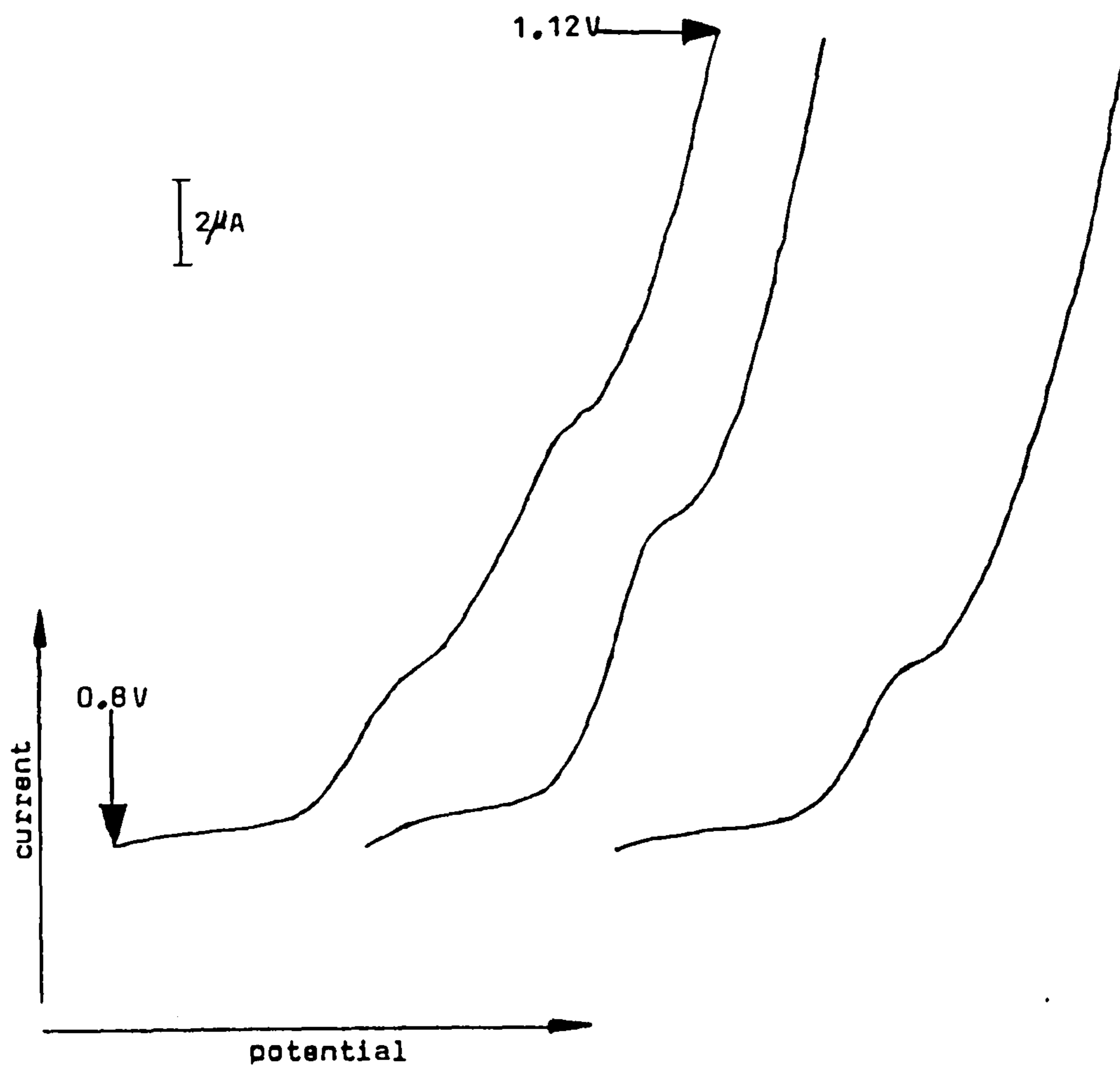


Fig. 3 LSV of 20ppm Sunset Yellow in pH 2 at Loaded-graphite-Araldite Electrodes Treated with 40% m/m Hydrofluoric Acid.

visible previously when untreated electrodes were studied (Fig. 1).

Hydrofluoric acid as a curing agent for loaded-epoxy base

Since hydrofluoric acid has the property of polymerizing the epoxy resin component of the two-tube Araldite system used so far it was decided to try the preparation of some electrodes with an epoxy base hardened with hydrofluoric acid alone without adding the common commercial hardener or catalyst. The following technique was employed for the first investigation.

A suitable amount (usually 0.5g) of spectrographic graphite powder was suspended in a small container inside a plastic reservoir containing in a second small cup approximately 2ml of 40% m/m hydrofluoric acid solutions which provided a HF vapour atmosphere inside the chamber. The carbon powder was left for a period of 6h to be saturated with hydrofluoric acid vapour. This type of graphite powder saturated with concentrated hydrofluoric acid vapour was shown to cause the complete curing of the epoxy resin system in the absence of any other hardener or catalyst. This graphite which has adsorbed HF vapour in the way indicated above has been termed graphite-HF here.

Prototype graphite-HF epoxy-based voltammetric electrodes

Graphite powder (0.5g) saturated with 40% m/m hydrofluoric acid vapour as described above was mixed thoroughly for 5min with 0.5g of epoxy resin adhesive (i.e. the contents of the adhesive tube of a two-tube Araldite commercially available from hardware shops). Small portions of this epoxy base were then forced into a nylon tube 6cm long and approximately 4mm bore to a length of up to ca. 1cm. A copper wire 1cm thick served as the electrical contact. The piece of copper wire was inserted directly into the graphite-epoxy mixture as close as possible to the electrode surface without affecting the performance of the electrode, i.e. about 0.5cm from the electrode surface. The prepared electrodes were left for a period of 9h overnight at ambient temperature to ensure complete curing of the matrices. Then they were polished

unloaded epoxy sealant _____

_____ copper wire

_____ nylon tube

graphite-loaded epoxy cured
with 40% m/m HF(aq)

with a fine abrasive paper, washed with distilled water and dried with a tissue. This prototype graphite-epoxy-HF electrode is depicted in Fig. 4.

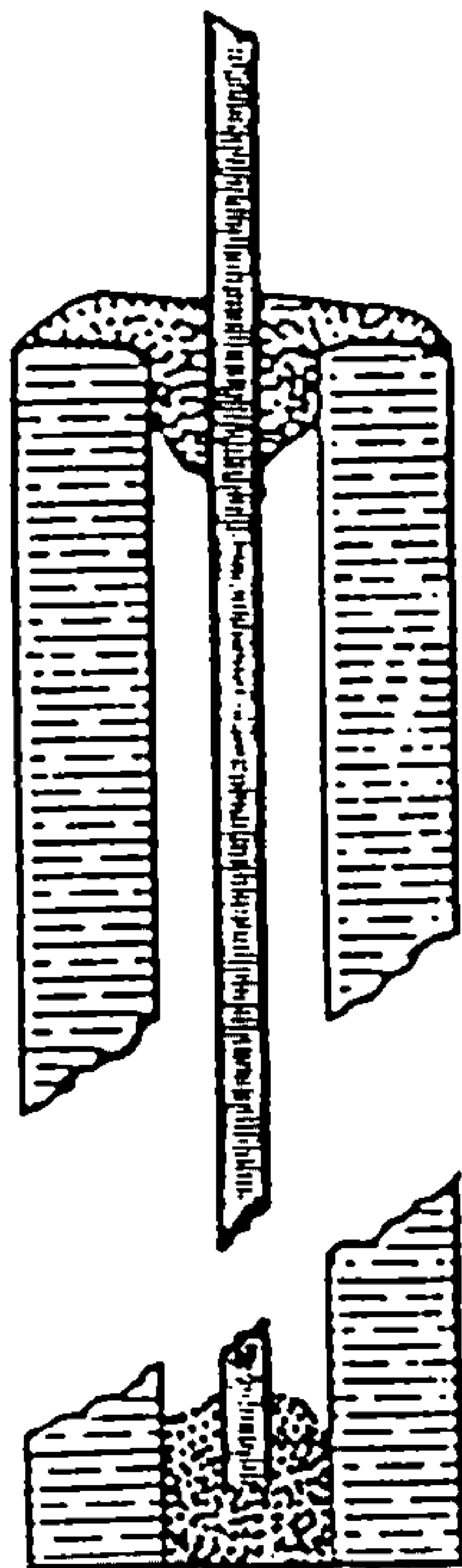


Fig. 4 Prototype Graphite-Epoxy-HF Voltammetric Electrode

with a fine abrasive paper, washed with distilled water and dried with a tissue. This prototype graphite-epoxy-HF electrode is depicted in Fig. 4.

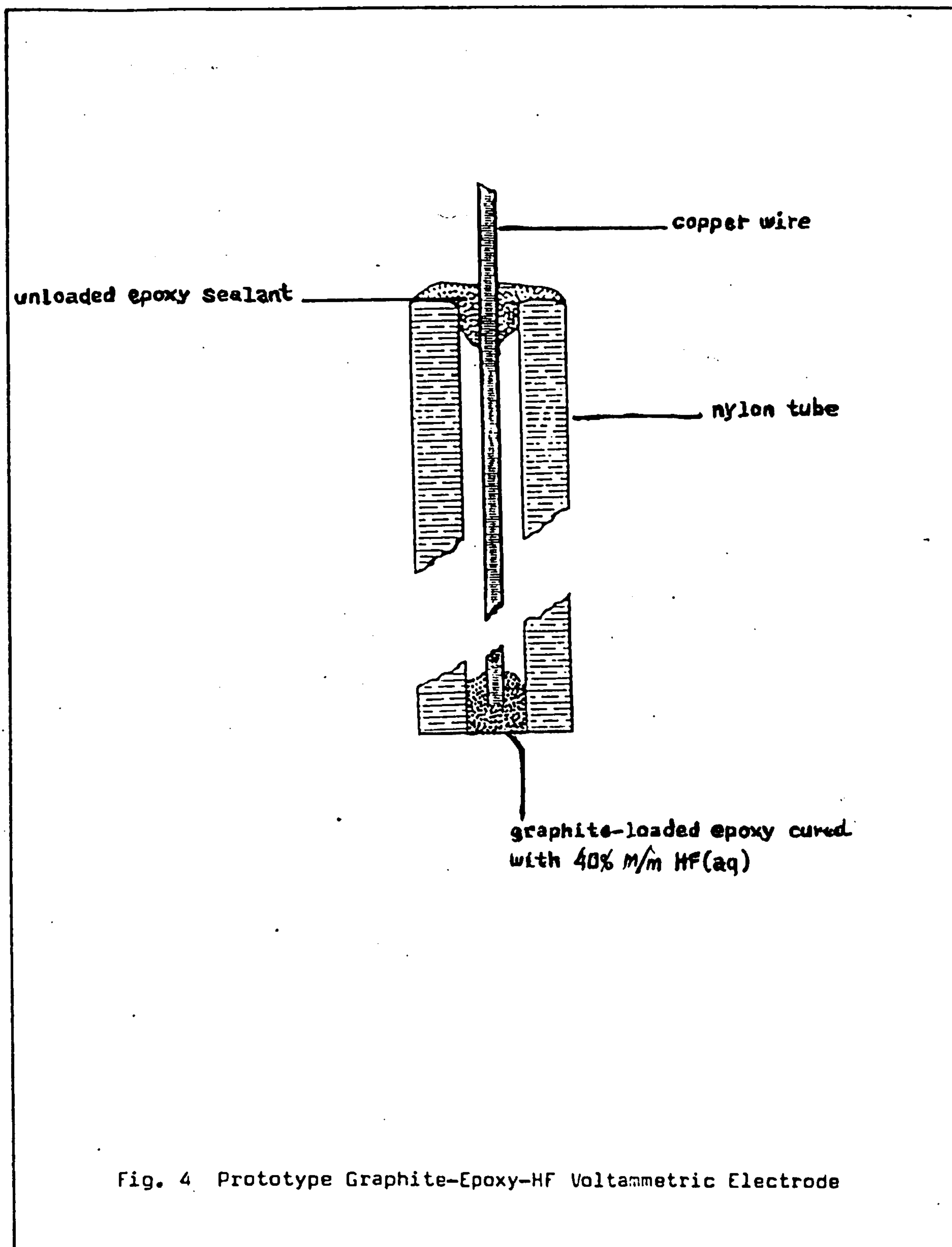


Fig. 4. Prototype Graphite-Epoxy-HF Voltammetric Electrode

Preliminary tests

The prototype electrode was tested in 30ppm tartrazine solution in pH 2.3 Britton-Robinson buffer. The LSV mode was used scanning at 25mVs^{-1} and sensitivity $0.2\mu\text{Amm}^{-1}$ from 0.8V to 1.12V. Fig. 5a shows a voltammogram obtained compared with the background. In Fig. 5b three consecutive scans are represented for one electrode of the same type under the same conditions. The electrode was cleaned before each scan with a tissue soaked in carbon tetrachloride. Using a similar technique three more electrodes were constructed with the only difference that they were cured for a period of 2h at 40°C .

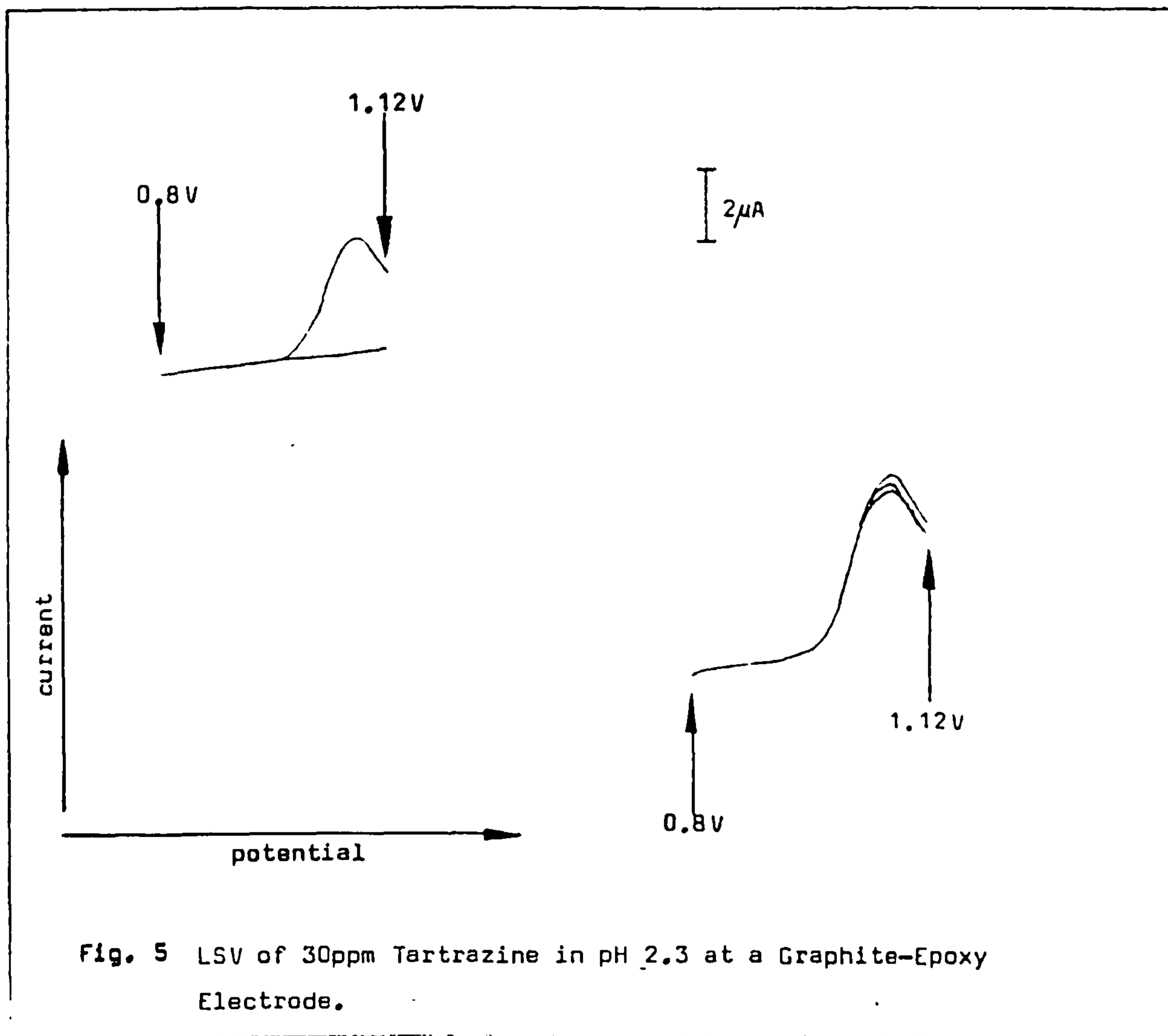
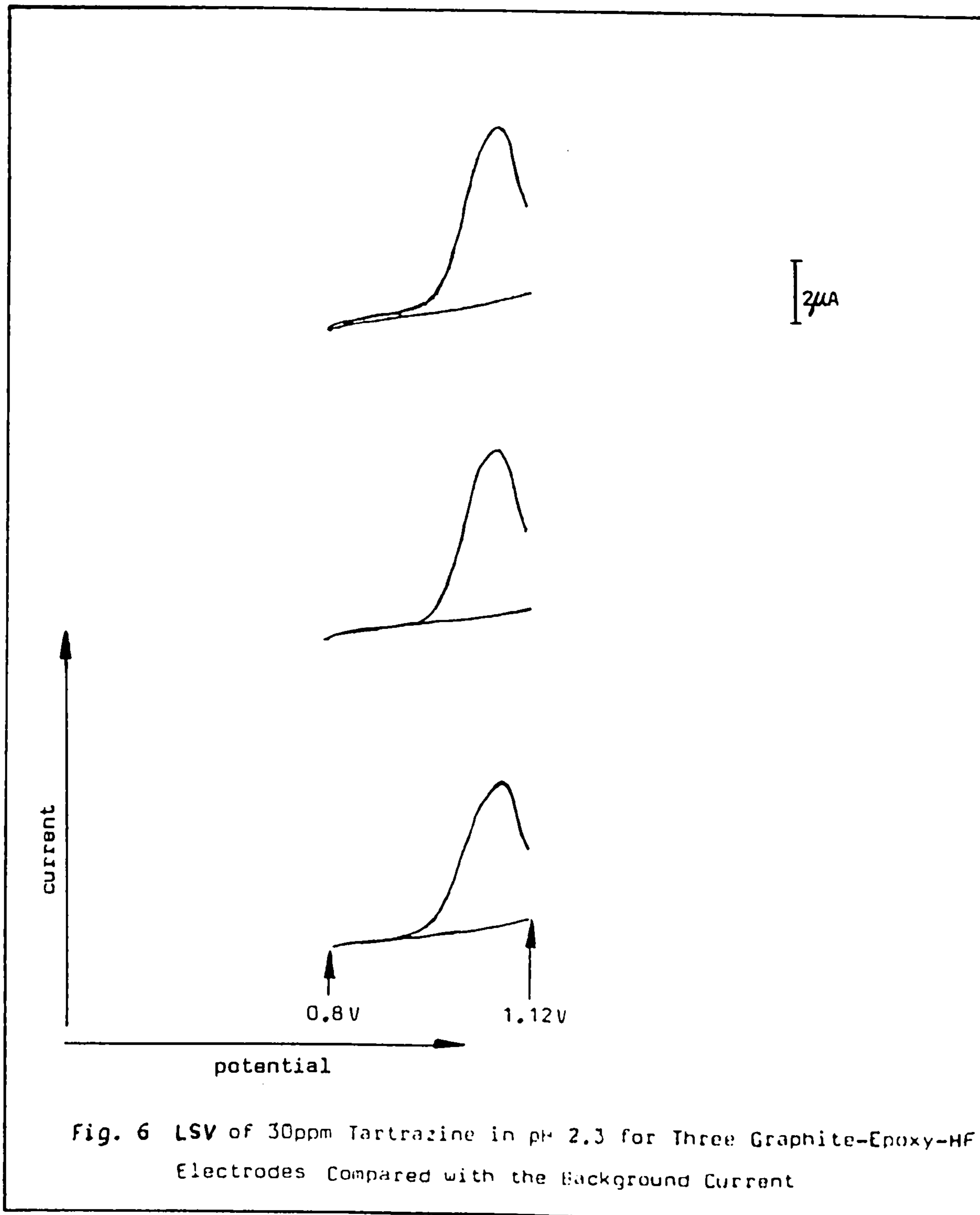


Fig. 5 LSV of 30ppm Tartrazine in pH 2.3 at a Graphite-Epoxy Electrode.

The finishing off of the electrode surfaces was accomplished as above and the electrodes were tested in the same way (see Fig. 6).



Discussion

Hydrofluoric acid was used as a hardener for epoxy adhesive and made the basis for a new type of loaded-graphite-HF voltammetric electrode whose characteristics were demonstrated to be superior compared with the performance of the common graphite-Araldite electrodes. They presented much lower background currents and well-shaped current-potential curves when tested using tartrazine aqueous solutions.

The reaction of hydrofluoric acid with simple epoxide compounds has been studied by Knunyants et al (290) and recently was reviewed by Olah et al (291). The polymerization of the epoxy resin presumably starts with the opening of the oxirane ring in the following way (292-294):



The polymerization reaction can proceed through the OH site as the active group according to the previous discussion (see pp. 51-55). In certain conditions epoxides and anhydrous liquid hydrogen fluoride react to form fluorohydrins and extensive polymerization can occur with the formation of polyethylene glycol (290). The organic chemistry of fluorine compounds is well established as an important field of intensive research because of its industrial significance. Besides the still growing applications of poly(tetrafluoroethylene), PTFE and of poly(chlorotrifluoroethylene), Kel-F especially for the construction of laboratory apparatus many important fluorine derivatives have been emerging and have been applied in many areas of industry and medicine (294). Nevertheless it seems that no special studies have been published in the literature concerning the reaction of hydrofluoric acid and epoxy resins. No mention has been made about this reaction in either specialized books

recently published or in special publications dealing with the chemistry and applications of hydrofluoric acid, inorganic fluorides and fluorine (257-262, 295). These publications describe the most common hardeners and catalysts for the curing of epoxides. Hydrofluoric acid does not seem to occupy an important position possibly because its great reactivity gives rise to a very brittle and highly cross-linked polymer. This kind of product appears to be of less commercial value so far. Two patents concerning the use of several halogenides, including HF(g) as the curing agent for epoxy resins were filed (296, 297). The authors described the invention of a technique for extruding epoxy resin mixed with other convenient ingredients to produce fibres and coatings when the system were hardened in an HF(g) atmosphere or a mixture of HF(g) and other gases, namely nitrogen or carbon dioxide. They did not indicate any mechanisms for the reactions and it is not clear from the articles which type of epoxy resin and what concentrations of hydrogen fluoride have been employed. The use of hydrofluoric acid (at different concentrations than those used in the present work) under several conditions or in mixtures with various chemicals have been applied for the curing of coatings, adhesives, fillers and other specific commercial products (298, 299).

In this chapter the use of 40% m/m hydrofluoric acid solution and the vapour above it to fabricate graphite-loaded epoxy electrodes has been described. This appears to be the first use of HF as a hardener for producing small electrodes. In this preliminary work the solution of HF was used simply to improve the surface characteristics after the electrode had been produced using non-conventional hardeners whereas the vapour was used by pre-adsorbing it onto the graphite before mixing the graphite with the epoxy adhesive. Better results were obtained using the vapour. However the problems of using this successfully were two-fold. The main problem is that the extent of adsorption of HF on the graphite is difficult to assess or control. Nevertheless this adsorption approach might have advantages in some situations or in some

applications. A minor problem is that whereas it would be advantageous to prepare a substantial quantity of graphite-HF for subsequent use, the material does lose HF on storage, and there is a difficult of weighing safely this HF-containing material.

In the first approach HF solution was used to improve the surface of electrodes already prepared with conventional hardeners. The logical extension of this approach is to use solutions of hydrofluoric acid as the hardener itself. This approach was investigated eventually with considerable success and these experiments are described in the later chapters of this thesis. Initially, however, owing to the difficulties of using graphite-HF, attempts were made to adsorb HF onto graphite-loaded epoxy adhesive already in situ on surfaces. This approach which proved to be extremely satisfactory and to present many possibilities for applications is described in the next chapters.

A NOVEL COATING AND CURING TECHNIQUE FOR THE PREPARATION OF ELECTROCHEMICAL SENSORS

Introduction

In view of the problems described in the previous chapter a novel technique of coating and hardening with hydrofluoric acid was developed. This is described in this chapter and the technique has been applied to the construction of coated wire and disc electrodes for voltammetric experiments.

Preparation of graphite-loaded epoxy base

The graphite-loaded epoxy base was prepared simply by mixing in appropriate proportions a suitable epoxy base with a suitable grade of spectrographic graphite powder. The contents of the adhesive tube of two-tube Araldite packs (Ciba-Geigy Plastics and Additives Company) obtainable from hardware stores were used as the epoxy base. According to the trade literature this base consists of a bisphenol-A epoxy resin containing a reactive diluent. The contents of the hardener tubes were not used in this application. The graphite powder used was Specpure graphite powder pelletable Grade 1 (Johnson Matthey Chemicals Ltd.). The optimum ratio of epoxy base and graphite to produce the most satisfactory electrodes was found to be 11:14 parts by weight. Thus 0.44g of epoxy base and 0.56g of graphite or proportional quantities were mixed on a suitable plastic or glass surface. A cellulose acetate or plexiglass sheet was found to be convenient for this purpose. The graphite-loaded epoxy base could be stored indefinitely in a glass or suitable plastic container and used when required.

Gaseous hardener vessel.

The surface to be coated was treated with a thin layer of the graphite-loaded epoxy base. The best way to do this depended on the shape of the

surface to be coated and this is discussed later. The hardener was hydrofluoric acid vapour and the article being coated was suspended in the vapour in order that hydrofluoric acid could be taken up by the graphite-loaded epoxy base.

A plastic container (approximately 10cm diameter and 19cm high) of the type used to transport glass reagent bottles, with a plastic screw cap, was used as the vapour chamber. Approximately 2ml of 40% m/m hydrofluoric acid solution was placed in a plastic cup which in turn was placed in the vapour chamber. Suspension of articles in the chamber was facilitated by means of a nylon string or a nylon net tied loosely across the mouth of the vessel. Later it was found convenient either to drill small holes in the cap and to suspend tubes and wires through these or to hook a plastic beaker over the side of the container with the help of a holder made of copper wire. Sufficient HF to cure the epoxy base was taken up by the epoxy base during 2-5min in the vessel. Safety precautions were taken when using hydrofluoric acid. Moreover care was taken not to handle directly electrode surfaces that might have retained some hydrofluoric acid.

Hardening the treated surface

The surface that had been coated with graphite-loaded epoxy base and treated with hydrofluoric acid vapour was then suspended over a hot plate in a fume cupboard in order to complete the hardening of the epoxy resin. The thermostat control position on the hot plate and the position in which the surface was suspended were predetermined such that the air temperature at the point of suspension was between 50 and 60°C. This heating step presumably eliminated any excess of hydrofluoric acid adsorbed on the surface. Hardening was complete after 2-5min, when further coats could be applied by repeating the above cycle in order to obtain a smooth surface by filling the pores and irregularities that usually were observed on the cured surfaces. Fig.7 and Fig.8 are the photographs of the system used as described in this work.



Fig. 7 Apparatus Used for Curing of the Epoxy Base:
7(a) HF vapour chamber. 7(b) Complete system.

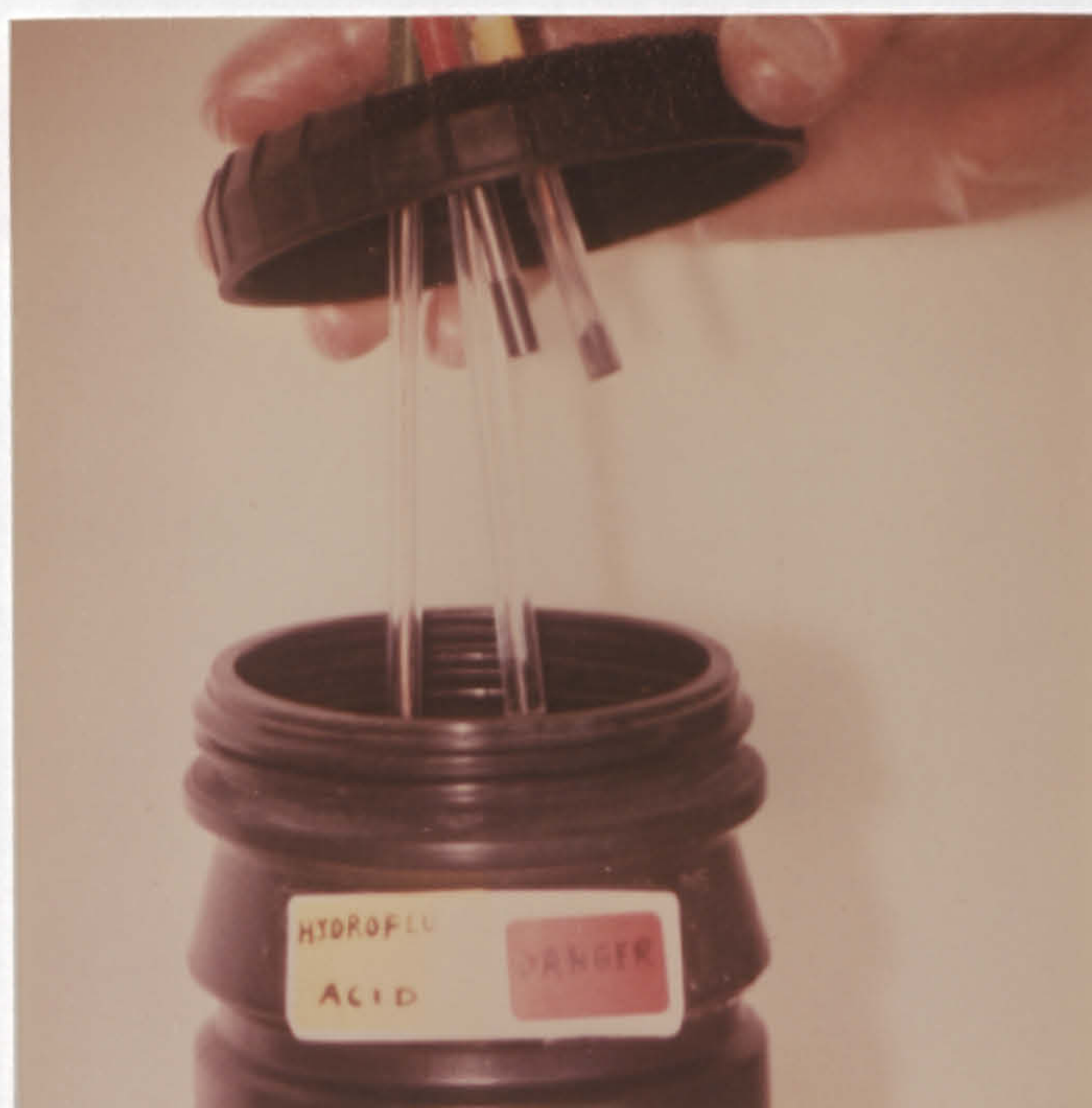


Fig. 8 Suspension of Articles for Hardening in the 40% m/m Hydrofluoric Acid Vapour Chamber.

Preparation of unloaded epoxy sealant

The unloaded epoxy sealant was prepared by mixing one drop of 40% m/m hydrofluoric acid solution with 0.5g of unloaded epoxy base: this hardened at room temperature (20°C) in approximately 40min. This time was observed to decrease with heating but it was found more convenient to allow 1-2h at ambient temperature to ensure the complete hardening of this sealant although sometimes the external layer of the sealant remained tacky. In this case the surface had to be exposed to hydrofluoric acid vapour again as described later.

Construction of coated wire voltammetric electrodes

Clean unused copper wire to be coated was treated first with 5M nitric acid solution and then rinsed thoroughly with acetone and allowed to dry in the air without washing it at any stage with water. A small amount of graphite-loaded epoxy base was placed on the wire and was then smoothed gently over the surface using a tissue. Any large graphite particles were removed with a tissue and the surface was smoothed finally and carefully with a thin flexible polythene or cellulose acetate sheet. A tissue could also be used for this purpose. A very smooth thin layer was produced by this means and this was then hardened as indicated above. The process was repeated several times to build up further hardened layers.

Obtaining adequate coverage of the tip of the wire is a general problem in producing good coated wire electrodes of any type. After the wire had been coated in this work the extreme tip was heavily coated with an unloaded epoxy sealant prepared as above so that in subsequent use the tip was isolated from the electrolyte solution. On occasion the surface remained tacky and in this case the surface was placed in the hydrofluoric acid vapour chamber for 2min and hardened at 50-60°C as before. After this further treatment the surface appeared completely cured and it was possible even to

polish it.

Usually approximately 20cm of copper wire (0.91mm thick) was coated with graphite-loaded epoxy and hardened as above and was then cut to make three electrodes each time. These were mounted in approximately 1mm bore glass capillary tubing as shown in Fig. 9, the wire being cemented in place at each end of the tube with unloaded epoxy. The tips of the electrodes were isolated as above.

Preparation of disc voltammetric electrodes

Very satisfactory disc electrodes were constructed from thick-walled glass capillary tubing of 2mm bore. The end of the tube at which the disc electrode was to be constructed was first polished with abrasive paper (fine grade abrasive, Acton and Borman) and with slurries of coarse and fine alumina, and then cleaned and dried. The coarser alumina was of 100-250 mesh (Fisons) and the fine alumina was that supplied with Metrohm glassy carbon electrodes (0.3 and 0.015 μ m). A graphite-loaded epoxy filler was prepared by mixing one drop (0.1ml) of 40% m/m hydrofluoric acid solution with 0.5g of graphite-loaded epoxy base prepared as above. A length of copper wire was bent as shown in Fig. 10 such that it reached close to the end of the glass tube. With the copper wire removed an amount of the graphite-loaded epoxy filler was pressed into the end of the tube to occupy a length of about 0.5cm. Whilst holding the end of the tube against a suitable surface to prevent the epoxy filler escaping the copper wire was inserted into the filler from the other end of the tube. The filler at the end of the tube was smoothed off by carefully rubbing the surface on a cellophane sheet and the glass tube was cleaned with a soft tissue. The filler was then allowed to harden for approximately 1h at room temperature (20°C). The filler hardened in 15-20min when heated at 50°C but hardening at room temperature was preferred here. The loop at the end of the copper wire anchored the wire very effectively in the epoxy

unloaded epoxy sealant



glass _____
capillary

graphite-loaded _____
epoxy coated
copper wire



unloaded epoxy sealant

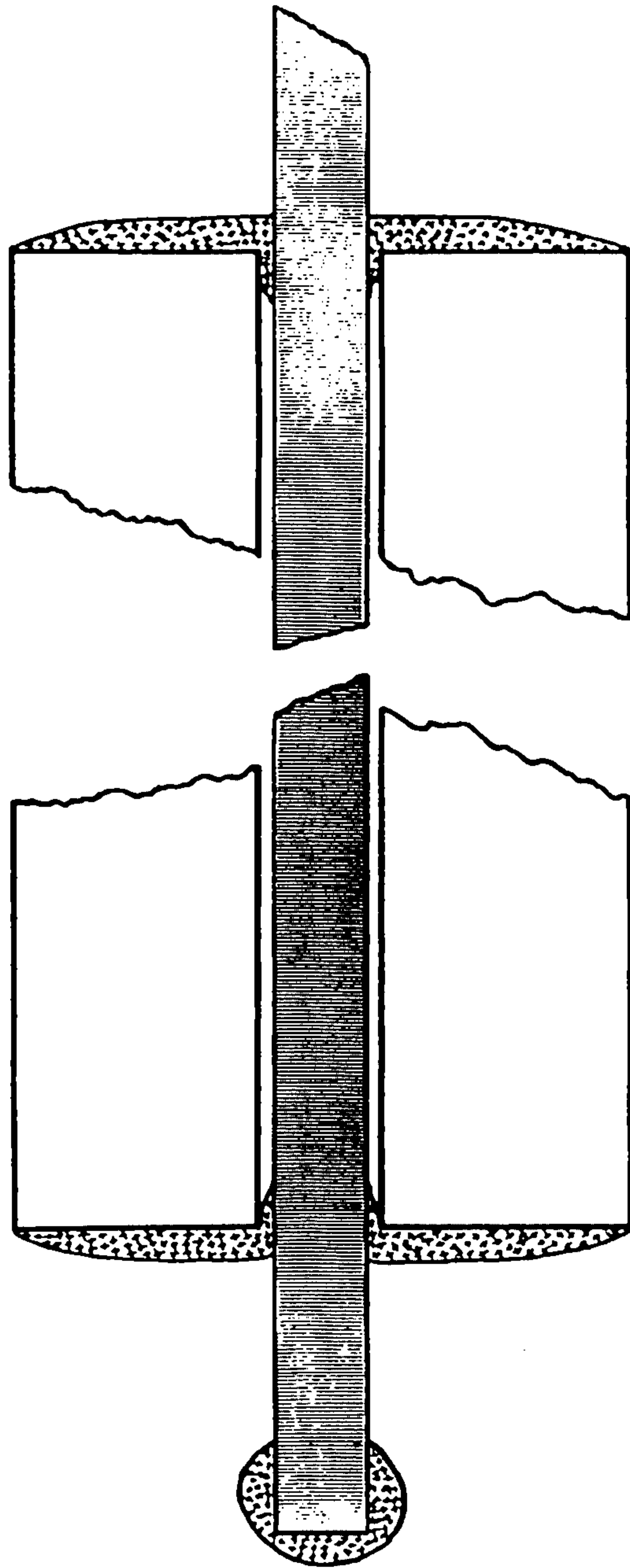


Fig. 9 Coated Wire Graphite-loaded Epoxy-based Electrode

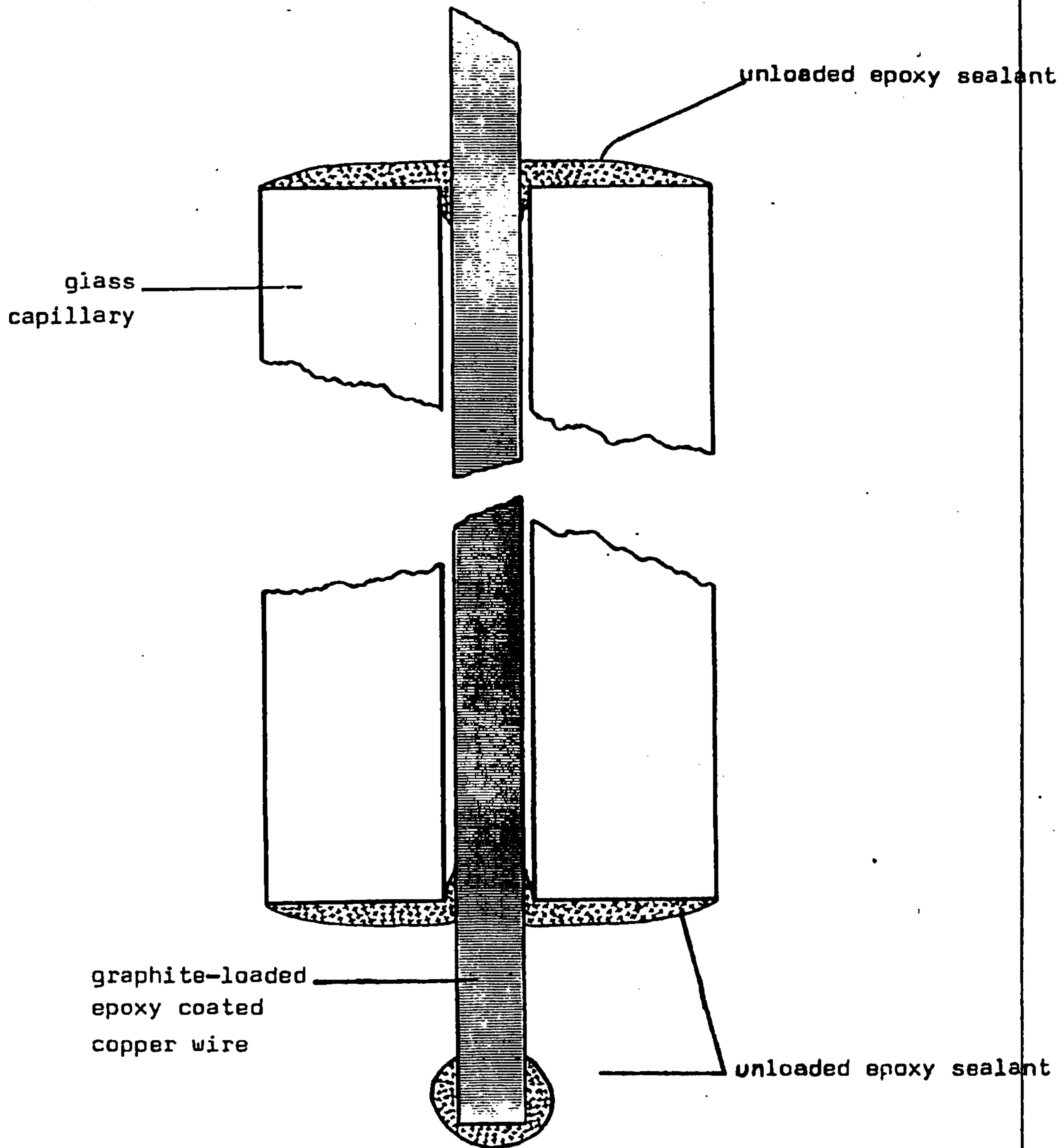


Fig. 9 Coated Wire Graphite-loaded Epoxy-based Electrode

_____ copper wire

unloaded _____
epoxy

graphite-
loaded
hardened
with 40% m/m
HF(aq)

_____ glass capillary

_____ graphite-loaded epoxy coating
hardened in HF chamber

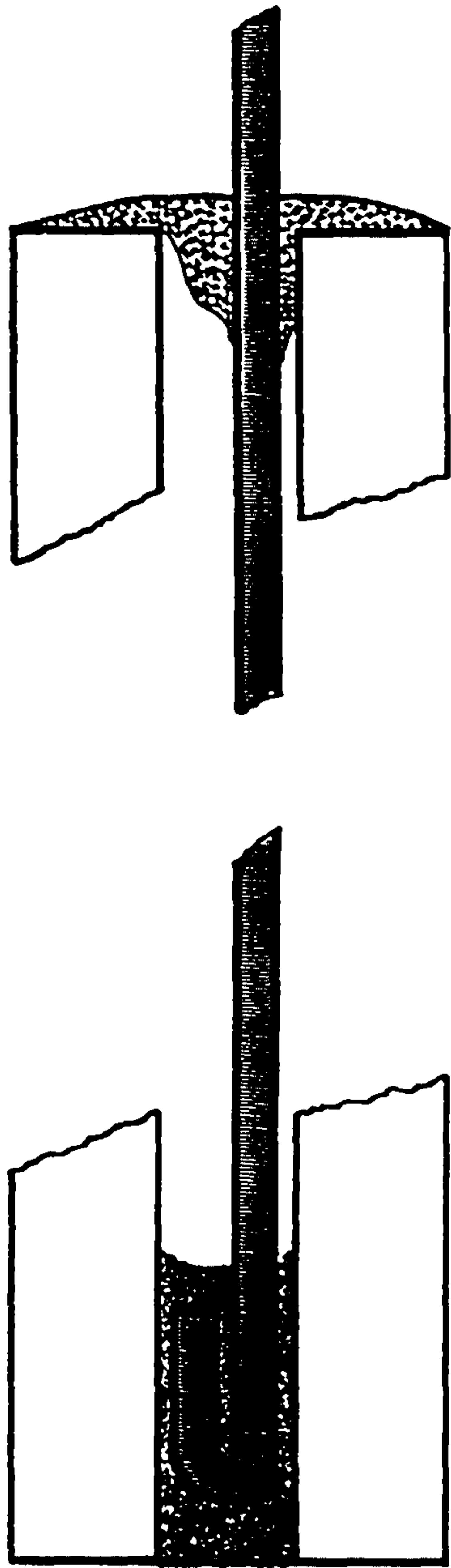


Fig. 10 Graphite-loaded Epoxy-based Disc Voltammetric Electrode

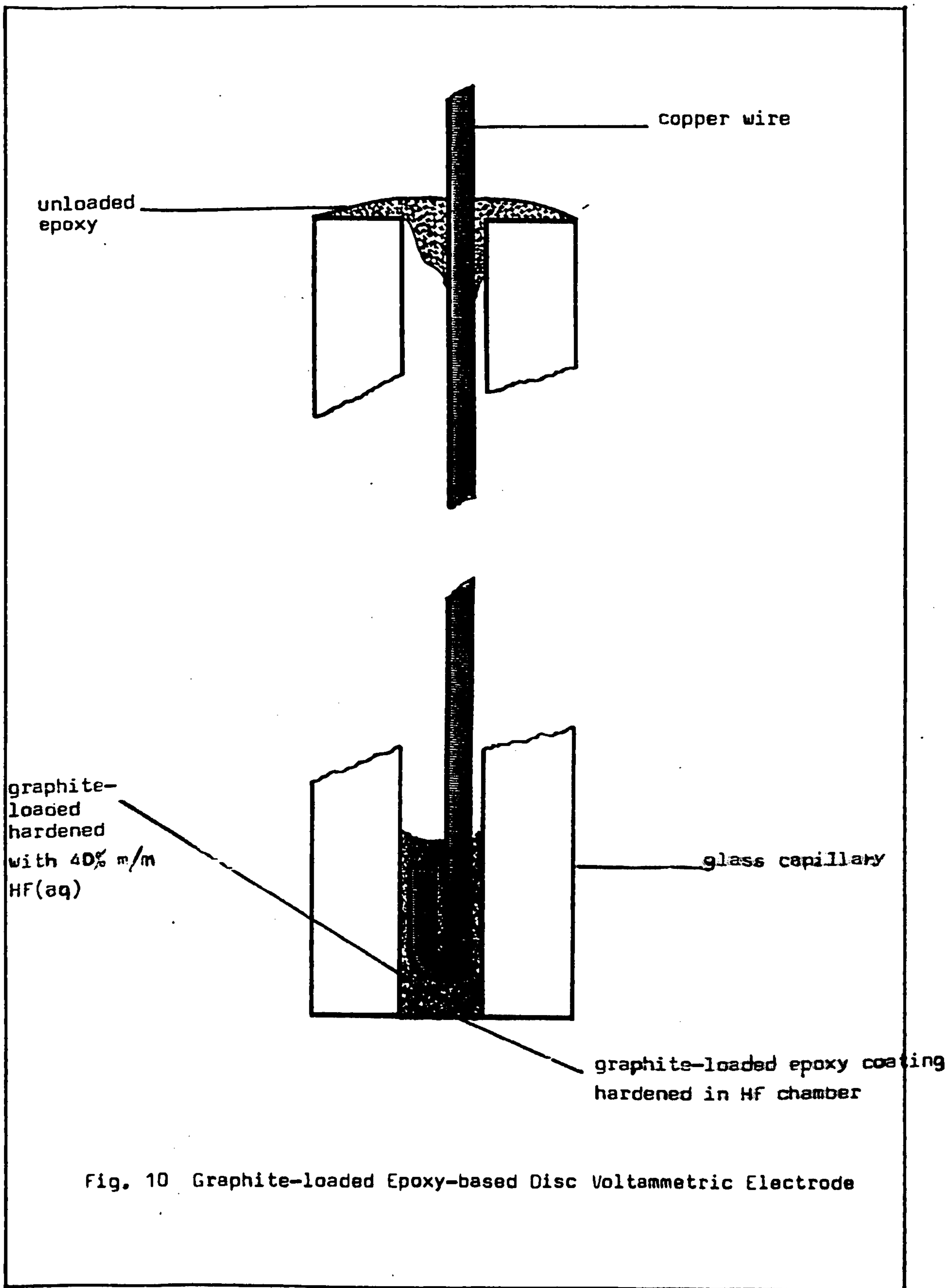


Fig. 10 Graphite-loaded Epoxy-based Disc Voltammetric Electrode

filler when the latter had hardened. The hardened surface was then polished with slurries of coarse and very fine alumina, washed with water and dried. Three layers of graphite-loaded epoxy were then coated successively onto this surface and hardened using the vapour chamber. After the application of each layer the surface was polished on a filter paper, washed with distilled water and dried. In general this produced a very smooth and shiny final electrode surface and no graphite remained covering the thickness of the glass tube owing to its having been polished previously. The smoothness of the surfaces obtained by this multilayer coating was confirmed by use of a scanning electron microscope as shown in Figs. 11-13 where three photographs of a graphite-loaded epoxy base hardened with 40% m/m hydrofluoric acid are depicted. Whilst hardening, a small portion of the mixture was kept covered with a cellulose acetate sheet and gently pressed against a small brass cylinder used as a base. After curing the sheet was removed as it did not stick on the hardened surface and the hardened plate obtained bound to the metallic base appeared flat and smooth but the magnified view (700 x 0.75) of this surface without any further treatment reveals several defects as presented in figure No. 11. The same surface after being polished with coarse and fine alumina as described here is shown in figure No. 12 (700 x 0.76). The application of one layer of the graphite-loaded epoxy base followed by curing in the hydrofluoric acid vapour chamber as indicated above improved considerably the smoothness of the hardened surface as shown in figure No. 13 (magnification 700x0.78) where the flaws observed in the first view have been removed. As mentioned above in general three layers of graphite-loaded epoxy were coated successively onto the electrode surface and this procedure was demonstrated to upgrade the electrodes tested here.

Originally disc electrodes were constructed on the end of nylon tubes but the use of glass capillary tubing was found to be superior. A very firm seal is produced possibly due to the etching of the glass by the action of HF.

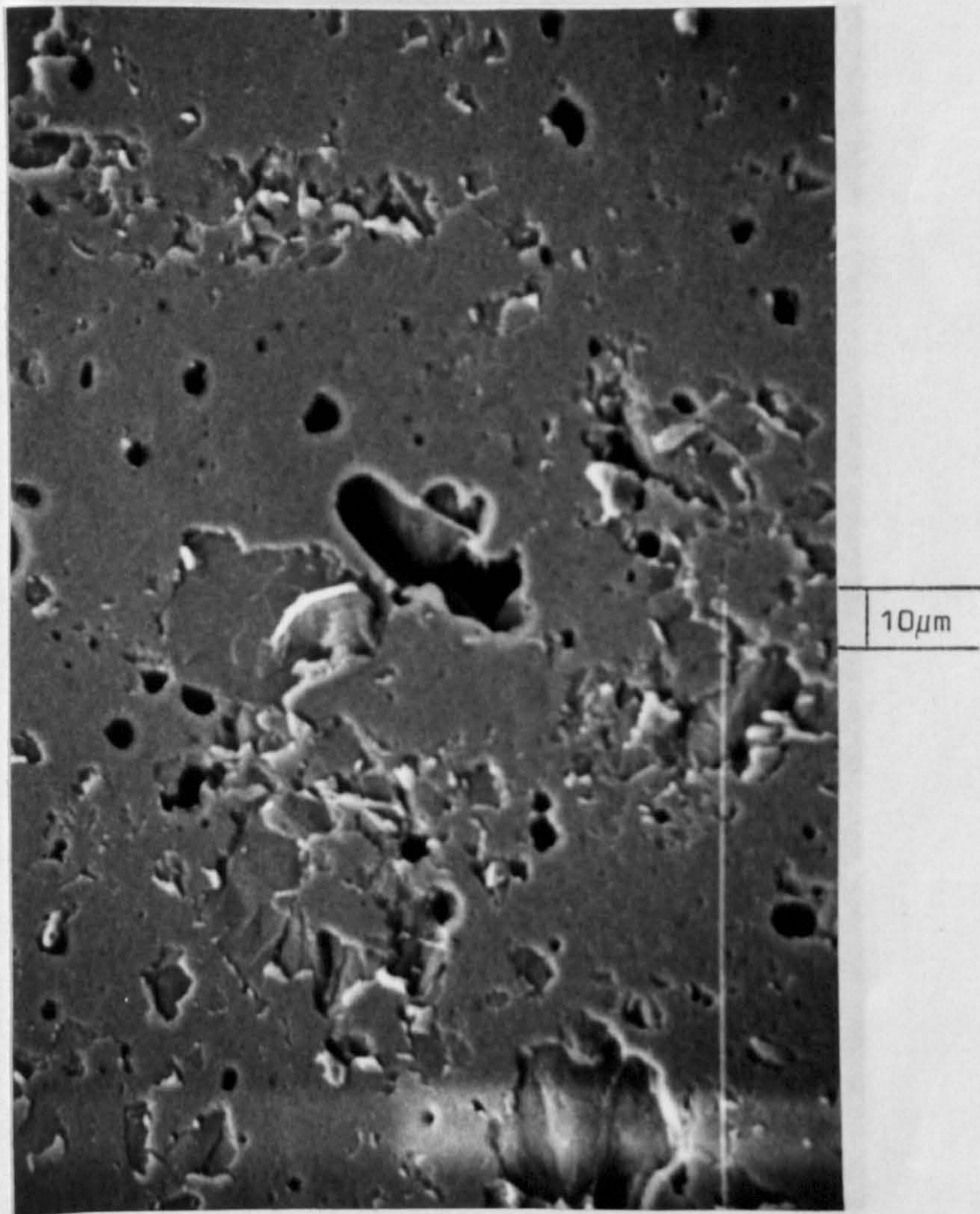


Fig. 11 SEM Electronmicrograph of a Graphite-loaded Epoxy Base Surface Hardened by 40% m/m Hydrofluoric Acid Solution. (upper bar = 10 μm).

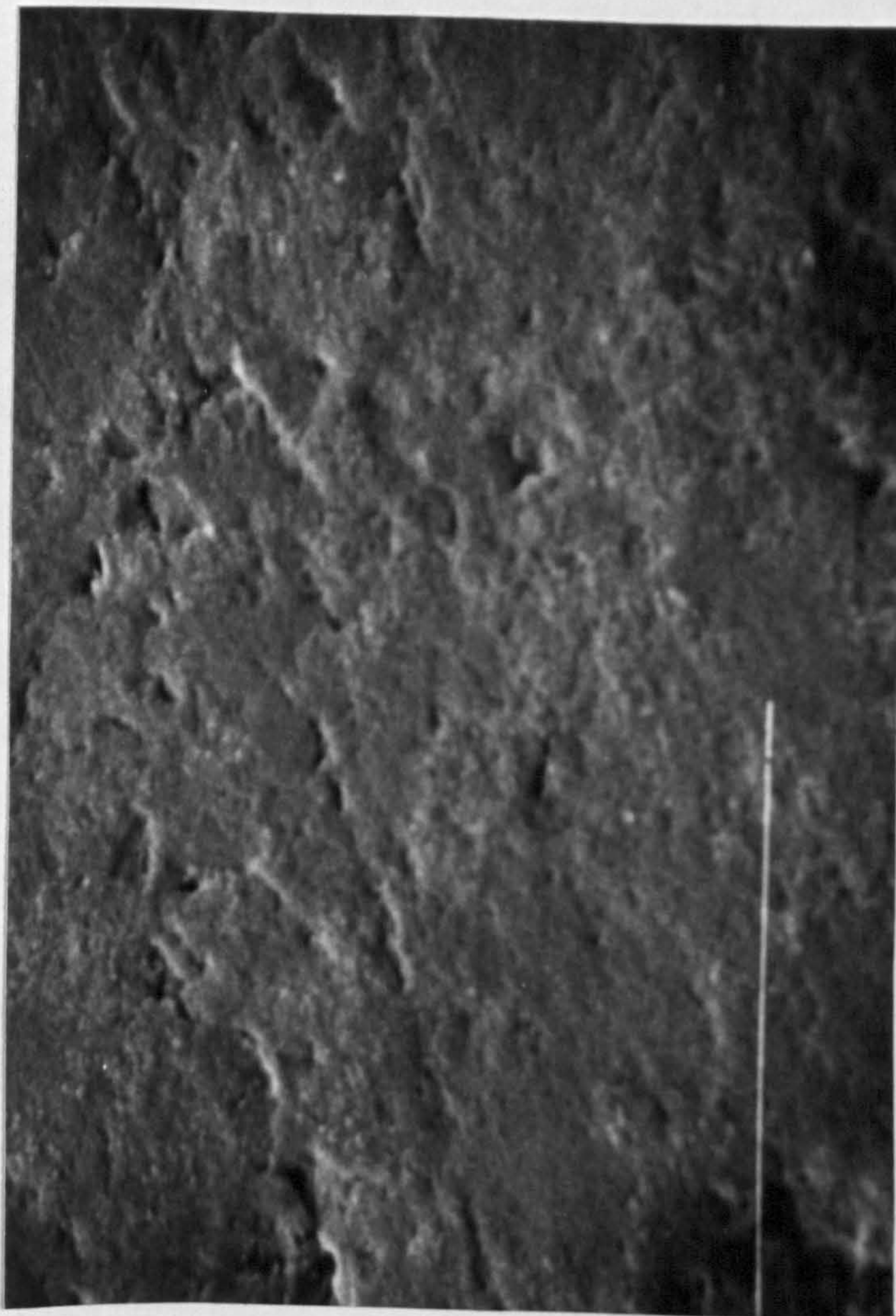


Fig. 12 SEM Electronmicrograph of the Cured Surface Shown in Fig.11
After Being Polished with Coarse and Fine Alumina.

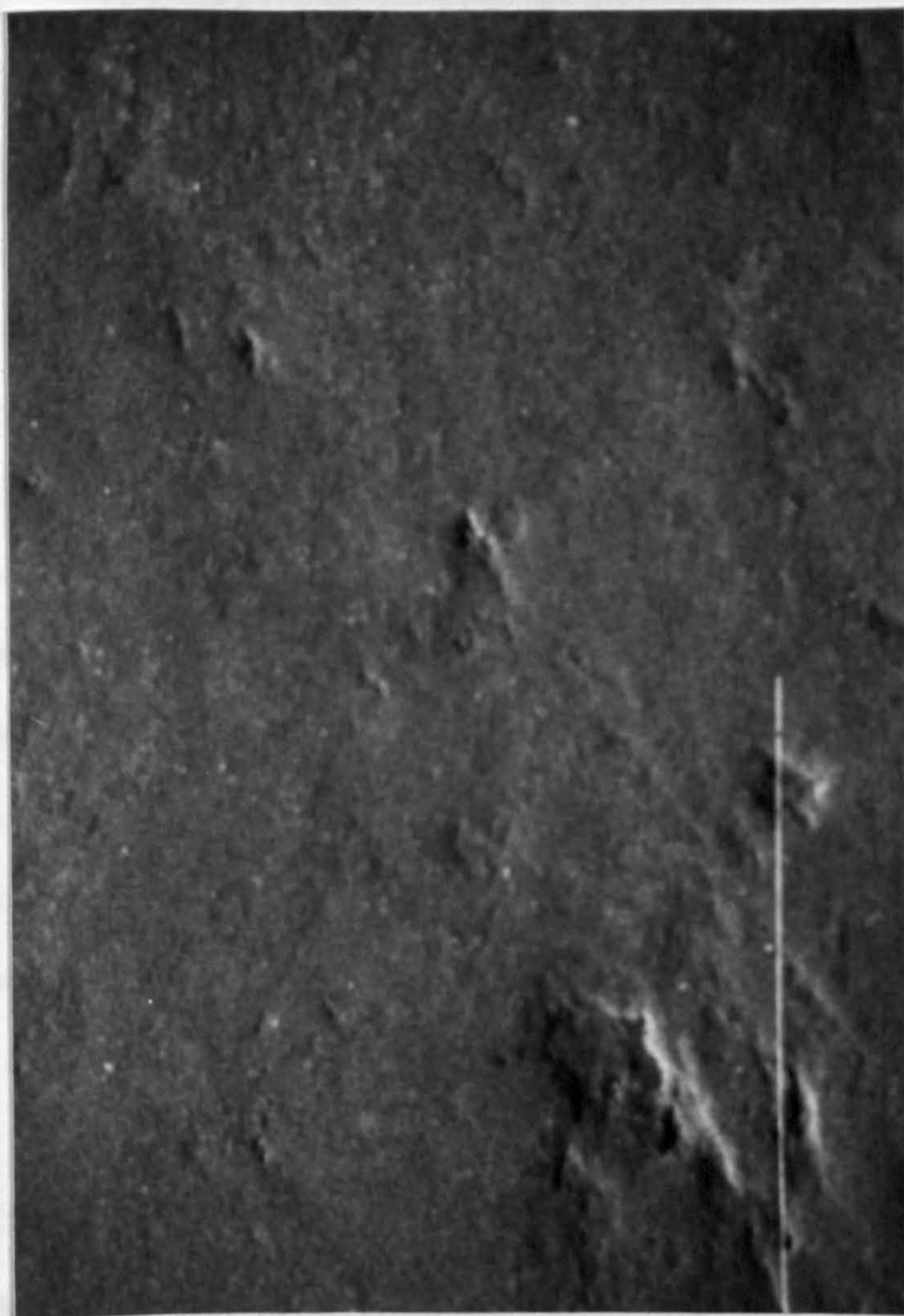


Fig. 13 SEM Electronmicrograph of the Surface Shown in Fig. 12 After the Application of one layer of Graphite-loaded Epoxy Base Cured in the HF Vapour Chamber.

Testing the electrodes

In this study the electrodes were tested in the static mode using slow LSV. The three electrode system consisted of the test electrode, a calomel reference electrode and a platinum counter electrode. The reference electrode was separated from the test solution by means of a salt bridge consisting of a ground glass joint containing an electrolyte of the same composition as the test solution but excluding any determinand such as iodide or Red 2G. Voltammetry was carried out by means of a Metrohm Polarecord 626. Before initial use the active surface of the electrodes were washed with water.

The background currents associated with the electrodes were tested first. This was carried out in various electrolyte solutions, namely 0.1M sulphuric acid solution, pH 2 Britton-Robinson buffer (0.04M in the three weak acid constituents) (300), 0.1M hydrochloric acid solution, 0.1M potassium chloride solution, 1M potassium nitrate solution, pH 7.5 Britton-Robinson buffer (300), 0.1M sodium hydroxide solution and 1M acetic acid solution. In general the potential was swept from zero volts to +1.2V, but some scans were made from -0.8V to +1.4V. None of the solutions was deoxygenated.

The use of these electrodes in voltammetry was illustrated by obtaining linear sweep voltammograms of 10^{-4} (or 10^{-3})M potassium iodide in 10^{-2} (or 10^{-1})M potassium chloride solution, and of 25ppm solutions of the permitted food colouring matters Red 2G containing 50% w/v Britton-Robinson buffer (pH2). Particular attention was paid to adsorption problems and to reproducibility.

Results

Several electrodes were constructed and tested in developing the methods recommended above for the construction of satisfactory electrodes. The tests reported here were carried out on twenty-three disc electrodes and six coated wire electrodes. All these electrodes behaved similarly and electrodes of both types can be prepared routinely and successfully.

Linear sweep voltammograms for a disc electrode in pH 2 Britton-Robinson buffer are shown in Fig. 14. These were run from 0 to +1.2V. At the sensitivity used for the measurements the background current is virtually zero up to +0.85V. Above this potential a small background current appears and this reaches a value of approximately $1\mu\text{A}$ at +1.2V on the first scan. On subsequent scans this background current becomes increasingly small and is constant on the third and subsequent scans. This was general with all the electrodes and freshly prepared electrodes were conditioned by carrying out three scans in pH 2 Britton-Robinson buffer from 0 to +1.2V.

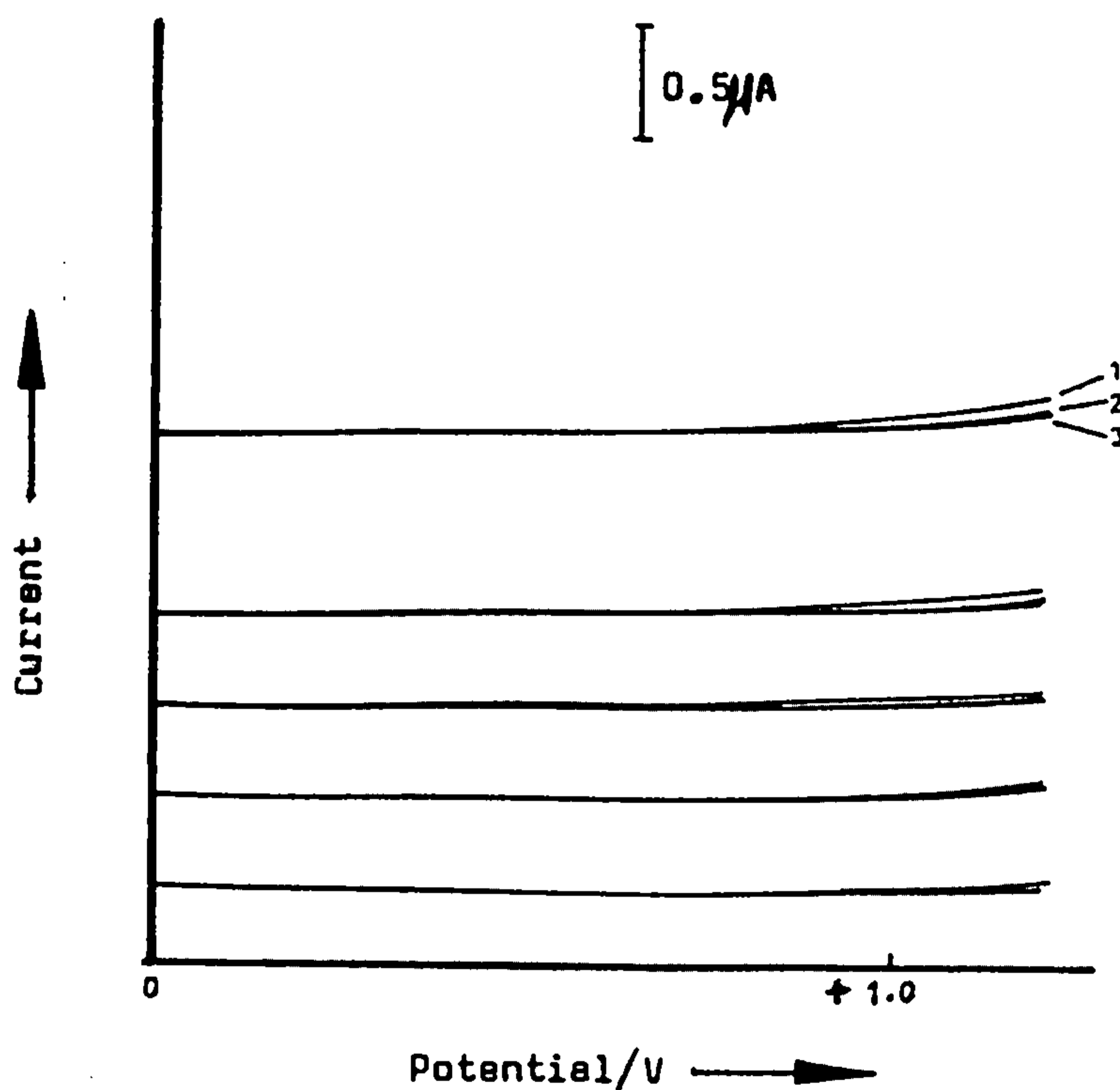
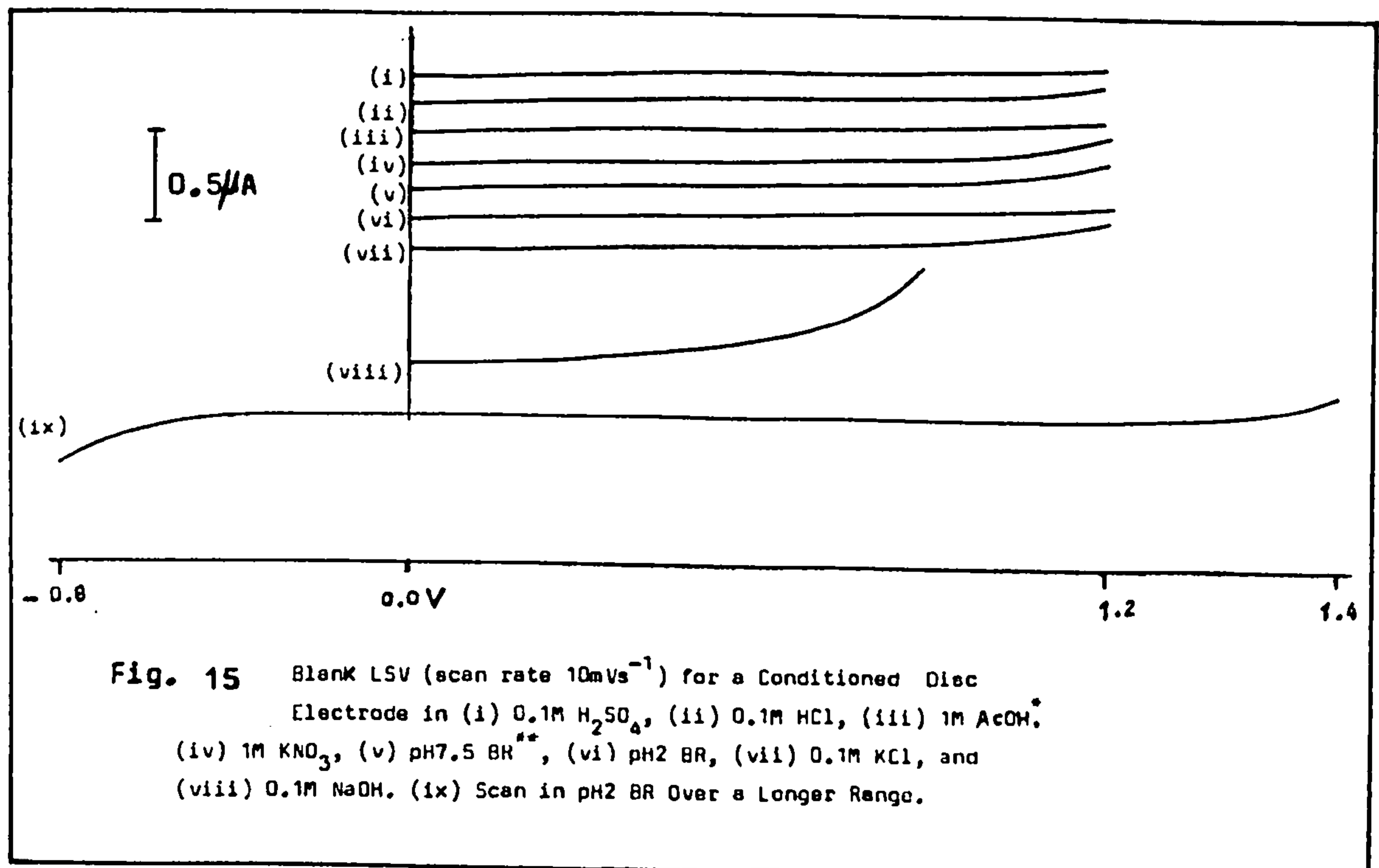


Fig. 14 Linear Sweep Voltammograms for a Disc Electrode in pH 2 Britton-Robinson Buffer Showing the order of Successive Scans.

One of the sweep voltammograms shown in Fig. 15 was obtained in pH 2 Britton-Robinson buffer over a slightly larger potential range (without deoxygenation) for a graphite-loaded epoxy-based disc electrode which had been previously conditioned as above. Clearly at this pH the electrodes are usable in the range $-0.4 - +1.2V$, possibly from $-0.6 - +1.3V$ for determinations of higher concentrations of determinand (coated wire electrodes acted similarly).

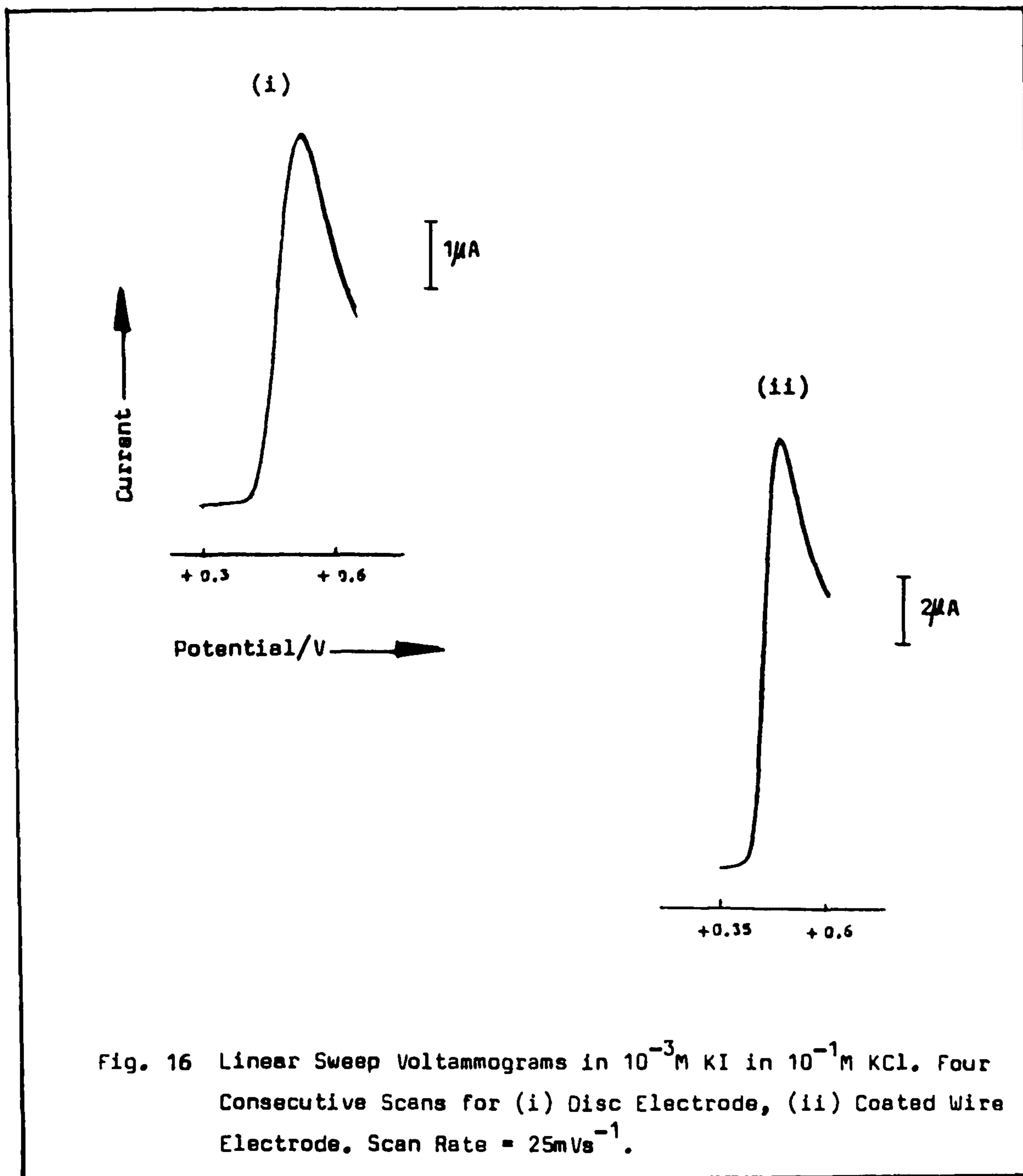
The other linear sweep voltammograms shown in Fig. 15 are for conditioned disc electrodes run in various supporting electrolytes. The background currents are very small generally in the range $0 - +1.2V$ except in the case of $0.1M$ sodium hydroxide solution for which the background current is very small up to about $+0.75V$ but above which a high cut-off current appears. The lowest background current over the full range was given in $0.1M$ sulphuric acid solution. At $+1.2V$ the size of the background current for the other solutions was in the order pH 2 Britton-Robinson buffer $< 0.1M$ hydrochloric acid solution $<$ pH 7.5 Britton-Robinson buffer, but it should be noted that even the background current of the pH 7.5 Britton-Robinson buffer is $< 1\mu A$.



* acetic acid

** Britton-Robinson buffer

The oxidation of iodide at these electrodes was very well-behaved with no adsorption difficulties. The electrode could simply be washed with water. The reproducibility of scans obtained with both disc and coated wire electrodes is shown in Fig. 16.



The oxidation of the permitted food colouring matters at carbon electrodes is frequently associated with adsorption of products (300, 301). Red 2G was used mainly in this study. The effect of adsorption was clearly seen in that if the electrodes were not cleaned between scans the signal decreased markedly. The possibility of cleaning the present electrodes chemically was investigated. For cleaning glassy carbon that had been used with food colouring matters (300, 301) and certain drug compounds (302, 303), cleaning with chloroform followed by 95% ethanol had been shown to be effective. In this work chloroform was found to remove the graphite surface and indeed could be used for this purpose prior to recoating the electrode. Excellent cleaning without removal of the carbon surface was obtained with carbon tetrachloride, with 3 + 2 V/V ethanol-water and with 1 + 1 V/V acetone-water. Cleaning with carbon tetrachloride normally takes the electrode back to its original state with regard to background current and for use above +1V the electrode requires reconditioning again. When either of the other two solvents is used reconditioning does not appear to be required. Nevertheless cleaning with carbon tetrachloride was adopted in this study as this cleaned the electrode more effectively. The effect of this cleaning on the reproducibility of blank linear sweep voltammograms is shown in Fig. 17. Treatment of the surface of the electrode with 0.1M sodium hydroxide solution does not affect the background current, whereas reconditioning is required when 1M sodium hydroxide solution is used. The need to recondition the surface when CCl_4 has been used is probably due to residual solvent remaining on the surface or might be caused by impurities from the solvent itself left on the electrode surface after evaporation of the solvent. Nevertheless it is well known that treatment with solvents, polishing of the electrode surface and electrochemical pretreatment usually change the properties of these surfaces. Washing with water or aqueous acetone or aqueous ethanol reduces the size of this background current before the use of

the reconditioning procedure. This proved to be essential in spite of the cleaning with solvents. Fig. 17 shows the effect of solvents on the conditioning of disc electrodes: blank linear sweep voltammograms in pH 2 Britton-Robinson buffer are presented in the following order.

- (i) and (ii) two electrodes (No. 21 and 22) treated with 1M sodium hydroxide solution.
- (iii) electrode (No. 20) treated with 0.1M sodium hydroxide solution.
- (iv) electrode (No. 19) treated with carbon tetrachloride and then 3 + 2 V/V ethanol-water.
- (v) electrode (No. 18) treated with 3 + 2 V/V ethanol-water.
- (vi) and (vii) two electrodes (No. 16 and 17) treated with carbon tetrachloride.
- (viii) five electrodes (No. 16-20) after washing copiously with water.

The use of other solvents was investigated. n-Heptane and cyclohexane did not remove the carbon surface but were less effective in cleaning the electrode in the present application. Ethanol, iso-amyl alcohol and 1-chlorobutane removed a small amount of graphite but could be used cautiously. Tetrahydrofuran, acetone, dichloromethane, n-butanol, iso-butanol, cyclohexanol, butanone, ethyl acetate, n-propanol and toluene all removed considerable amount of carbon. The cleaning with solvents appeared difficult to control as the same treatment did not reproduce the expected cleaning effect. When the electrodes were left for longer in the test solutions or scanned several times without being removed from the test solutions it became more difficult and time consuming to clean the electrodes with solvents. The use of a special electrochemical treatment to renew the electrode surface during voltammetric experiments with dopamine is reported later.

Four consecutive linear sweep voltammograms at a disc electrode of a $25\mu\text{gml}^{-1}$ solution of Red 2G in pH2 Britton-Robinson buffer are shown in

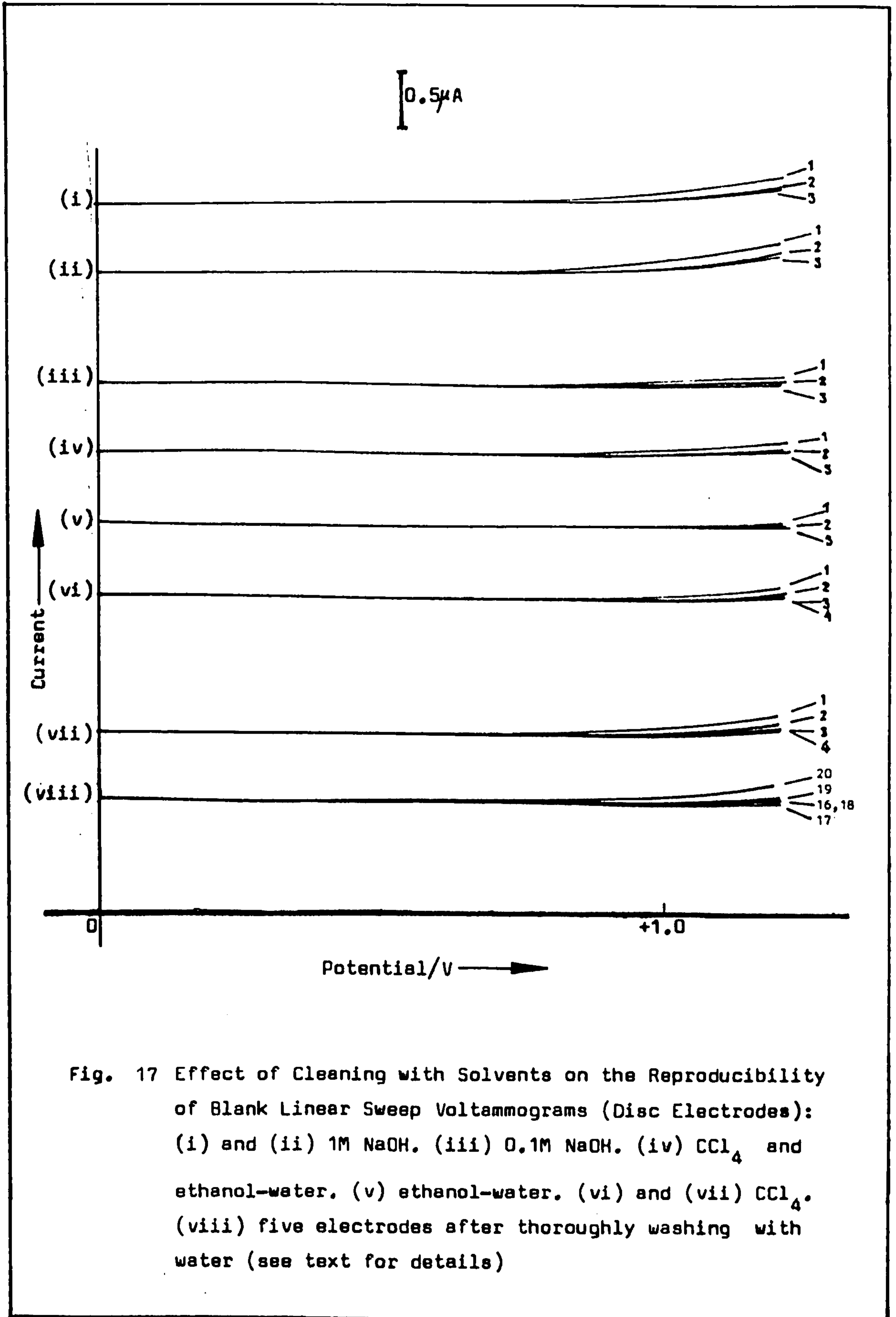
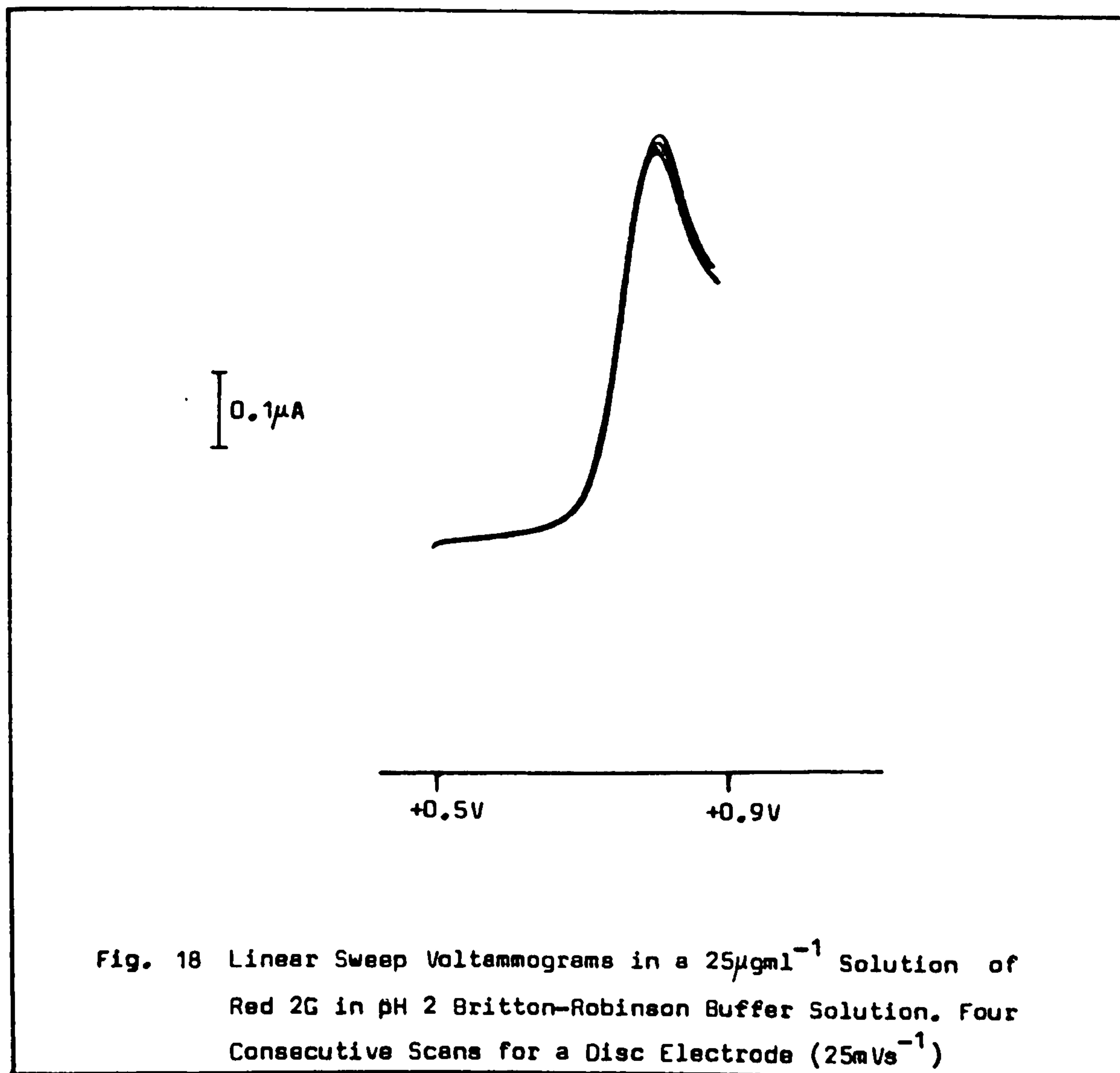


Fig. 18. In this case the electrode was washed thoroughly with carbon tetrachloride and dried between scans without washing with water. When the electrode was also washed with water between scans repeated scans were not as reproducible. This behaviour was found to be the case also when a glassy carbon electrode was studied here. Indeed the behaviour of the present disc and coated wire electrodes and glassy carbon electrodes was very similar except that glassy carbon could be treated physically more aggressively and therefore cleaned more readily.



Discussion

Coated wire and disc electrodes constructed by this novel coating and hardening procedure have been shown to be as good as commercially available well-polished glassy carbon disc electrodes in terms of low background currents and the quality of linear sweep voltammograms. The advantage of the present technique is that smooth electrodes can be produced on surfaces of a variety of shapes and sizes as has been demonstrated by the production of coated wire and disc electrodes described here. The materials are inexpensive and the electrodes, which are very easily prepared can be considered as disposable, or alternatively, as renewable by resurfacing. Clearly glassy carbon electrodes are more resilient to attack by a wider range of solvents than are these electrodes although in some cases they have to be polished and this usually modifies their electrochemical behaviour (244). The use of a hardener in gaseous form as described here and its application to an epoxy base for the preparation of electrochemical sensors appears to be novel, but there are two patents published concerned with the use of hydrogen fluoride as a hardener (296, 297). Mixed epoxy base and hardener of the type obtained from the hardware shops is generally quite viscous and difficult to spread. The epoxy base, alone or loaded with graphite, however, can be spread smoothly, thinly and uniformly. The repeated coating and hardening procedure allows a graphite-loaded epoxy surface with excellent electrical properties to be built up. Further, in using commercial epoxy/hardener mixes it is difficult to avoid the entrainment of air bubbles. Gas bubbles also seem to form in epoxy resins hardened with amines and other curing agents. These problems do not occur seriously with the new electrodes. Besides this multilayer technique developed and presented here is very effective for the filling of the irregularities which are present on the cured surfaces as demonstrated by microscopic examination. The smoothness of the electrode surface seems to be

vital for their electrochemical performance especially for stripping analysis.

The use of 40% m/m hydrofluoric acid solution as a hardener in producing the curing of a graphite-loaded and unloaded epoxy base has been demonstrated in the construction of the disc and coated wire electrodes described in this work. This mixture is also more fluid than the commercial epoxy/hardener mix and is easier to use and is more versatile in use. Early in this work graphite of a cheaper grade was used in constructing the filler for the disc electrodes. Unsatisfactory electrodes frequently resulted, however, presumably owing to incomplete coverage of the polished (impure) surface during the subsequent coating and hardening procedure. The main improving property of the coating procedure as applied to the disc electrodes seems to be the filling in of the small pits remaining after the polishing procedure. In a continuation of the present work an epoxy filler containing 40% m/m hydrofluoric acid solution and loaded with a cheaper grade of graphite has been shown to be an excellent substitute for silver-loaded epoxy for use away from electrode surfaces as a conductive resin.

Unloaded epoxy base containing 40% m/m hydrofluoric acid solution is extremely useful for isolating parts of an electrode surface preventing their subsequent contact with electrolyte solutions. This was demonstrated here in the case of the coated wire electrodes. Where the tip was not isolated in this way, greater difficulty was experienced in producing good electrodes. An excellent property of this hardened epoxy is that adsorption of organic compounds from solution occurs only slightly. Food colouring matters, for example, are adsorbed strongly by conventional epoxy resin but not in great extent by this material. It was observed that a surface coated with common Araldite mixture soaked in Red 2G solutions immediately became coloured whereas epoxy resin surfaces cured with 40% m/m hydrofluoric acid solution remained practically colourless in these solutions for at least 24h.

USE OF GRAPHITE-LOADED AND UNLOADED EPOXY BASE
TO RECLAIM USED GLASSY CARBON DISC ELECTRODES
EXHIBITING HIGH BACKGROUND CURRENTS

Introduction

The background currents showed by certain types of commercial glassy carbon electrodes become unacceptably high after extensive use mainly due to leakage of electrolyte solution between the glassy carbon disc and the plastic body in which the disc is encapsulated.

A method of resetting the disc in such electrodes using both graphite-loaded epoxy base and an unloaded epoxy base sealant is described in this chapter.

Commercial glassy carbon electrodes frequently consist of a short cylindrical rod of glassy carbon pushed into a tightly fitting plastic tube. The revealed front face of the glassy carbon rod, which acts as the electrode surface, is highly polished.

Electrical contact is made at the rear face, via a compressed metal spring, to a close fitting metal rod inserted into the other end of the plastic tube. The properties of the electrode vary with the origin of the glassy carbon used but it is also important that the surface of the electrode is highly polished to a mirror-like smooth finish and that electrolyte comes into contact only with this polished surface and not with other parts of the glassy carbon rod.

Used electrode surfaces can generally be cleaned chemically with a range of solvents and reagents, or electrochemically, but from time to time they should be repolished with fine alumina to renew the surface. When this repolishing is carried out over a period of time, the plastic tube as well as the sealant surrounding the glassy carbon are polished away faster than the

glassy carbon disc. For this reason and because of other problems originating during the fabrication of the electrodes electrolyte eventually enters between the glassy carbon disc and its plastic tube support. The extent to which this occurs determines the increase in the size of the background current and the quality of the response of the electrode up to a point that it becomes useless.

In the previous chapter a new multilayer coating and hardening technique was described and applied to the preparation of highly satisfactory graphite-loaded epoxy-based voltammetric electrodes. Here the use of both the loaded and the unloaded epoxy base containing 40% m/m hydrofluoric acid solution to repair or reclaim used commercial glassy carbon electrodes showing high background currents is described and the signals of four such electrodes after repair are compared with the corresponding signals obtained before repair. It seems that the procedure reported in this section can be adapted readily to other types of glassy carbon electrodes especially those mounted in glass. The Metrohm electrodes are constructed as indicated above. The metal contact rod and the glassy carbon cylinder are contained in a plastic tube presumably made of nylon or PTFE, and contact is made via a metal spring. This construction is depicted in Fig. 19.

Before attempting to reclaim these electrodes they were first tested by the procedure described later which were also used to test the reclaimed electrodes.

The graphite-loaded epoxy base and the unloaded epoxy sealant were prepared as described in the previous chapter.

The reclamation of glassy carbon electrodes

The glassy carbon electrodes reclaimed in this work were Metrohm electrodes (type EA 286) with 5mm diameter glassy carbon surfaces. These had been used extensively over a long period of time in a variety of linear sweep

_____ metal rod with
compressed spring

_____ plastic body

thin
layer
of sealant

_____ glassy carbon electrode

and flow-injection voltammetric applications and their condition in respect to background currents was verified to be either bad or very bad.

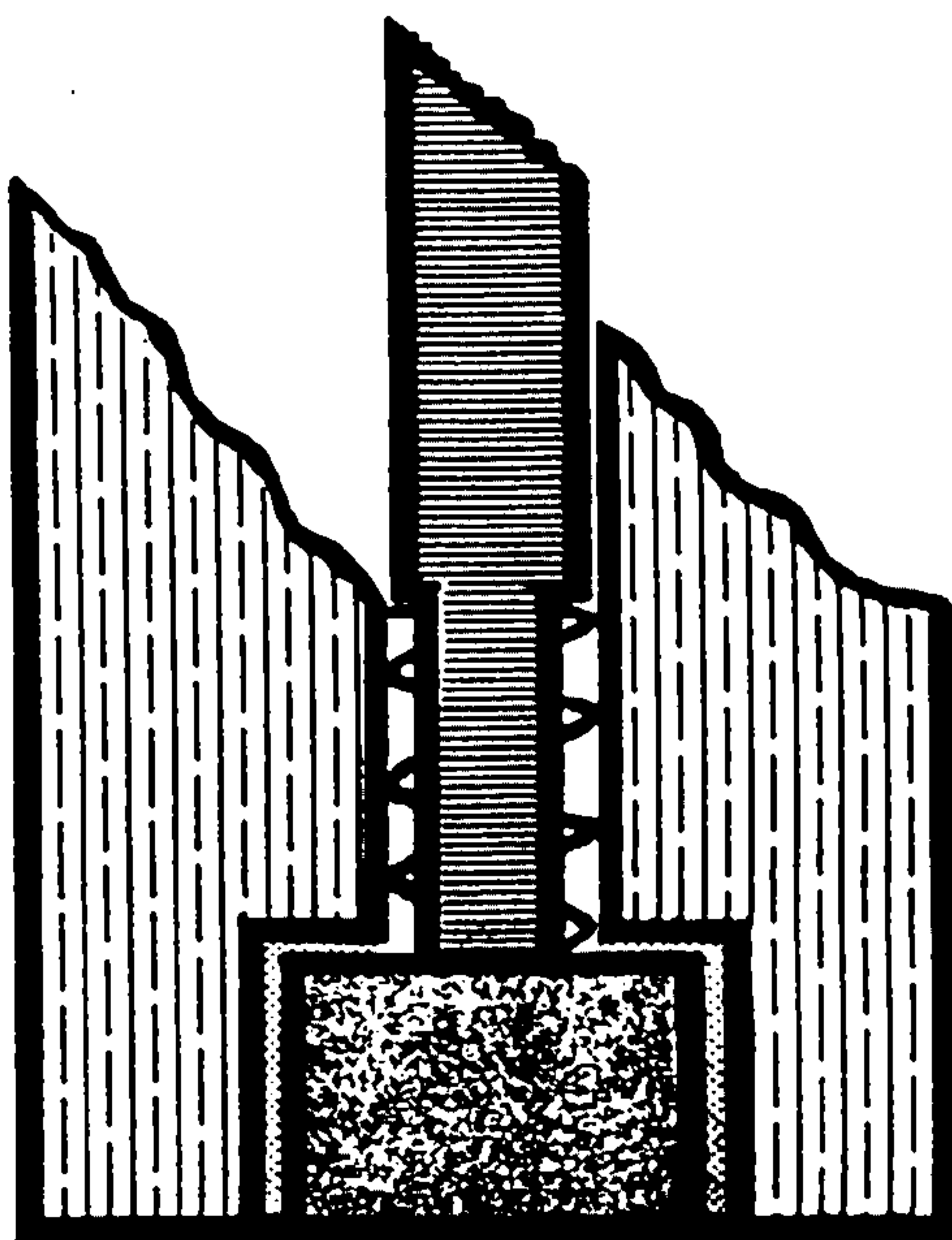


Fig. 19 Schematic of Construction of a Typical Commercial Glassy Carbon Electrode.

and flow-injection voltammetric applications and their condition in respect to background currents was verified to be either bad or very bad.

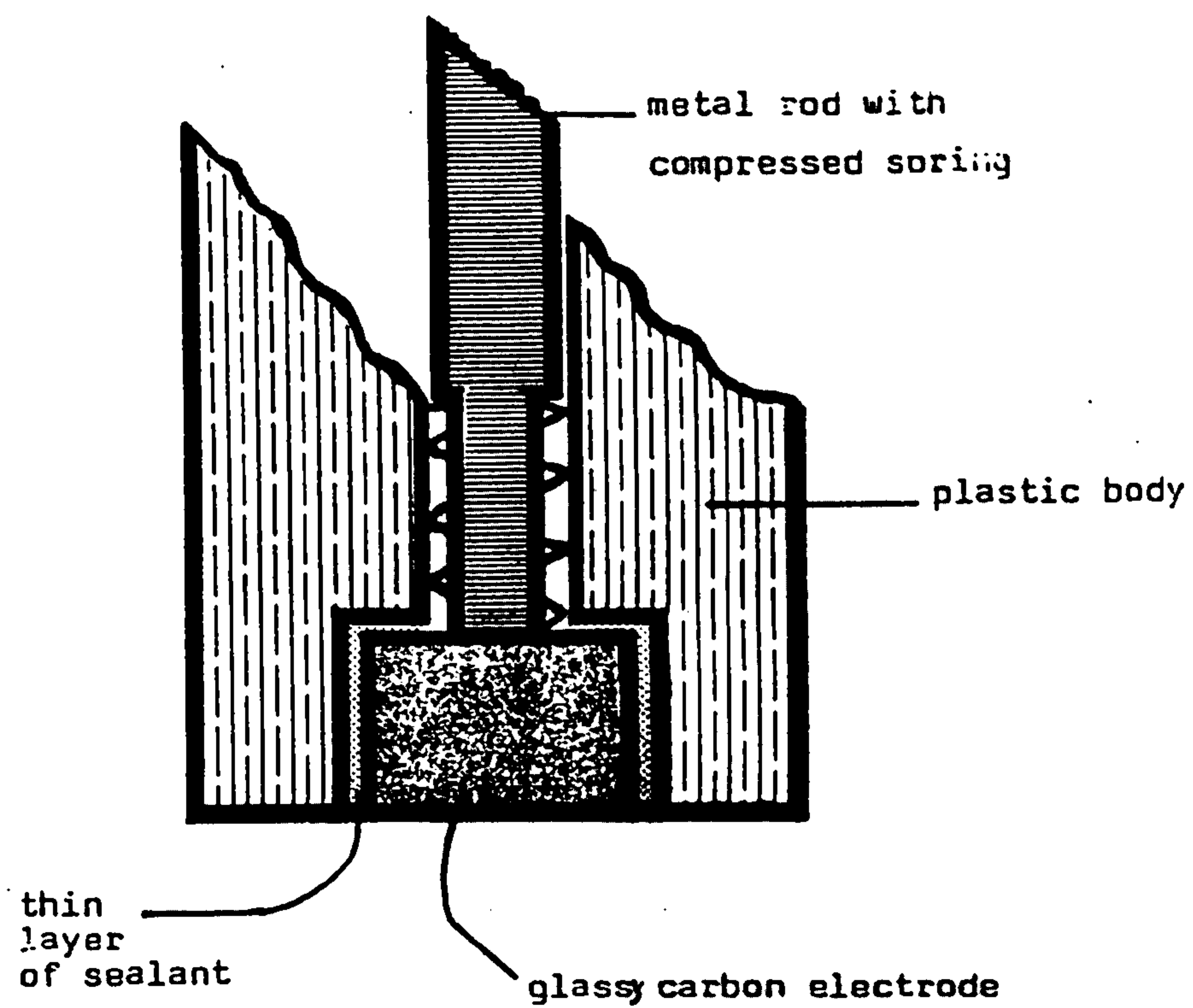


Fig. 19 Schematic of Construction of a Typical Commercial Glassy Carbon Electrode.

The electrode was placed in boiling water for about 15min. After this time it was usually possible to remove the metal contact rod from the plastic tube. A narrower metal rod could then be used to push the glassy carbon cylinder out of the plastic tube. For one electrode a longer heating time was required and a pair of pliers had to be used to ease the plastic tube off the glassy carbon cylinder. The spring were discarded in all cases.

The end of the metal rod, which in all cases had rusted, was cleaned with abrasive paper or a file and then treated with 5M nitric acid solution and then acetone. The reverse face of the glassy carbon cylinder wall were roughened with medium grade abrasive paper (No.240 silicon carbide paper, Acton and Borman Ltd.). The inside of the plastic tube and also the electrode end of the tube were roughned with a coarse grade abrasive paper (No.180). Loose powder was removed with a tissue.

The metal rod was replaced in the tube as shown in Fig. 16. An amount of graphite-loaded epoxy base containing 40% m/m hydrofluoric acid solution was placed into the top of the plastic tube followed by the glassy carbon cylinder. Correct positioning of the metal rod and the use of a suitable amount of epoxy base ensures that about 1mm of the glassy carbon cylinder remains exposed (Fig.20). The epoxy was allowed to harden partially for 1h at room temperature and then for 15min over a hot plate at 50-60°C in the same way as described in the previous chapter. Unloaded epoxy base sealant containing 40% m/m hydrofluoric acid solution in the appropriate amount as described earlier in this work was then applied to the top of the tube around the electrode face as shown in Fig.20 to isolate the glassy carbon with the exception of the electrode face from subsequent contact with electrolyte. The unloaded epoxy was allowed to harden for a period of 40min at room temperature. To remove any tackiness in the unloaded epoxy surface the electrode was suspended in the vapour chamber over 40% m/m HF_(aq) for 2min and was then removed and held at 50-60°C over a hot plate for a further 5min.

metal rod

plastic body

unloaded epoxy
sealant

glassy carbon
disc

loaded-graphite
epoxy base + HF(aq)

To obtain a levelled and flat surface with the sealant and glassy carbon disc two alternatives were devised and examined. In the first one an auxiliary tube into which the electrode was inserted and completely covered with a portion of the sealant was employed. After the curing of the system this tube was removed and then the covered tip was polished with coarse and fine alumina until the flat and shiny glassy carbon surface appeared free from the isolation epoxy which therefore remained only surrounding the disc as a sealant. A second way to obtain a final and flat surface was achieved by pressing the electrode with the glassy carbon cylinder already in place on the surface of a plastic sheet. With the electrode kept in this position upside down the sealant was poured around the glassy carbon disc and conveniently fixed in place until its complete hardening. This alternative method eliminates the need for a further rigorous polishing of the reclaimed unit. Nevertheless the simpler procedure indicated above was demonstrated to be satisfactory for the present application of the reclaimed electrodes.

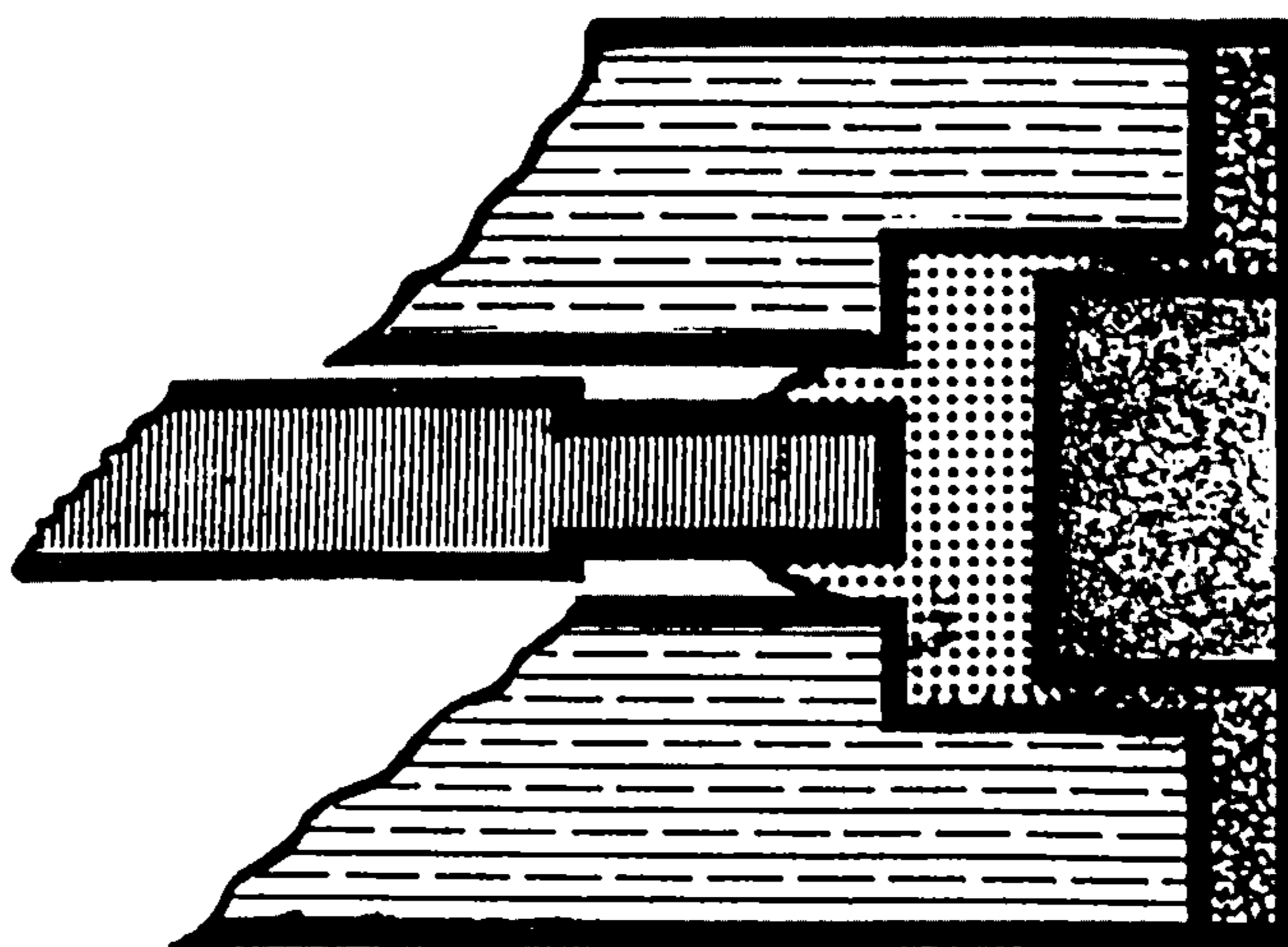
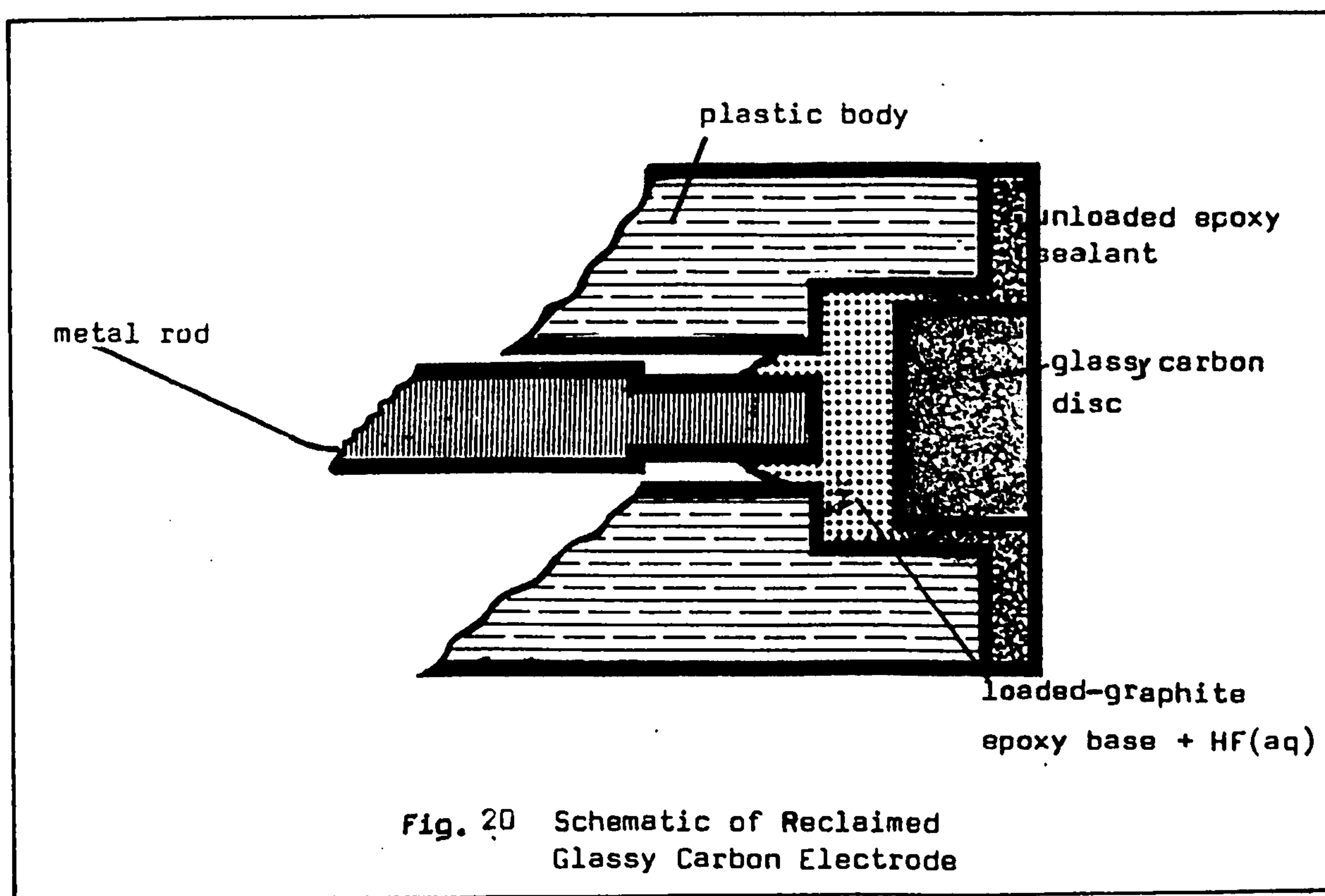


Fig. 20 Schematic of Reclaimed
Glassy Carbon Electrode

To obtain a levelled and flat surface with the sealant and glassy carbon disc two alternatives were devised and examined. In the first one an auxiliary tube into which the electrode was inserted and completely covered with a portion of the sealant was employed. After the curing of the system this tube was removed and then the covered tip was polished with coarse and fine alumina until the flat and shiny glassy carbon surface appeared free from the isolation epoxy which therefore remained only surrounding the disc as a sealant. A second way to obtain a final and flat surface was achieved by pressing the electrode with the glassy carbon cylinder already in place on the surface of a plastic sheet. With the electrode kept in this position upside down the sealant was poured around the glassy carbon disc and conveniently fixed in place until its complete hardening. This alternative method eliminates the need for a further rigorous polishing of the reclaimed unit. Nevertheless the simpler procedure indicated above was demonstrated to be satisfactory for the present application of the reclaimed electrodes.



Testing of reclaimed electrodes

The electrodes were tested in the static mode in a similar way to that used previously with the graphite-loaded epoxy-based electrodes by running slow (5 to 25mVs⁻¹) linear sweep voltammograms. The three electrode system consisted of the test electrode, a calomel reference electrode and a platinum counter electrode. The reference electrode was separated from the test solution by means of a ground glass sleeve joint salt bridge, containing an electrolyte of the same composition as the test solution but excluding any determinand. Voltammetry was carried out by means of a Metrohm Polarecord 626.

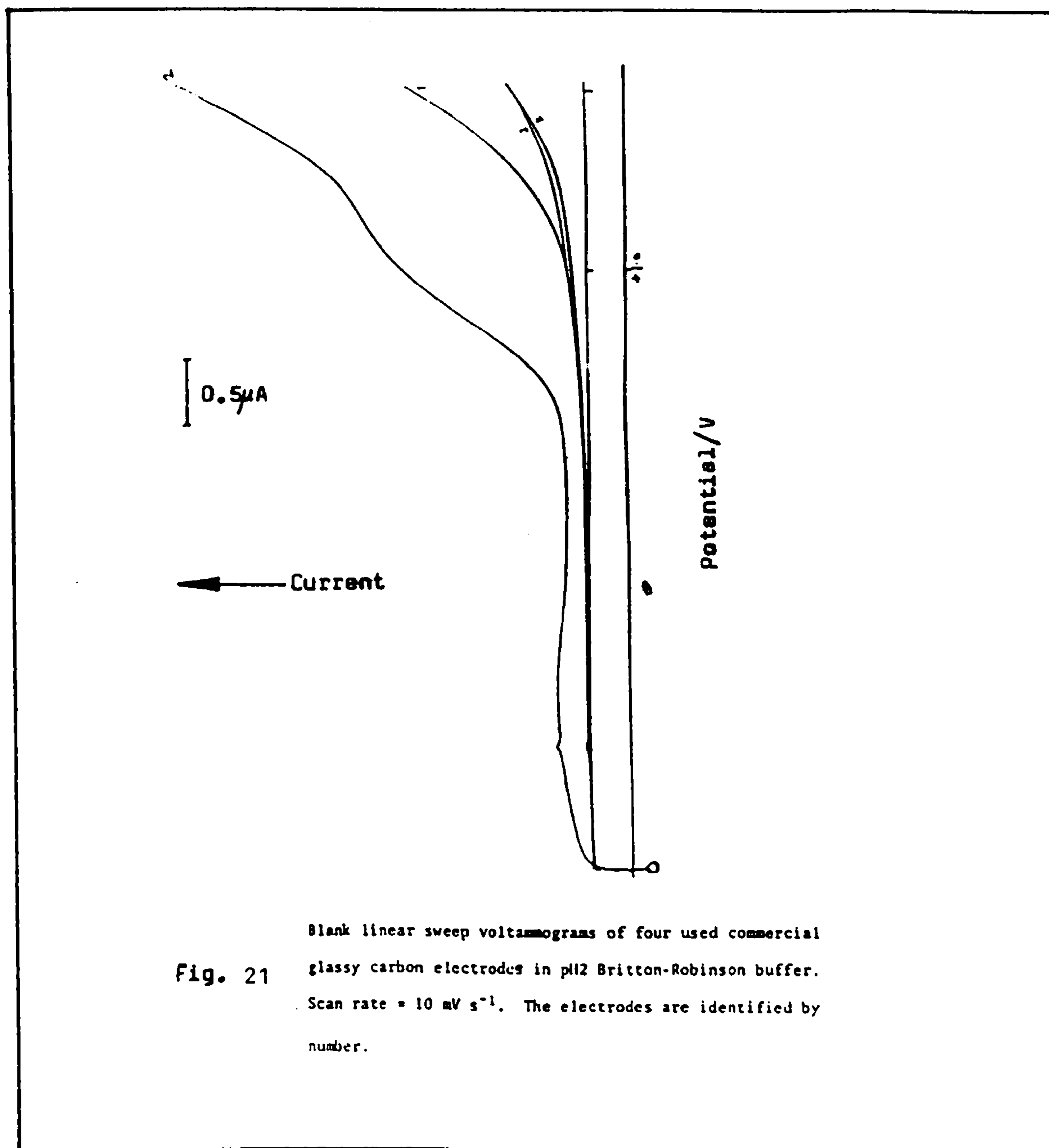
The background current associated with the glassy carbon electrodes before and after reclamation were determined for pH 2 Britton-Robinson buffer (0.04M in the three weak acid constituents). The potential was swept from zero to +1.2V. The solutions were not deoxygenated. The reclaimed units were tested further by obtaining linear sweep voltammograms in 10⁻³M KI in 10⁻¹M KCl solution and in a 40 gml⁻¹ solution of dopamine in pH 6.2 Britton-Robinson buffer.

Results

Four electrodes were reclaimed using the procedure described. The background of the four electrodes were studied after chemical cleaning and re-polishing before reclamation. The linear sweep voltammograms obtained with these four electrodes in pH 2 Britton-Robinson buffer are shown in fig. 21. Clearly the background currents were high in all cases and very high in one case.

The linear sweep voltammograms obtained in pH 2 Britton-Robinson buffer after reclamation for the four electrodes are shown in fig. 22. Clearly the reclamation technique has been successful in producing electrodes with low background currents and with similar voltammetric behaviour to

the graphite-loaded epoxy-based electrodes described in the previous chapter. The background currents are virtually zero (i.e. $< 0.1 \mu\text{A}$) up to +0.85V but a small background current is present at +1.2V. The size of this background current is highest on the first scan and a minimum of three successive scans conditions the electrode and reduces the background current at +1.2V to its lowest value.



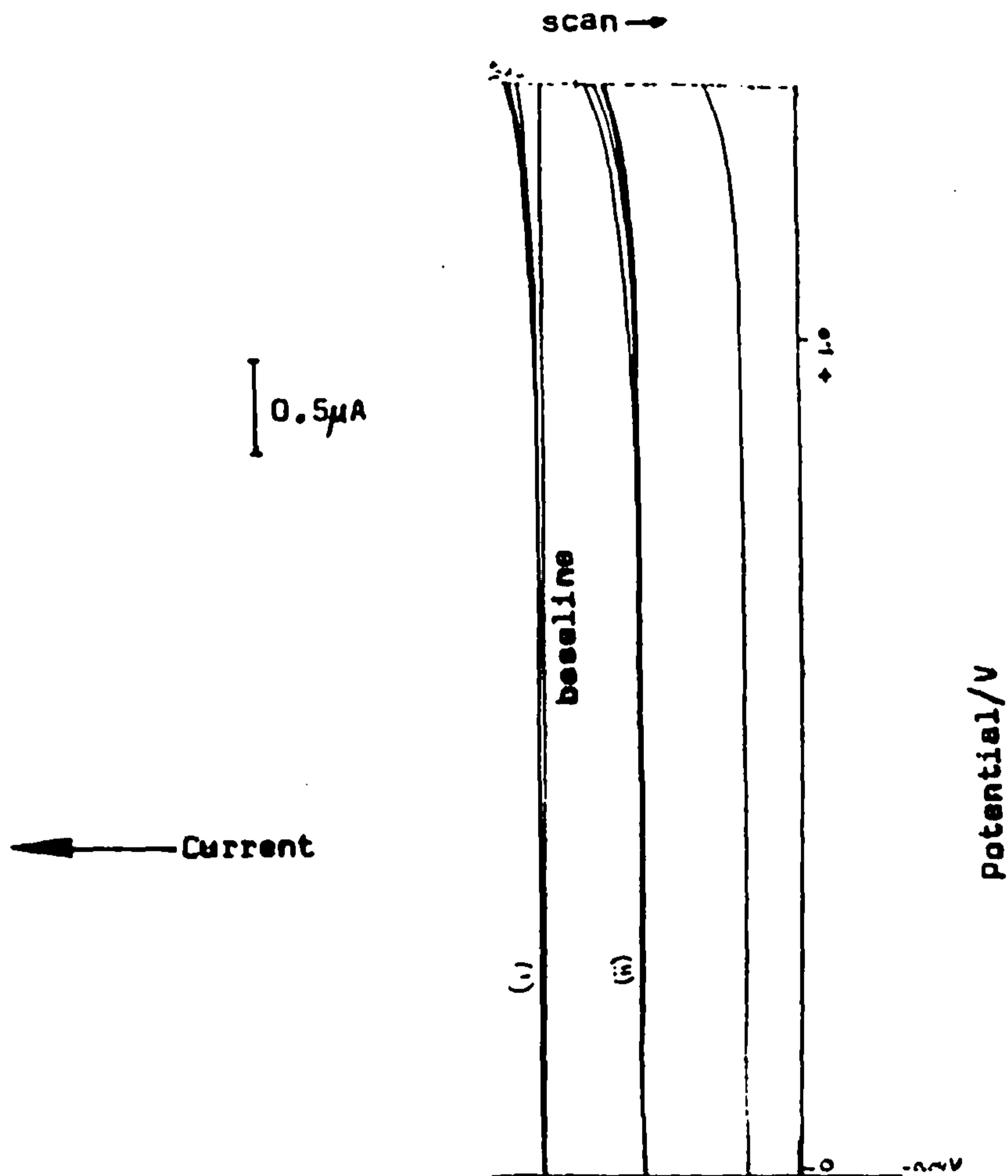


Fig. 22

Blank linear sweep voltammograms in pH2 Britton-Robinson buffer of reclaimed glassy carbon electrodes. Scan rate = 10 mV s^{-1} .

- (i) Scans for four electrodes after conditioning. The electrodes are identified by number.
- (ii) Six consecutive conditioning scans for electrode number 1.
- (iii) Scan for a conditioned new commercial electrode for comparison.

Linear sweep voltammograms for the electrodes in 10^{-3} M KI in 10^{-1} M KCl solution and in $40\mu\text{gml}^{-1}$ of dopamine (pH 6.2 Britton-Robinson buffer) are shown in Fig. 23. Cleaning of the electrodes between scans in dopamine solutions was carried out with carbon tetrachloride.

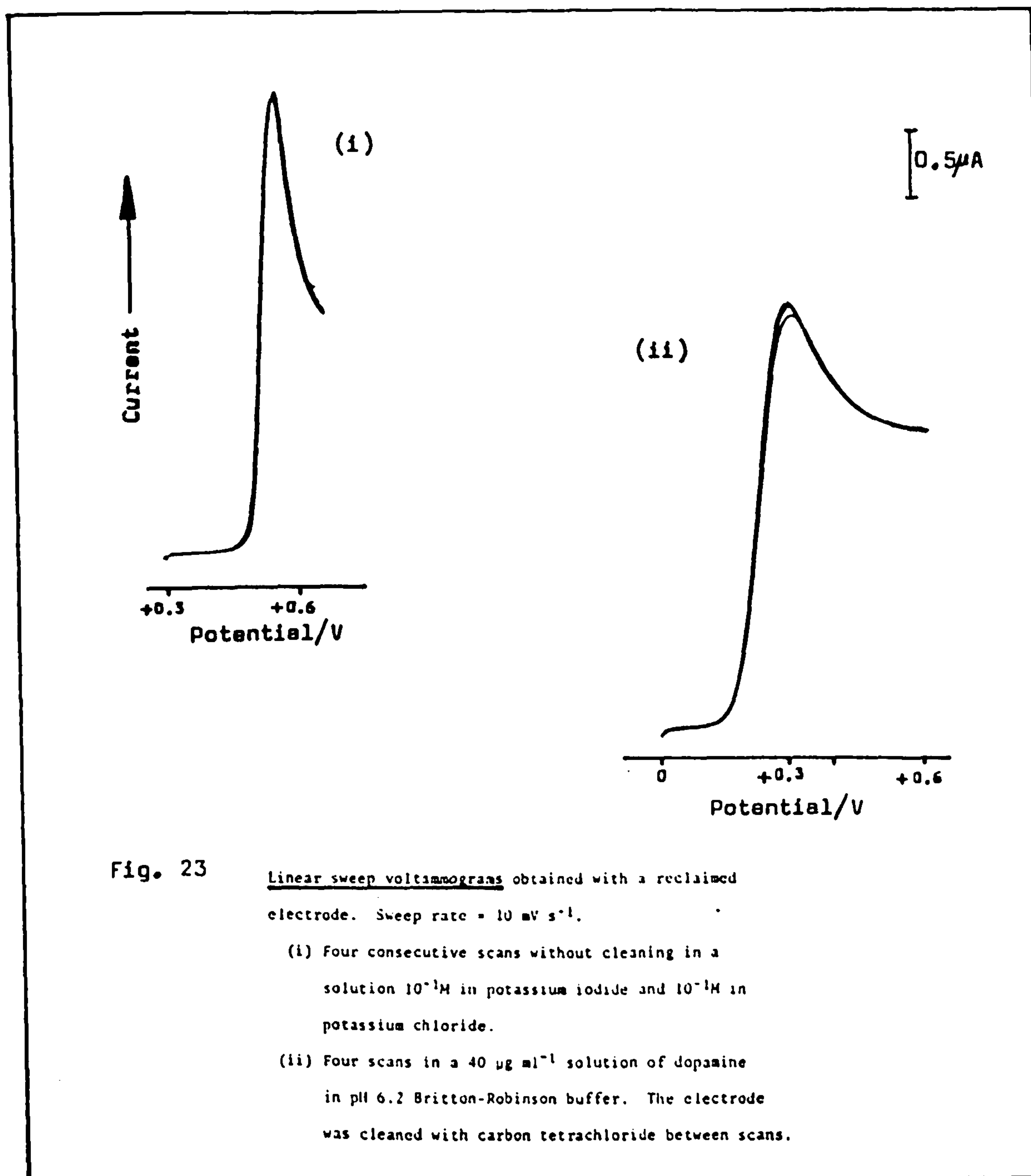


Fig. 23

Linear sweep voltammograms obtained with a reclaimed electrode. Sweep rate = 10 mV s^{-1} .

- (i) Four consecutive scans without cleaning in a solution 10^{-3} M in potassium iodide and 10^{-1} M in potassium chloride.
- (ii) Four scans in a $40\mu\text{g ml}^{-1}$ solution of dopamine in pH 6.2 Britton-Robinson buffer. The electrode was cleaned with carbon tetrachloride between scans.

Discussion

The performance of commercial glassy carbon electrodes of some makes deteriorate with use. The usual reason for deterioration has been shown to be due to permeation of electrolyte between the electrode body and the glassy carbon disc. Electrical contact is then established between the electrolyte and other parts of the glassy carbon cylinder and the internal metallic parts in addition to the electrode face, and, as a consequence, high background currents are produced. In this application of the novel coating and curing technique it was assumed that if these electrodes are dismantled and then remounted in such a way that parts of the glassy carbon cylinder and internal contacts are isolated effectively leaving only the electrode face in contact with the electrolyte then satisfactory performance can be re-established with a financial saving. Another assumption is that an unloaded epoxy resin cured by addition of 40% m/m hydrofluoric acid solution is particularly suitable for effecting this isolation as its fluid characteristics before it has hardened allow it to be smoothly applied, it is highly resistant to attack by a range of acids and solvents and it has a much lower tendency to adsorb organic compounds than has epoxy resin cured conventionally. Furthermore, a graphite-loaded epoxy resin hardened by addition of 40% m/m HF solution has excellent fluid characteristics, is of course electrically conducting and can be used with advantage where silver-loaded epoxy is normally employed to provide electrically conducting connection. In this work Specpure graphite was used as a precaution as difficulty had been experienced in coating properly a graphite-loaded epoxy surface prepared with a cruder graphite. In the present application, however, the graphite-loaded epoxy is well away from contact with the electrolyte and no difficulty is predicted arising from the use of a cruder graphite. A graphite-loaded epoxy can be used liberally as its cost is negligible. Numerous other applications are possible and some of them are discussed in continuation of the present studies.

GRAPHITE-LOADED EPOXY-BASED COATED PLASTIC AND COATED GLASS VOLTAMMETRIC ELECTRODES

Introduction

In this chapter the multilayer coating and vapour technique has been extended to the production of coated plastic and glass rod electrodes. An advantage of using plastic or glass instead of wire is that it is not so critical to coat the surface thoroughly because the plastic or glass is non-conducting. A disadvantage arises from this non-conductivity, however, in that coated-plastic rod or coated-glass rod electrodes produced in a similar way to the coated-wire electrodes have too high an electrical resistance. This difficulty has been overcome here by enriching the first few epoxy layers with graphite powder immediately after they have been hardened. Electrodes produced in this way have a sufficiently low resistance. The preparation of graphite-loaded epoxy base and the use of 40% m/m hydrofluoric acid solution as the hardener for the graphite-loaded and unloaded epoxy resin are described earlier (see previous chapter) and the same technique was employed here. A crude graphite-loaded epoxy base was used in some circumstances as a conductive epoxy base and the unloaded epoxy sealant was used conveniently for the isolation of the electrodes.

Preparation of coated plastic and coated glass electrodes

In this work plastic and glass rods (2-3mm diameter) were used in 7cm lengths. The plastic rods used were knitting needles made of polystyrene. The surface of the rods were roughened using an abrasive paper as mentioned previously; the ends of plastic rods were flattened using this abrasive paper. The surfaces were then wiped with a tissue, washed with ethanol and dried. A very small amount of graphite-loaded epoxy base was placed on the

cylindrical surface and thoroughly smoothed over most of the length using a thin flexible cellophane sheet. It was essential that only a thin film was left in order to obtain effective hardening. The coated rod was suspended in the vapour chamber over 40% m/m hydrofluoric acid solution for 5min. The rods were then removed and hardened at 50-60°C over a hot plate for ca. 5min. For some types of electrode the end of the rod was also coated.

A small portion of Specpure graphite was then placed on the hardened surface and smoothed into the layer using a tissue. The graphitised layer was then rubbed intensively with a tissue in order to remove excess of graphite powder. The surface now had a shiny mirror-like finish owing to the entrapment of graphite in the surface. The process of coating the surface with graphite-loaded epoxy, and of hardening and graphitising the coating was repeated twice. Then the coating and hardening process was repeated twice more without the graphitisation process. The combination of three graphitised layers and two normal layers produces electrodes of low resistance ($< 150\text{ohm}$ for a 6cm length) with a sufficiently robust surface.

Three types of plastic and glass electrode were prepared here: a disc electrode and two different cylindrical electrodes. These are illustrated in Fig.24(a). In type (i) both the cylindrical and end surfaces were coated with graphite, but the cylindrical surface was isolated subsequently from later contact with the electrolyte by coating it with the isolating epoxy resin. This electrode is thus a coated disc electrode. In types (ii) and (iii) the end surface was left uncoated. The type (ii) electrode can be considered essentially an end cylinder, the rest of the cylindrical surface being treated with unloaded epoxy sealant: the end surface which is uncoated plastic or glass was cleaned finally with an abrasive to remove any graphite particles. Type (iii) electrode is of the central cylinder type. In this work the coated glass-rod electrodes that were prepared were of types (ii) and (iii).

plastic or glass

sealant
(isolation)

graphite-loaded
epoxy coating

graphite-loaded
epoxy resin

metal foil

metal wire

Electrical contact was made at the end of the rod away from the electrode surface. Three methods of making contact used here are illustrated in Fig. 24(b). In type (i) the graphite coating at the end of the electrode was covered with graphite-loaded epoxy resin which was allowed to harden. Electrical contact was then made conveniently by means of a crocodile clip. In type (ii) metal foil (e.g. aluminium foil) was wrapped round the coated surface and was held firmly in position by some means: electrical contact was made to this, again possibly with a crocodile clip. In type (iii) a copper wire was fixed to the coated surface by means of graphite-loaded conductive epoxy base. The latter was much simpler and more resistant as it is fixed permanently in position. As the graphite-loaded epoxy base employed has low electrical resistance this third type of contact was preferable for the majority of electrodes tested.

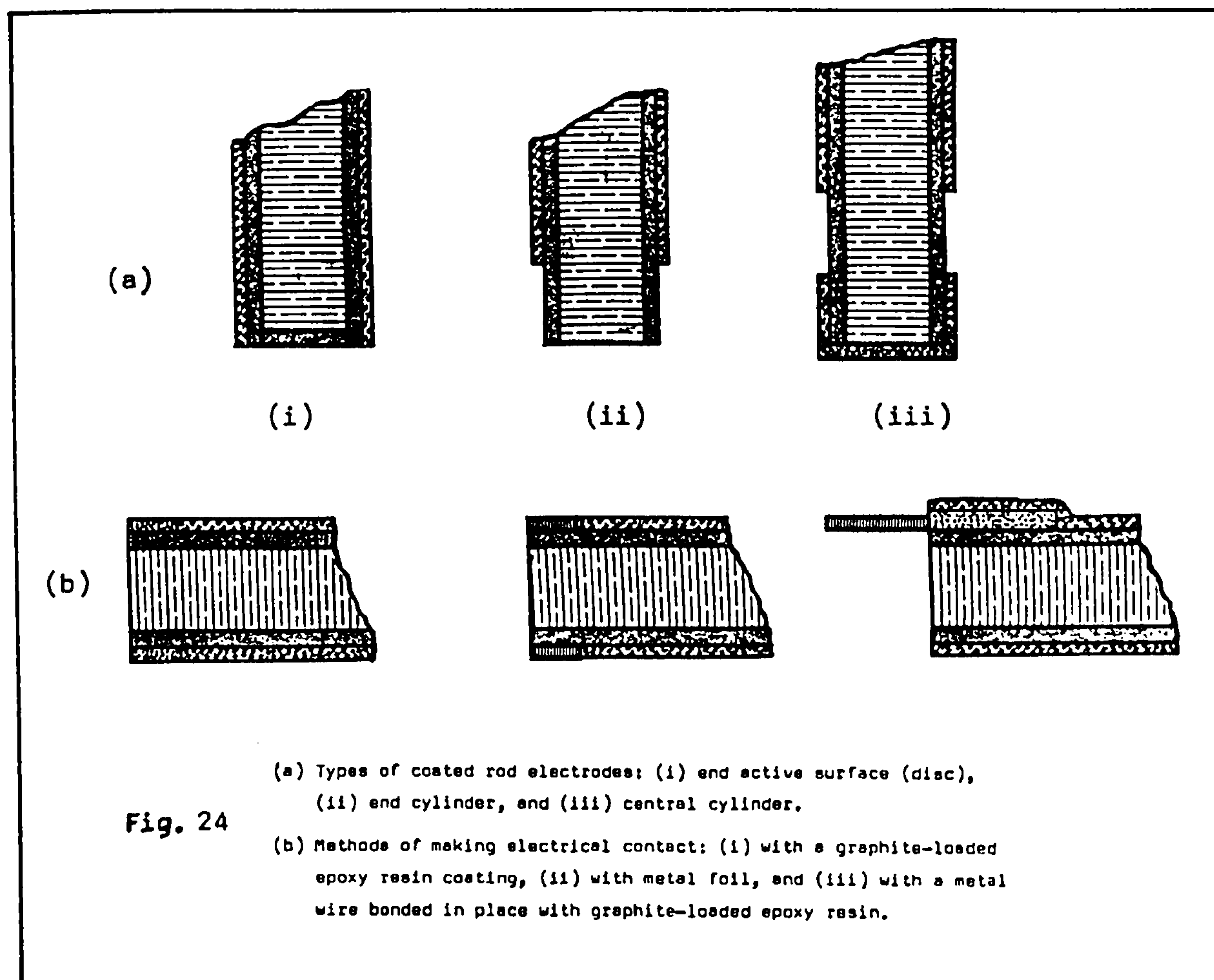
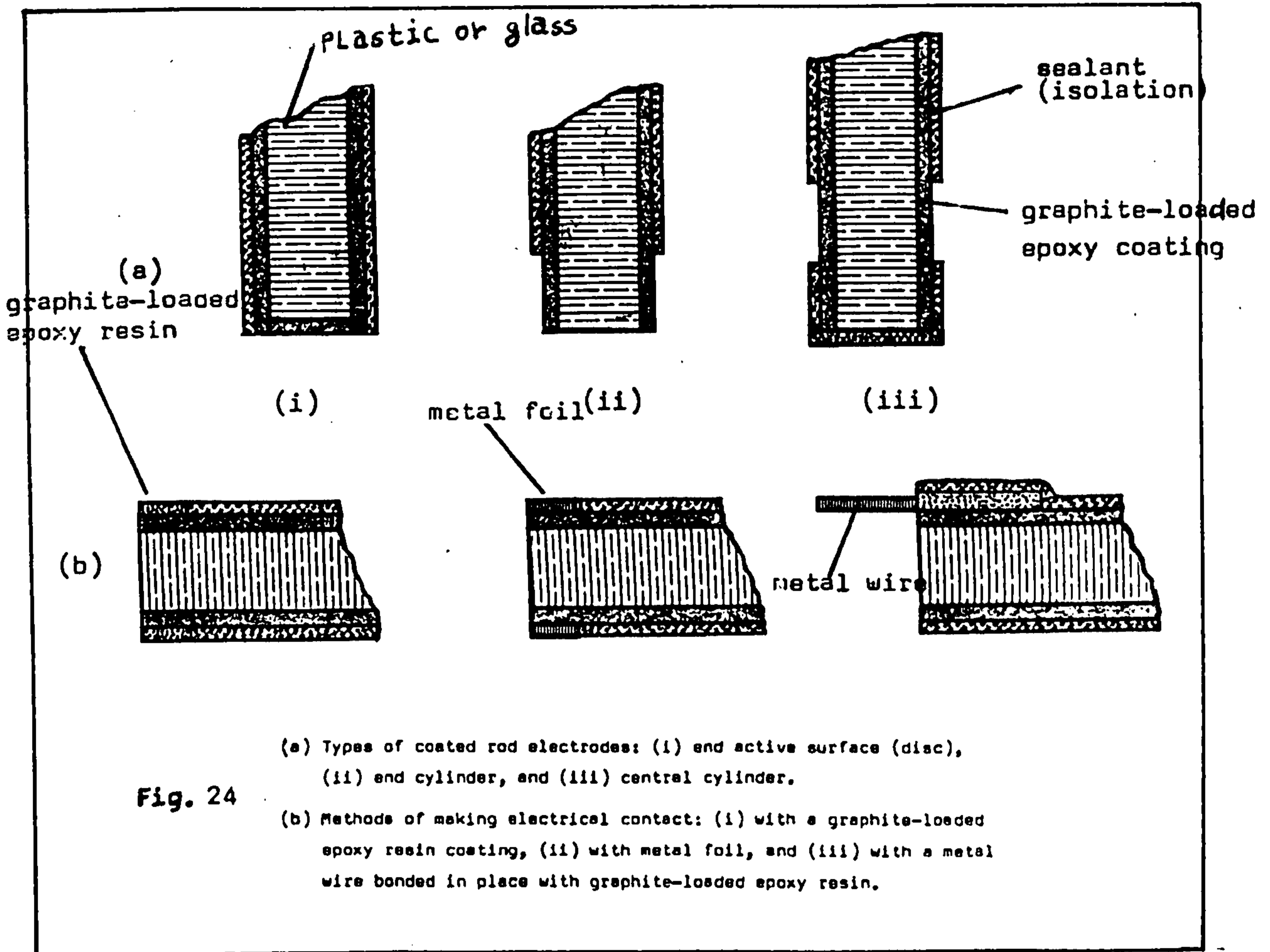


Fig. 24

Electrical contact was made at the end of the rod away from the electrode surface. Three methods of making contact used here are illustrated in Fig.24(b). In type (i) the graphite coating at the end of the electrode was covered with graphite-loaded epoxy resin which was allowed to harden. Electrical contact was then made conveniently by means of a crocodile clip. In type (ii) metal foil (e.g. aluminium foil) was wrapped round the coated surface and was held firmly in position by some means: electrical contact was made to this, again possibly with a crocodile clip. In type (iii) a copper wire was fixed to the coated surface by means of graphite-loaded conductive epoxy base. The latter was much simpler and more resistant as it is fixed permanently in position. As the graphite-loaded epoxy base employed has low electrical resistance this third type of contact was preferable for the majority of electrodes tested.



Testing of electrodes

In this work the electrodes were tested in static mode using slow ($5\text{--}25\text{mVs}^{-1}$) linear sweep voltammetry and differential pulse voltammetry. The three electrode system consisted of the test electrode, a calomel reference electrode and a platinum counter electrode. Voltammetry was carried out by means of a Metrohm Polarecord 626.

The background currents associated with the electrodes in a range of buffer solutions were investigated, and the oxidation of iodide, food colouring matters and dopamine were studied as examples.

Results

The preparation of graphite-loaded epoxy-based coated wire electrodes was discussed previously (see p. 81). The resistance of a 6cm length of plastic rod coated in the same manner even with eight to ten coatings was typically 1000ohm or more. Using the present graphitisation procedure the resistance of similar electrodes with only five coatings was 150ohm. Coated-plastic and coated-glass rod electrodes have an advantage over coated wire electrodes in that the material of the rod does not interfere with the response of the electrode. Thus, highly satisfactory electrodes can be made without the same degree of care to ensure that the original surface is covered adequately.

Numerous plastic rod electrodes of the three types shown in Fig. 24(a) have been prepared. All are readily produced and behave similarly. Most of the later tests were carried out using the end-cylinder type and the results presented are for this type. Coated glass rod electrodes behaved similarly. The coating and vapour hardening procedure works particularly well on slightly roughened glass presumably owing to the etching action of the hydrofluoric acid.

The electrodes behave very similarly to the graphite-loaded epoxy-coated

electrodes already described and to well-behaved glassy carbon electrodes. Three slow linear sweep scans from 0 to +1.2V were used to condition the electrodes. Background currents associated with a typical conditioned electrode in pH 2 Britton-Robinson buffer, 0.18M sulphuric acid solution, pH 3 ammonium citrate buffer and pH 7.5 Britton-Robinson buffer are shown in Fig. 25. In all these buffers without deoxygenation the background current between -0.3 and +1.1V was less than $0.2\mu\text{A}$.

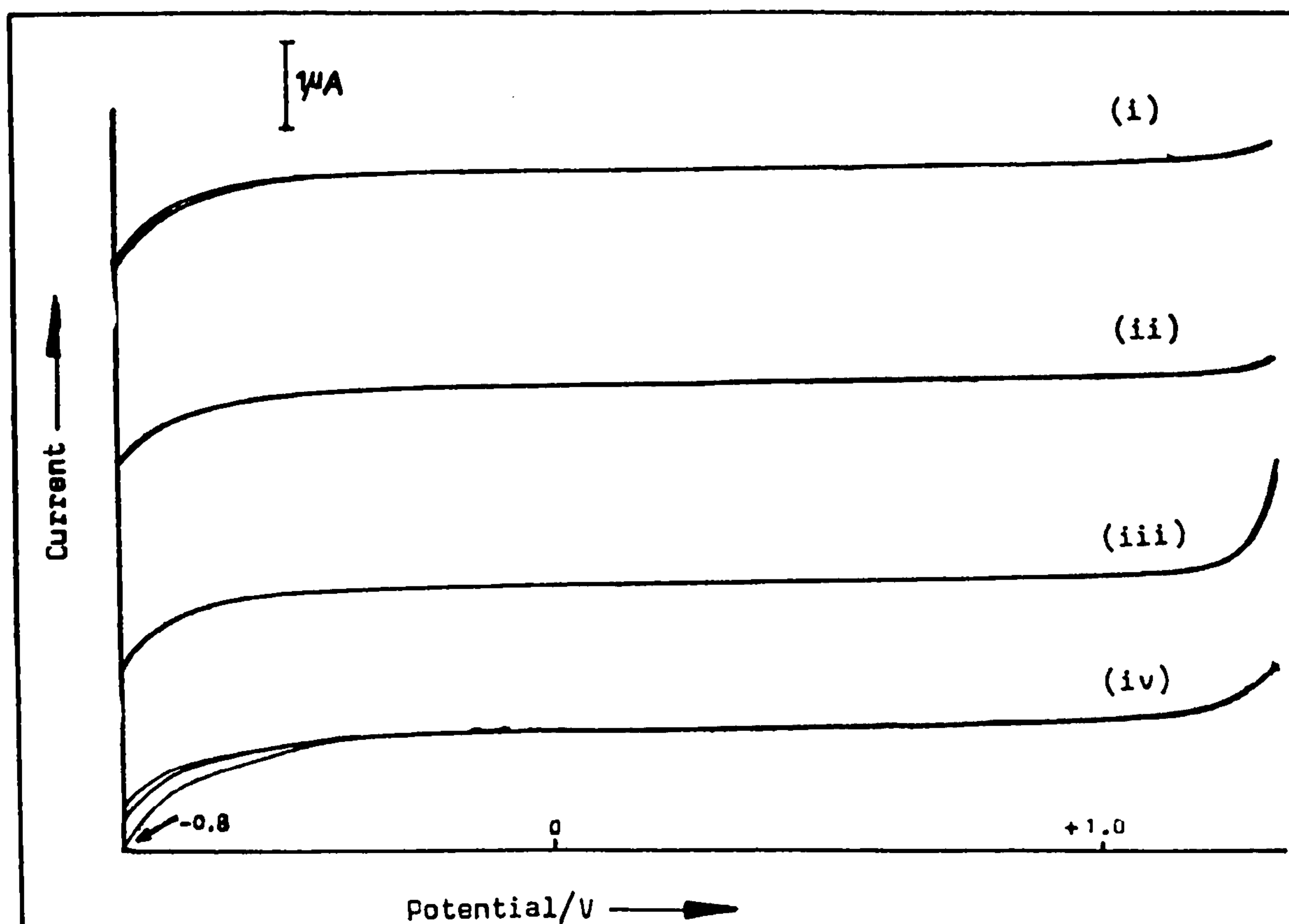
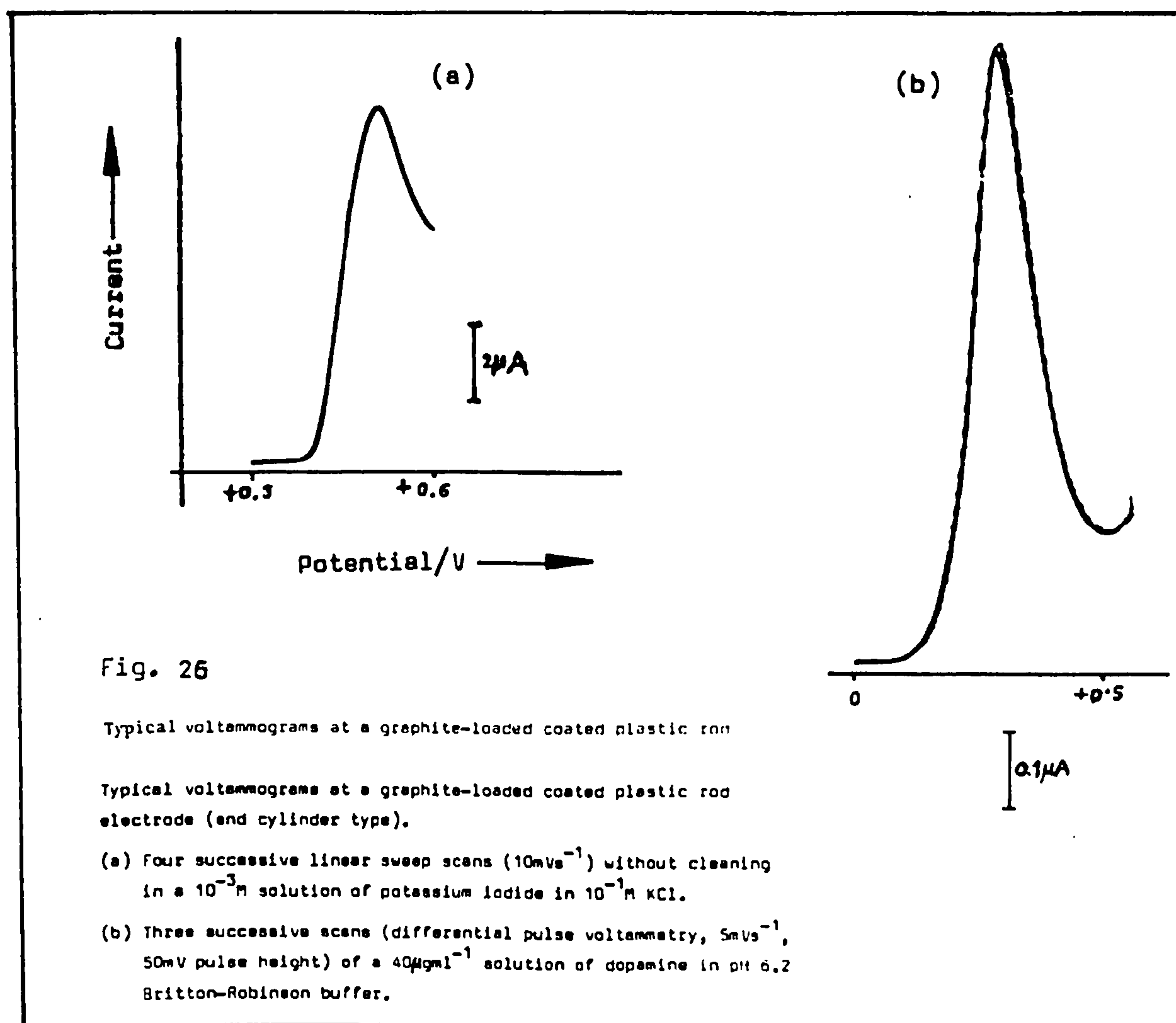


Fig. 25 Background currents (linear sweep voltammetry) for a conditioned graphite-loaded coated plastic rod electrode (end cylinder type). No deoxygenation. Three successive scans in: (i) pH 2 Britton-Robinson buffer, (ii) 0.18M sulphuric acid solution, (iii) pH 3 ammonium citrate buffer, and (iv) pH 7.5 Britton-Robinson buffer. Scan rate 10mVs^{-1} .

Typical linear sweep voltammograms for the oxidation of 10^{-3} M KI in 10^{-1} M KCl solution are shown in Fig. 26 (a) without cleaning the electrode between scans.

In this work an effective way of cleaning of electrodes that had been used with dopamine was to place them in 0.1M sodium hydroxide solution or 1.5M sodium sulphite solution and hold them at a potential of +1.5V for ca. 5min. Differential pulse voltammograms for dopamine shown in Fig. 26(b) illustrate this point. Linear sweep voltammograms obtained with food colouring matters were similar to those obtained with graphite-loaded epoxy-based disc electrodes discussed previously.



Discussion

A method has been described here for producing coated plastic and glass rod voltammetric electrodes of low resistance and comparatively good electrochemical behaviour. Their main advantage over coated metal wire electrodes is that complete coverage of the material of the rod is not essential. Indeed in one type of electrode described here the plastic or glass end of the rod is left uncovered. The electrodes described are easy to construct and may^{be} regarded as disposable. There is the possibility of making them very small and the contamination problems observed here are expected to become minimal at the low determinand concentrations that are measured in flow systems. Preliminary experiments on the use of these electrodes in flow-injection analysis are reported later.

GRAPHITE-LOADED EPOXY-BASED COATED FABRIC ELECTRODES

Introduction

In this chapter the new multilayer coating and hardening technique was extended to the coating of various surfaces including nets and fabrics. A procedure is described for the preparation of a coated fabric as a master source for the construction of disc voltammetric electrodes as an extension of the previous work. Several other applications were devised for the system developed here.

Coating polyester and other plastic nets

An epoxy base and an epoxy sealant were prepared in the same way as described in the previous chapters. The gaseous hardener inside the so-called vapour chamber was employed in the usual manner. Graphite-loaded epoxy sheet was prepared by coating polyester net fabric (dressing making fabric). Spreading of the graphite-loaded epoxy base on the fabric was carried out using a flat metal spatula of the same width as the strip of fabric coated with hardened graphite-loaded epoxy. A layer of base was placed on one side of the fabric. This was hardened and then further coatings were built up on this first side. Later, layers were built up on the reverse side of the fabric. The smoothness of the final coated fabric surface was improved by polishing with slurries of coarse alumina (aluminium oxide of 100-250 mesh) and with very fine alumina (0.3 and 0.015 μm). This coated fabric constitutes a master electrode source.

Preparation of voltammetric coated fabric disc electrodes

Discs were cut conveniently from the master membrane source by means of an office paper punch or by using a wad punch. Larger discs were cut out with scissors. Copper wire was soldered onto the back of a copper or brass disc:

glass
tube

epoxy sealant

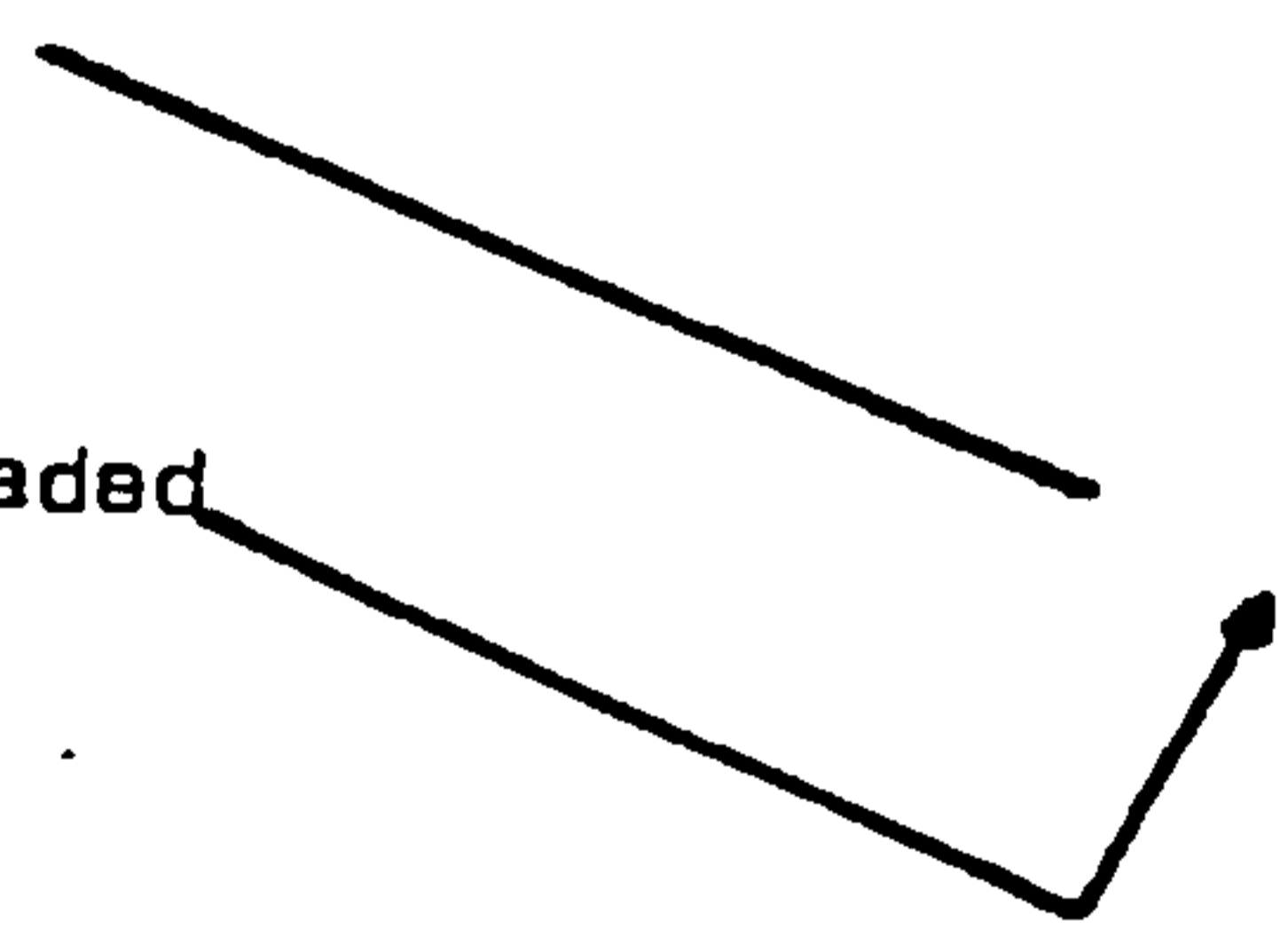
copper wire soldered
to rear of copper or
brass disc

conductive
loaded-graphite
epoxy resin

graphite-loaded
epoxy disc

copper or brass disc

epoxy sealant



the copper disc was usually slightly larger than the graphite-loaded epoxy fabric disc to facilitate fixing. The graphite disc was then fixed onto the copper disc by means of graphite-loaded epoxy resin. The assembly was then sealed into a suitable glass tube as shown in Fig. 27 using the unloaded epoxy resin sealant as described in the previous sections.

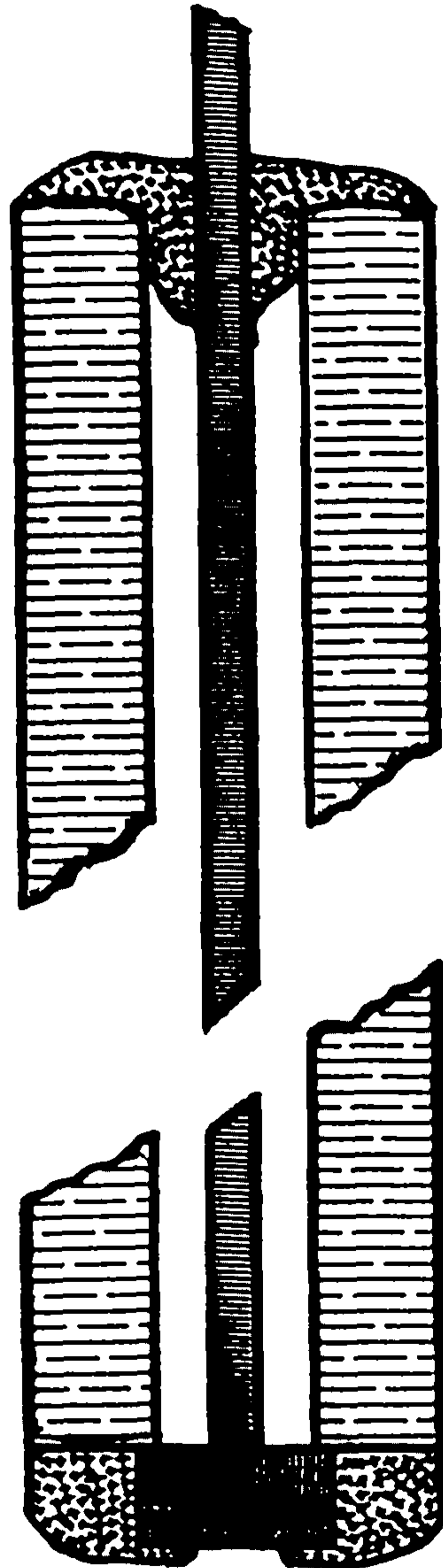


Fig. 27

Construction of disc electrode.

the copper disc was usually slightly larger than the graphite-loaded epoxy fabric disc to facilitate fixing. The graphite disc was then fixed onto the copper disc by means of graphite-loaded epoxy resin. The assembly was then sealed into a suitable glass tube as shown in Fig. 27 using the unloaded epoxy resin sealant as described in the previous sections.

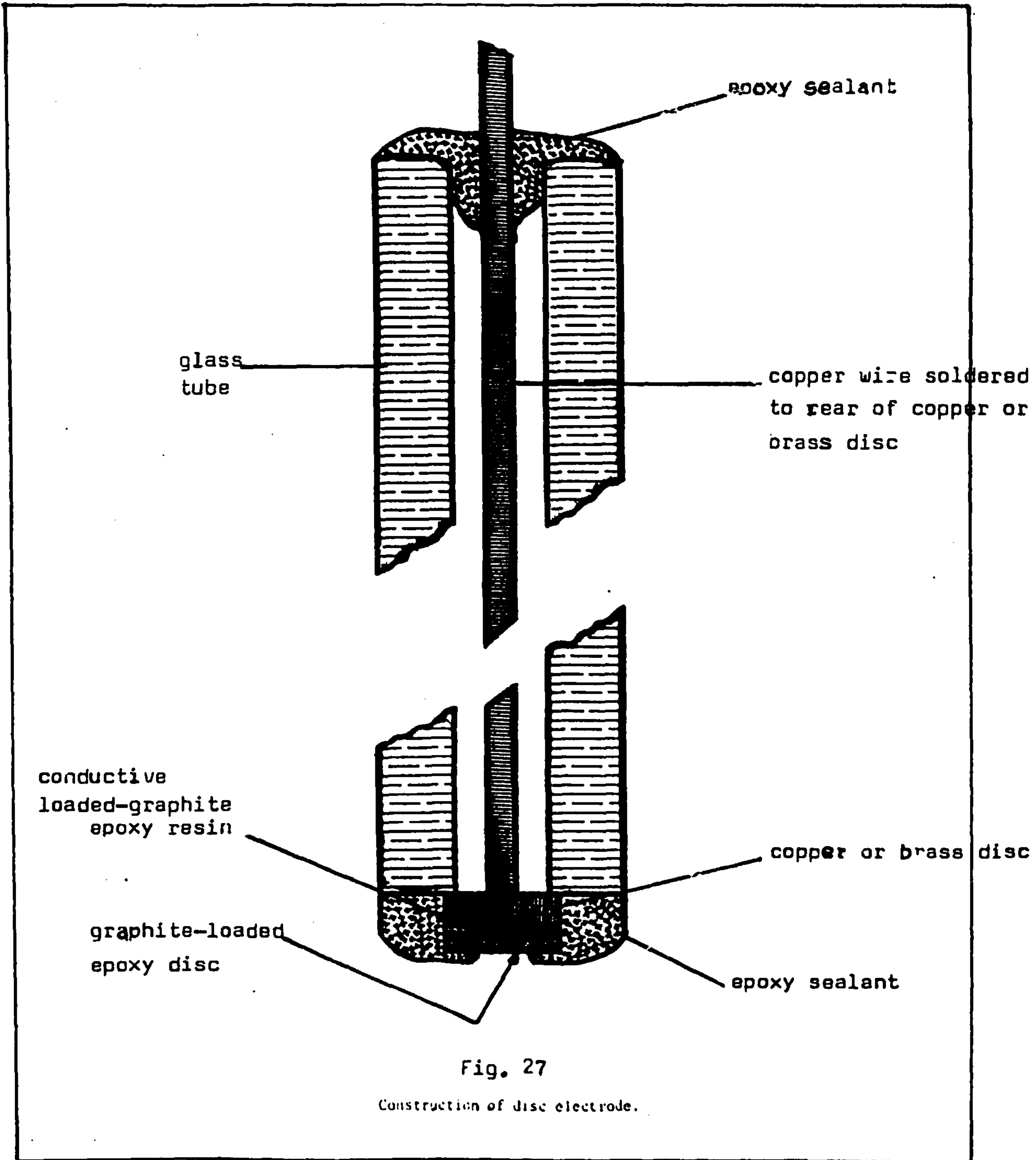


Fig. 27

Construction of disc electrode.

Testing of electrodes

The electrodes were tested in a similar manner to that used in previous studies of the use of hydrofluoric acid hardened electrodes. The background current was determined in the static mode in several electrolytes: slow LSV and, in this case, differential pulse voltammograms were obtained for iodide, food colouring matters and dopamine. A three electrode system was used with a Metrohm Polarecord 626.

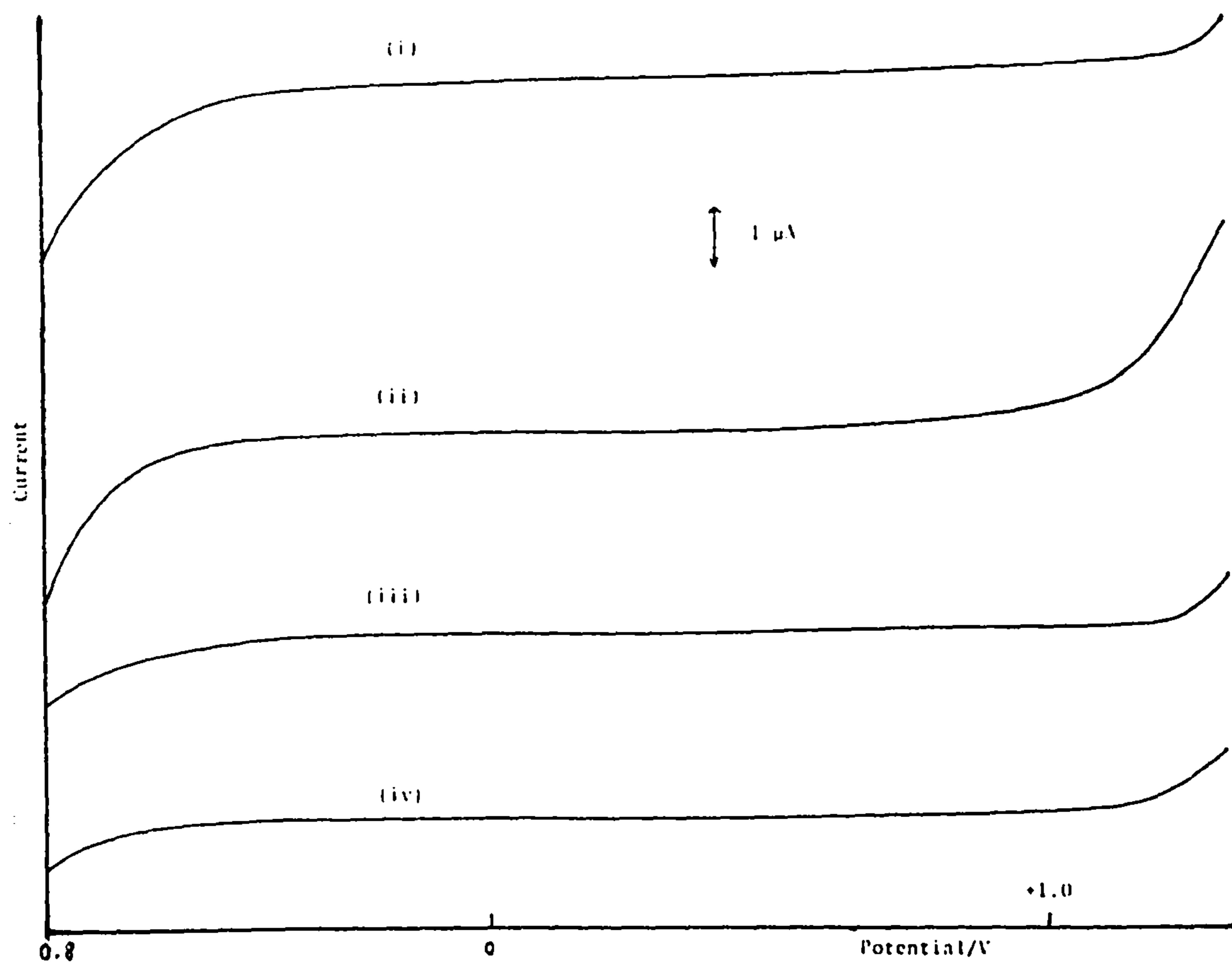
Results

Numerous electrodes of this type were prepared. Two sizes of electrode were constructed with active surfaces of 4 and 6mm diameter prepared from epoxy discs 5 and 9mm in diameter respectively (see Fig. 27). Typical blank linear sweep voltammograms obtained in 0.18M sulphuric acid solution and in pH 7.5 Britton-Robinson buffer solution are shown in Fig. 28. Clearly very low background currents are obtained between -0.4 and +1.0V without deoxygenating the solutions.

The linear sweep voltammograms are very similar to those given previously for this type of surface. Successive linear sweep voltammograms in 10^{-3} M KI in 10^{-1} M KCl solution are identical. The electrodes responded as well as glassy carbon electrodes in food colour solutions when cleaned with ethanol, chloroform and carbon tetrachloride between scans. Adsorbed products from dopamine oxidations could be removed effectively by holding the electrode at +1.5V in a 1.5M sodium sulphite solution for 2-5min between scans. Differential pulse voltammograms of dopamine for four successive scans at one of the smaller disc electrodes are shown in Fig. 29.

Discussion

An advantage of this type of disc electrode is that the disc itself is readily replaced. Numerous discs can be cut from the master source and these have virtually identical surface properties and can be polished very readily.



Background currents obtained for linear sweep voltammetry.
Sweep rate 10mVs^{-1} .

Fig. 28

(i) and (ii) large disc; (iii) and (iv) small disc.

Electrolyte: (i) and (iii) 0.18M sulphuric acid solution;

(ii) and (iv) pH 7.5 Britton-Robinson buffer.

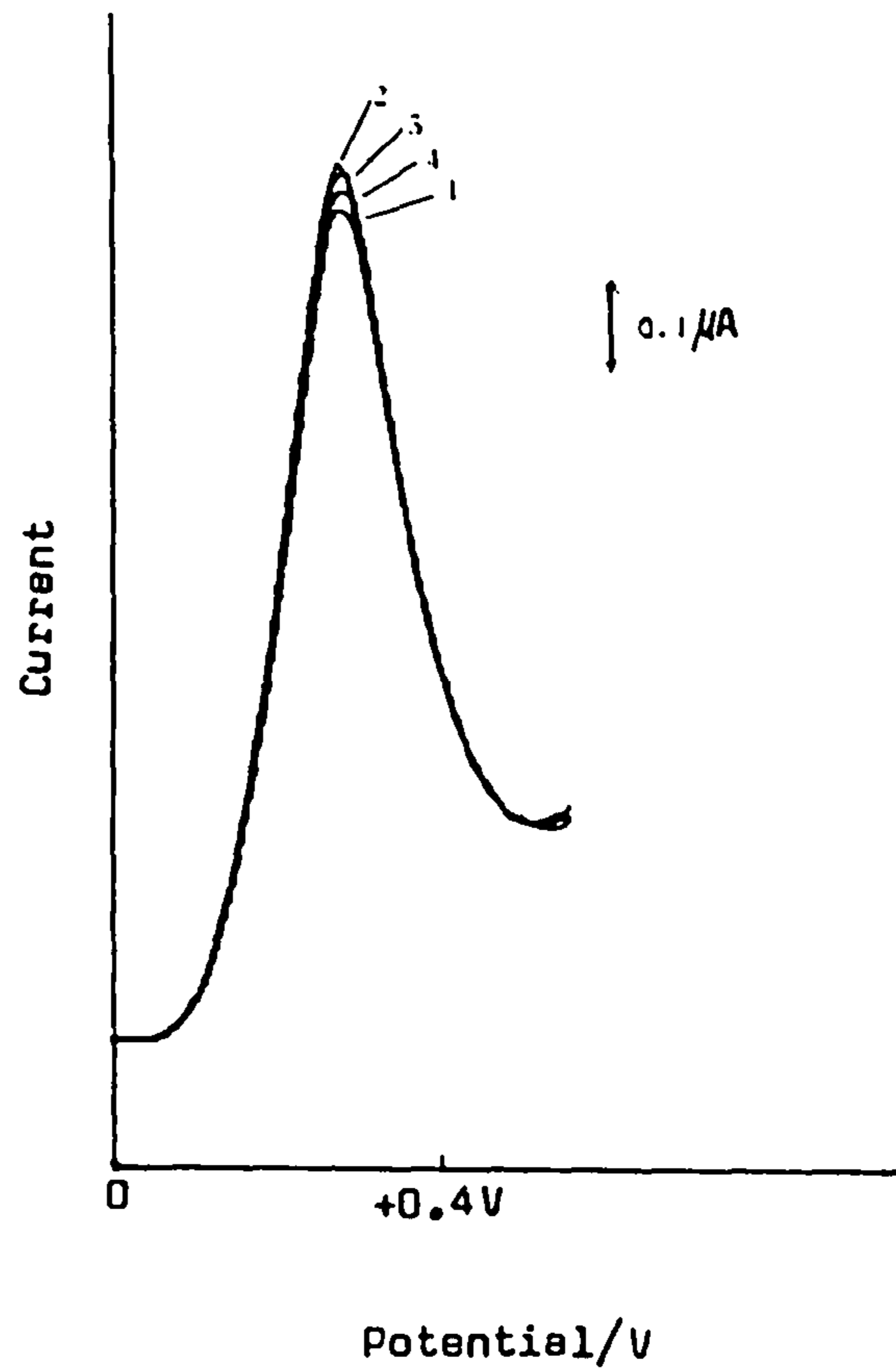


Fig. 29

Four consecutive differential pulse voltammograms in pH 7.5 of dopamine (40ppm). Scan speed 5mVs^{-1} ; Pulse amplitude 50mV. Cleaning in 1.5M sodium sulphite solution at +1.5V for five minutes between scans. The scan numbers are indicated.

The discs are very robust owing to the reinforcing action of the fabric net, and more physical pressure can be applied during chemical cleaning than is the case with the disc electrodes described previously. The previous disc electrodes can be recovered also by renewing the surface using the coating and hardening technique.

The disc are quite thin (ca. 0.2mm) and the electrical resistance across them is small (ca. 30ohm). The successive layers of graphite-loaded epoxy could be enriched with graphite powder to lower the resistance even more as described previously during the preparation of coated plastic electrodes but this does not appear to be necessary.

PRELIMINARY STUDIES OF FURTHER SYSTEMS AND USES OF GRAPHITE-LOADED
EPOXY BASE AND EPOXY-BASED ELECTRODES

Introduction

In the previous chapters the development of a new coating and curing technique has been presented and evaluated and new voltammetric epoxy-based electrodes of the type shown in Fig. 30 below have been described.



Fig. 30 Different types of Epoxy-based Voltammetric Electrodes.

Left to Right: coated-fabric disc electrode, coated-plastic (central cylinder), coated-wire electrode, coated-plastic (end cylinder) and glass capillary disc electrode.

Among the electrodes developed the coated wire voltammetric electrode and the disc voltammetric electrode (Fig. 31) are particularly suited for further development.

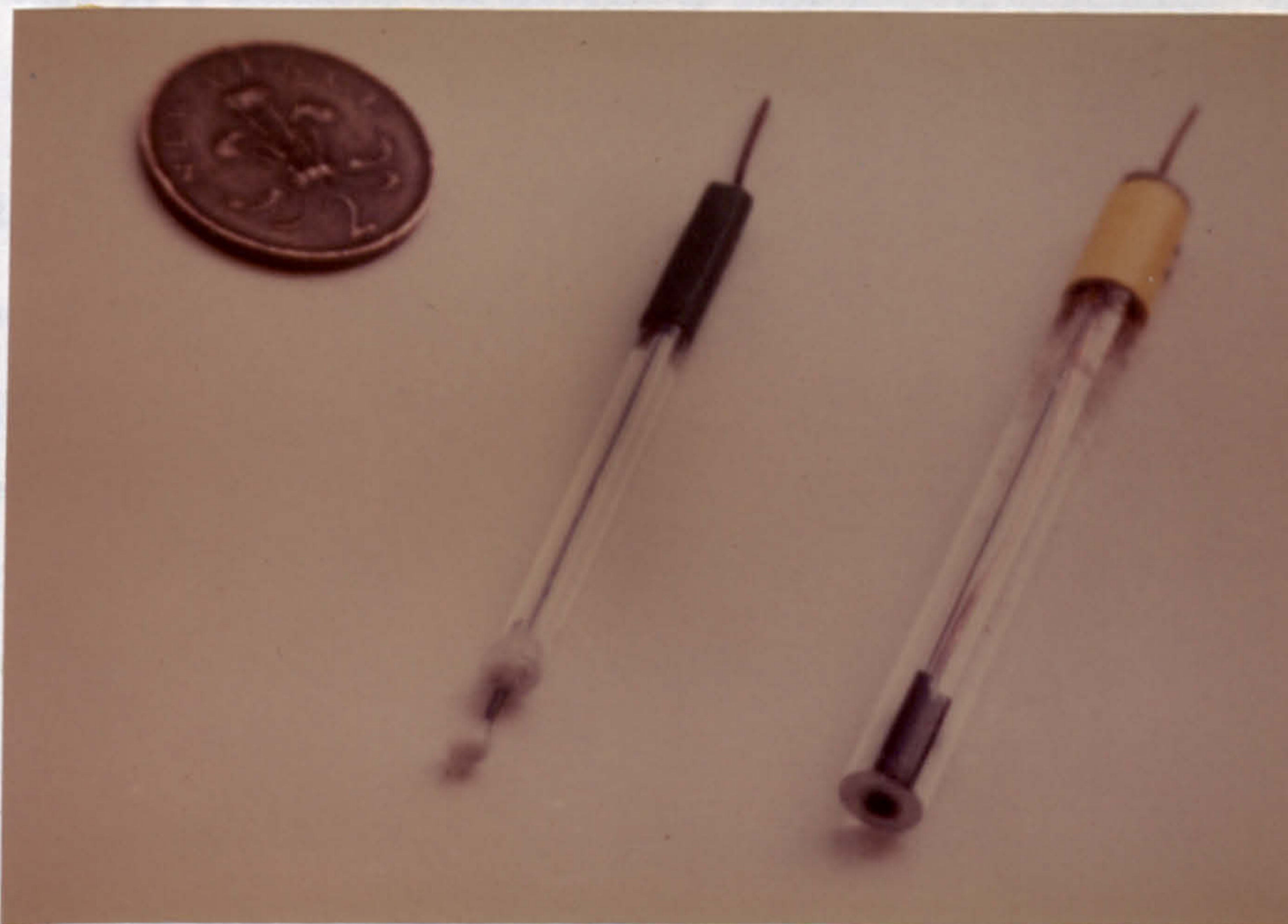


Fig. 31 Epoxy-based Coated Wire and Disc Voltammetric Electrodes.

In this section the application of these electrodes to chemical analysis of different systems is described. An epoxy-based disc voltammetric electrode and an epoxy-based rotating disc electrode was applied to anodic stripping voltammetry and the preliminary results are reported here. The first steps on the preparation of microsystems including the design of a microcell for voltammetric analysis of small volume samples and the description of the technique of coating fibres and thin wires is considered. A new version of an electro-

chemical detector for flow-injection analysis is proposed and its prototype is shown together with the results of the first tests performed to measure the size of its electrochemical response. A general assembly convenient for the preparation of epoxy-based ion-selective electrodes is suggested and the initial test of a sulphide ion-selective electrode is described. The extension of this model to the construction of other types of ISEs is discussed.

The coating of fibres and wires for microelectrodes

The importance of microelectrodes is well documented (135, 304, 305). Their preparation and application in the analysis of biological samples have been reported by several authors and this subject constitutes a specialized area of intense research work.

Coated wire electrodes have been claimed to be suitable for miniaturization (148, 149) but have been regarded by some authors as inconvenient for the fabrication of microelectrodes for intracellular measurement (306). Nevertheless the new coating and curing technique described in the present work provides a means of application of very thin layers of sensors on wires and these layers are physically much more resistant than PVC and other similar films that are produced without hardening. The coating of thin silver wires is being examined in the course of this work as a possibility of producing coated wire minielectrodes and presumably microelectrodes. These have been fabricated by the use of the technique indicated earlier (p. 81). A commercially available PTFE coated silver wire (Clarck Electromedical Instruments, Reading, UK, cat No. AG-10T) will be used for the preliminary tests.

Glass fibres and other synthetic fibres seem to be a better choice for producing very thin microelectrodes. The problems arising from the non-conductive nature of these fibres appear to be overcome by the use of the

graphitization approach previously described (see p. 108). These electrodes are now being produced and tested in simple standard solutions and their use in biomedical analysis is being considered in collaboration with other groups of researchers.

Carbon fibres have been used for the preparation of microelectrodes and have been applied recently to in vivo electrochemical detection of neurotransmitter compounds in brain research (7, 307). They seem to offer a more attractive alternative for the preparation of microelectrodes for several reasons, mainly because their small size (o.d. = 8 μ m). Nevertheless they are porous materials and this property generally causes many problems when they are utilized in electrochemical reactions and this certainly constitutes a drawback of these electrodes. Because of that they become more susceptible of contamination and rapid deterioration. Furthermore the inserting and sealing of carbon fibres in glass capillaries or any other suitable support involves many difficulties. These problems have been examined here. The coating of carbon fibres with graphite-loaded epoxy base using the coating and hardening technique with the help of the HF vapour chamber was verified as being viable. On the other hand after covering the carbon fibres with epoxy it will probably be more convenient to seal them by the use of the unloaded epoxy base cured with 40% m/m hydrofluoric acid solution as mentioned in this work. This sealant has been shown already to produce a good signal from the electrode which is not the case when common sealants are used as they cause an increase in the background current and at the same time are more susceptible of adsorption from the solutions. These studies on the coating of carbon fibres also constitute a collaborative project with other research group. It is well known that the coating and manipulation of thin fibres for the preparation of microelectrodes require a special technique and the test of the electrodes needs more sophisticated equipment.

Microcell for voltammetry with small volume samples

The application of electroanalytical methods to biological samples frequently require a special technique adapted to small volumes, due to limited availability of sample (308). An arrangement for microanalysis with inverted ion-selective electrodes was described by Vogel et al (309, 310). A microelectrolytic cell for voltammetric analysis was proposed by Wang and Frelha (311). These authors reviewed and discussed the adaptation of electroanalytical techniques to analyses of very small sample volumes indicating the problems concerned in using the thin layer cell configuration. They reported the results of the analyses of dopamine, chlorpromazine and ferrocyanide with 50 μ l solution volumes. They used a carbon paste electrode as the working electrode and a capillary silver-silver chloride reference electrode. Recently Jarbawi et al reported on the DPV of chlorpromazine in biological fluids employing a thin-layer microcell (312) and reviewed the importance of this determination.

In the present work a much simpler microcell is described on the basis of the new techniques established for the preparation of voltammetric sensors in different geometries as mentioned previously. A small nylon block (7x3x1cm) was used as the base of the cell. On one side of this block several coatings were applied successively and cured in the HF chamber as described in the procedure recommended for the preparation of coated fabric disc electrodes (p. 114). Usually five to eight layers were applied producing a surface with very low electrical resistance between their extremities. The graphitization technique (p. 108) could be used to increase the conductivity along the surface coated but this was not employed for the construction of this prototype microcell. The configuration of the proposed cell allows the rapid analysis of several samples (with a drop of solution) and permits the prompt renewal of the surface functioning as the working electrode. This cell is

depicted in Fig. 37 (see p. 137). Basically it consists of a nylon support covered on one side with the graphite-loaded epoxy base which after being cured in the usual manner becomes the working electrodes for several units defined by the holes made in a plexiglass sheet and by a PTFE or rubber made spacer as shown. The plexiglass top cover together with the suitable spacer define the volume of the cell. In this preliminary construction 18 holes were produced (ca. 2mm i.d.) making rapid multiple microdeterminations possible. This can be performed with a three electrode system using a micro reference electrode (usually a Ag/AgCl reference electrode) and a platinum wire as the counter electrode. A variation of this construction is shown in the same figure. This consists of a brass rod metallic base (1.5cm o.d.): one of its surface is covered with the graphite-loaded epoxy base in the same manner as used to prepare coated wire voltammetric electrodes described earlier in this work. This variation offers certain advantages namely higher conductivity and more facility for contact with the working electrode. In this second case contact can be made via the metallic base itself without the need to clamp the contact on the graphite surface as is essential in the case of the plastic base. (In that cell the contact with the working electrode is provided by a reinforced point with a conductive graphite-epoxy filler as shown in Fig. 20b(i)). Both types of microcells discussed here are being evaluated and it is expected that the results will be as satisfactory those obtained with voltammetric electrodes of the normal size and configuration used here.

Anodic stripping voltammetry

Electrodes for stripping analysis were reviewed earlier in this work (see p. 38) and in that chapter the technique of stripping voltammetry was discussed together with the importance of this technique for the analysis of

trace metals in natural waters and in biological systems in general. Here the first results of the use of a disc voltammetric electrode developed using the new coating and curing technique are reported. A disc electrode with a longer body was specially constructed to be adapted for use in the cell employed in this experiment. Discs with different diameters were made and tested. The best results were obtained with a disc electrode of 2mm diameter of active surface prepared as described in this work (p. 82). The disc electrodes constructed and used in this experiment are shown in Fig.32 together with a coated wire and a coated plastic rod ready to be used for the fabrication of electrodes. Coated wire and coated plastic electrodes will be employed later in ASV determinations to compare their responses with that of flat disc electrodes.



Fig. 32 Disc Electrodes Used in ASV Shown Together with a Coated Wire and a Coated Plastic Rod.

ASV determinations are usually performed with a rotating disc electrode. Glassy carbon is frequently used for this purpose and on this electrode surface a mercury film is deposited as the preliminary step for the performance of the ASV analysis. In the tests reported here an epoxy-based disc electrode (Fig. 32) was used in some experiments performed simply using a magnetic stirrer inside the cell which agitated the solution at high stirring speed (313) and increased the convection of the solution towards the electrode surface. Other experiments were carried out using an epoxy-based rotating disc electrode constructed with the same features of the Metrohm rotating disc electrode with the same dimensions so that it could be fitted in the Metrohm rotating unit employed. This was achieved using the technique described for the preparation of graphite-loaded epoxy-based disc electrodes (p. 114) with the difference that the glass tube of the common stationary disc electrode was replaced by a machined glass-PTFE rod. The rod was provided with a central hole filled with a portion of the graphite-epoxy base and having a metallic tube at the top of the electrode which was conveniently threaded so that it could be screwed on to the Metrohm rotator. This graphite-loaded RDE is shown in Fig. 33.

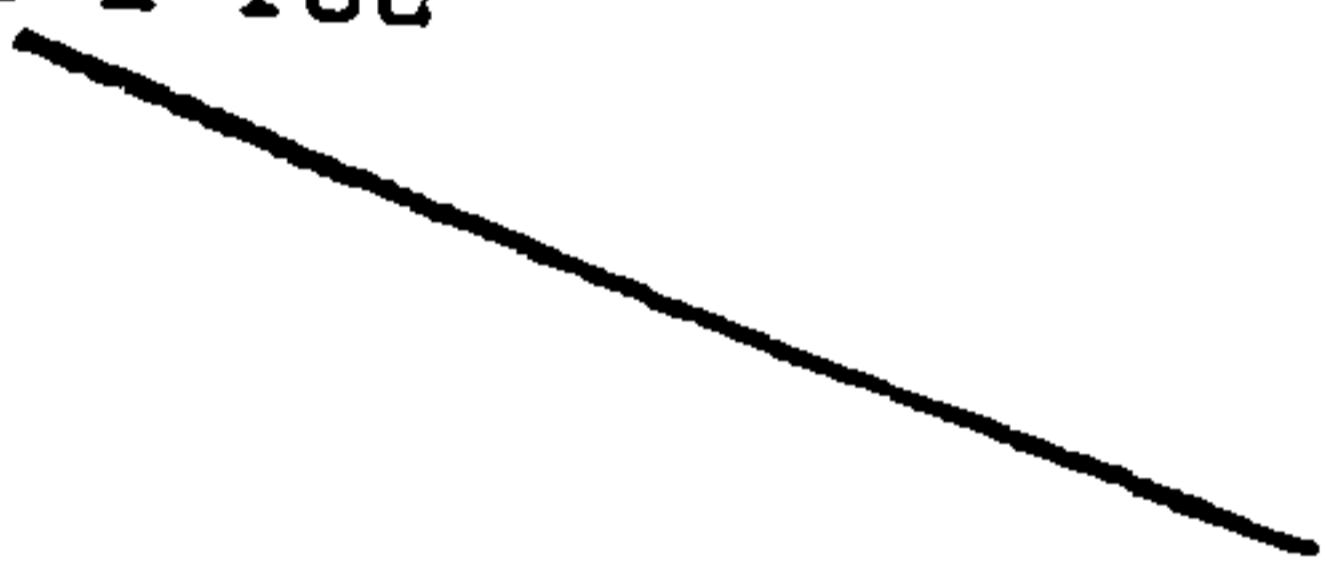
The results presented below have confirmed that the stationary and the rotating discs made as described here are viable alternative for anodic stripping voltammetry for the results obtained were in some cases better than those obtained with the rotating disc glassy carbon Metrohm electrode. This was verified in terms of lower background currents and a higher overpotential for hydrogen evolution when the graphite-epoxy electrode was used. It is considered that this behaviour is associated with the smoothness of the electrode surfaces and the complete absence of poros. This assumption was verified by observing the improvement of the electrode performance as a function of the increasing in the number of epoxy layers applied as usual.

rotator



PTFE-glass body

metal rod



graphite-loaded epoxy-HF

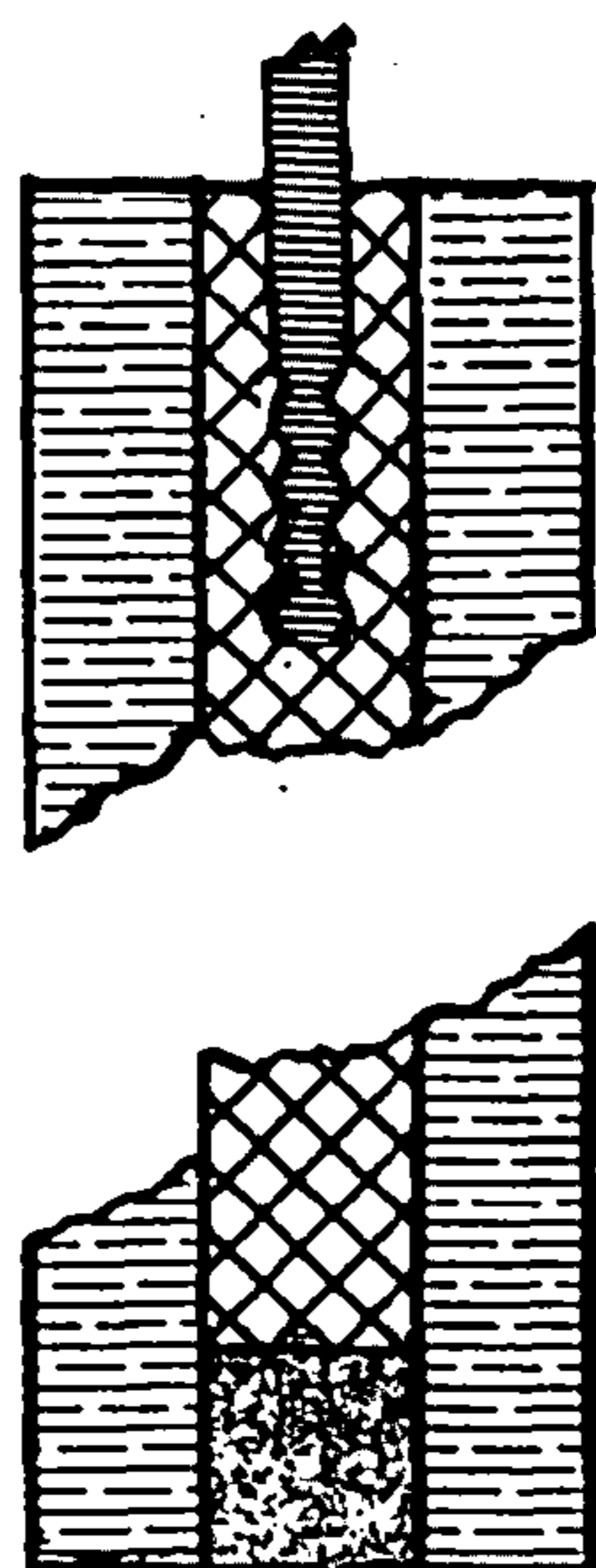


Fig. 33 Graphite-loaded Epoxy-based
Rotating Disc Electrode

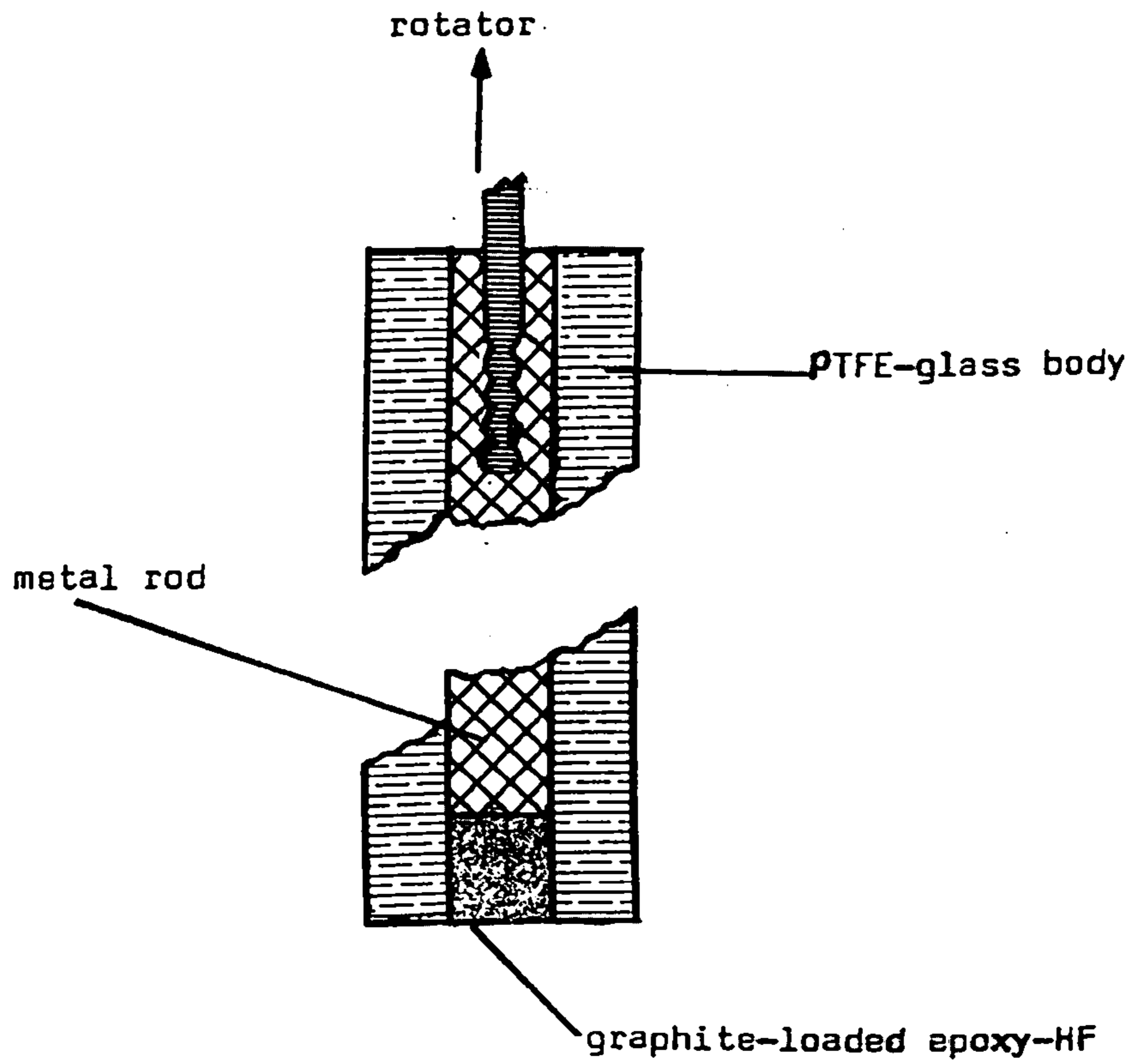


Fig. 33 Graphite-loaded Epoxy-based
Rotating Disc Electrode

As previously discussed in the section on Electrodes for stripping analysis (p. 38) the ASV (CSV is less common) involves two main steps: in the first stage the plating of a mercury thin film on the working electrode surface is accomplished by the use of a mercury(II) nitrate solution. A small amount of this solution is placed in the voltammetric cell and the plating step (deposition of $\text{Hg}_{(l)}$) is carried out by the reduction of Hg^{2+} to Hg^0 at a negative potential (usually from -0.9 to -1.0V). This step is conducted with magnetic stirring at high speed (unnecessary with rotating disc units). After the formation of a thin mercury film onto the working electrode surface (5 to 15min) the stirring is stopped and after the restoration of quiescence in the solution (15sec) the deposition of trace metals follows at -1.0 to -1.3V for a period of 3min. This deposition step sometimes is carried out simultaneously with the plating of mercury. Both can be seen as only one step (the deposition step). After this period of 3min to complete the deposition of impurities (background) or trace metals to be determined (for low concentrations or with flow-injection the deposition time can be greatly increased) the stripping step is carried out by scanning the potential to 0.0V and then the re-oxidation of the metals deposited on the mercury film can be observed, and the elements identified and quantified. Voltammograms are usually obtained in the differential pulse mode (DPASV) which is more sensitive than LSV mode. Usually concentrations in the order of 10^{-10}M can be determined, mainly for cadmium, lead and copper.

The experiments performed provided some information about the electrochemical behaviour of the graphite-loaded epoxy-based electrodes constructed here. The deposition potential and the reproducibility of scans as well as the linearity of responses were investigated. Standard addition was used in order to verify the possibility of quantitative analysis using these units. The results obtained and the conditions applied are shown in Figs. 34 and 35.

The solutions were deaerated by purging with nitrogen for a period of 10min before the plating of metals. The cell was cleaned with nitric acid and washed with double distilled water. The reagents used were of analytical grade or Aristar. The experiments were conducted in pH 3 citrate buffer and for the plating of the mercury thin film a approximately 10^{-5} M mercury(II) nitrate solution (1gl^{-1}) was used. ($50\mu\text{l}$ in 20ml of electrolyte solution).

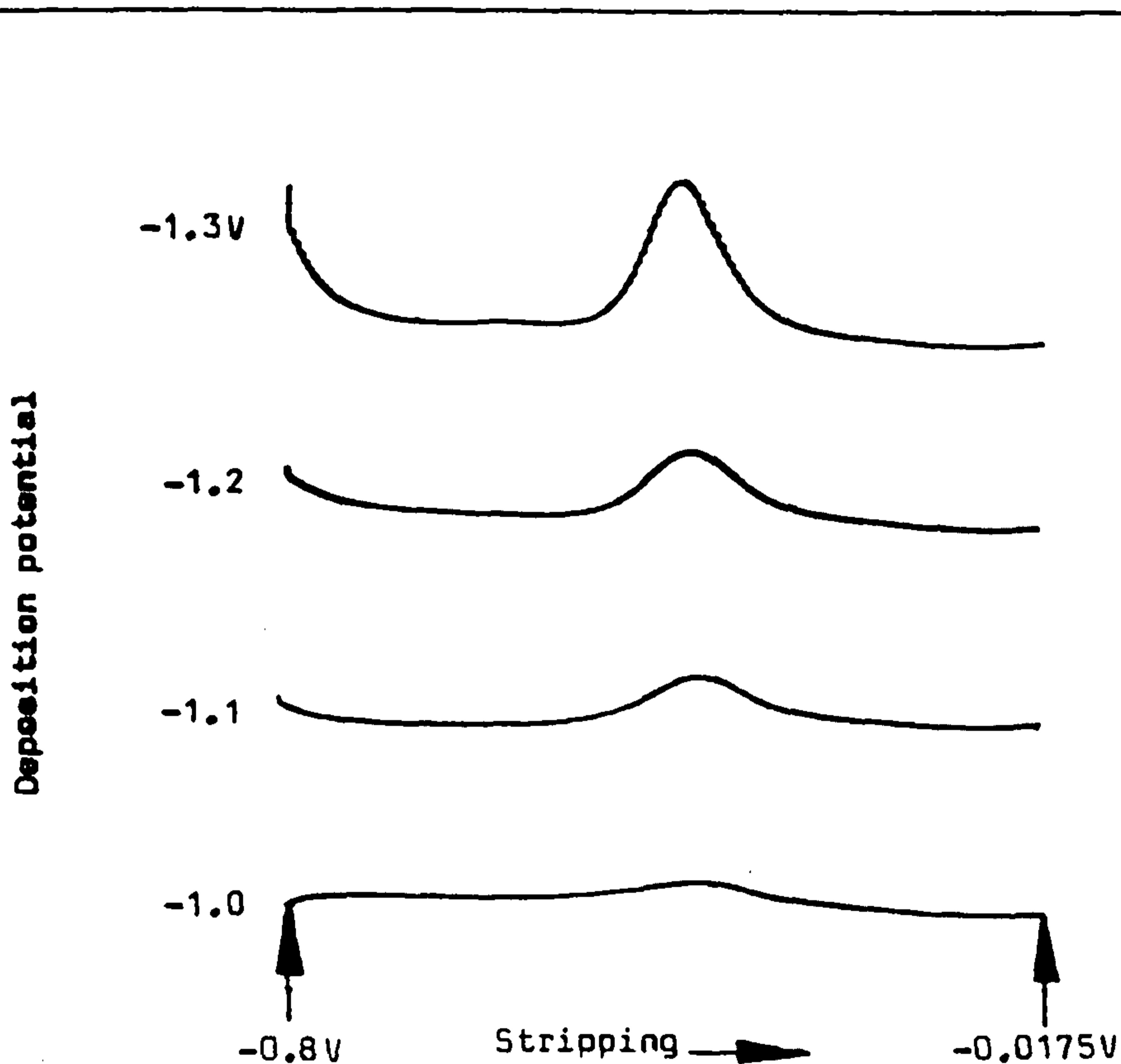


Fig. 34 Anodic Stripping Voltammetry with a Graphite-loaded Rotating Disc Electrode: influence of deposition potential. Citrate buffer pH 3, scan from -0.8 to -0.0175V . Sensitivity 10^{-8}Amm^{-1} , DPVASV with pulse amplitude of 50mV using a Metrohm E506 instrument. Active surface diameter 5mm . Deposition potentials: -1.0 , -1.1 , -1.2 and -1.3V . Stripping peak for lead (usually at $\approx -0.45\text{V}$).

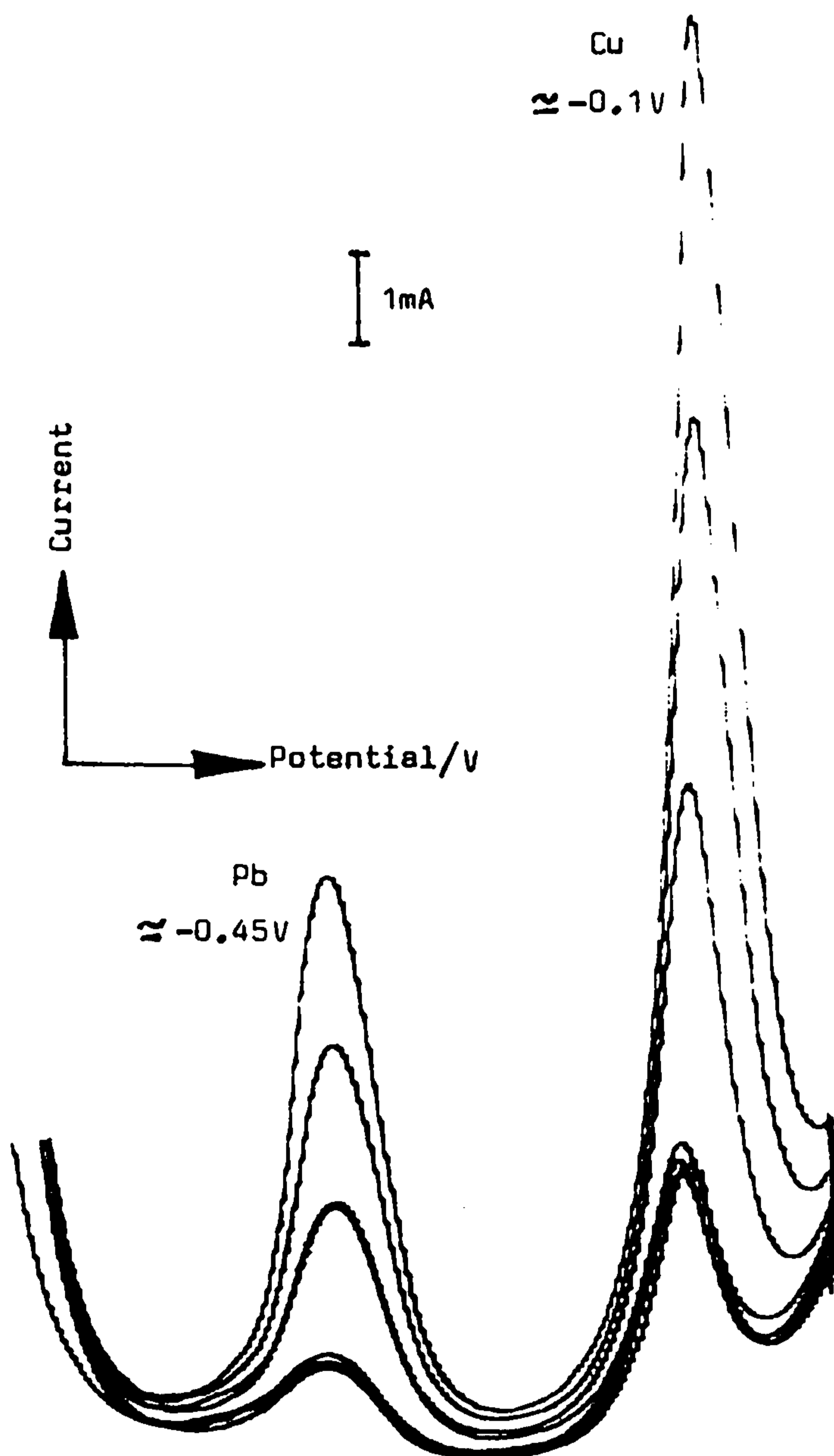


Fig. 35 Determination of Lead and Copper Using ASV at a Graphite-loaded Epoxy-based Disc Electrode (diameter = 3mm). Three standard additions of 100µl (Cu = 1ppm std. soln., Pb = 0.5ppm). Scanning from -0.8V to 0.05V. DPV ASV with pulse amplitude of 50mV. Deposition potential -1.3V. Stirring of solution with a magnetic stirrer. Citrate buffer pH 3.

Flow-injection analysis

Recently, during the presentation of a plenary lecture in the International Symposium on Electroanalysis (Cardiff, April 1983), Pungor (314) compared flow-injection analysis today to a new religion. In fact since the development of automatic methods of analysis (194) to which Pungor et al offered a great contribution and after the introduction of the "new concept" of FIA by Růžička and Hansen (315) this technique has been applied to almost all the field of analysis and has been adapted to numerous techniques. Voltammetry, polarography, atomic absorption and spectrophotometry are those frequently performed in conjunction with flow-injection mode. The main applications of FIA were reviewed recently during a meeting (316) and several comprehensive reviews appeared in the literature. Two reviews describe the fundamentals of the technique and applications giving about 140 references (317, 318). Růžička and Hansen's book (319) constitutes a major source of information on the theoretical and practical aspects of this technique. Recently Růžička reviewed the historical development of FIA and presented a very interesting discussion of the method with many illustrative diagrams together with 29 references (320).

The simplest flow-injection analysis system is composed of a carrier stream of reagent, a pump to propel the flowing stream, an injection port (rotary injection valve), a detector (working electrode, photocell, etc.), and a recorder (to record the signal generated by the detector during the rapid passage of the sample (≈ 30 sec after the injection)). The detector is chosen in accordance with the mode of operation and the nature of the sample. FIA systems have been described for example in the previously mentioned references (315-320). Nowadays these systems are being commercialized in several different models which in general maintain more or less the basic construction. Fig. 36 shows the results of FIA with a graphite-loaded epoxy-

based disc electrode with the help of a wall-jet cell (321).

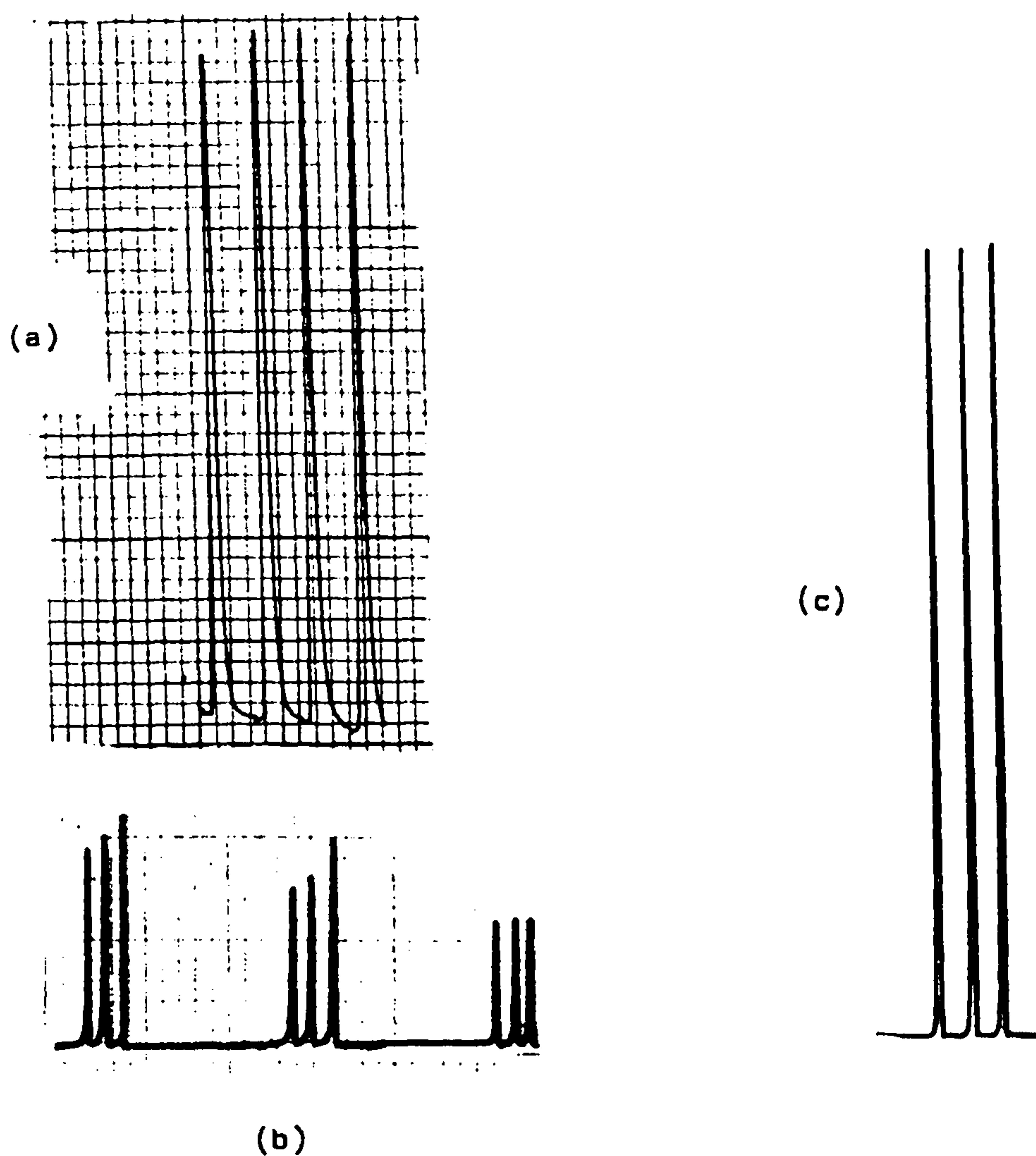


Fig. 36 FIA with Graphite-loaded Epoxy-based Disc Electrodes in a Wall-jet cell (312).

(a) $25\mu\text{gml}^{-1}$ Red 2G in 10% pH 2 Britton-Robinson buffer. Sensitivity $1\text{nA}\mu\text{mol}^{-1}$, flow-rate = 6mlmin^{-1} at 1.17V.

(b) 30, 20 and $10\mu\text{gml}^{-1}$ Tartrazine. $5\mu\text{A}\mu\text{mol}^{-1}$, 6mlmin^{-1} and 1.08V.

(c) 10^{-3}M KI in pH 2 Britton-Robinson carrier stream with flow-rate = 5.8mlmin^{-1} , sensitivity of $0.2\mu\text{A}\mu\text{mol}^{-1}$ at 0.5V.

Prototype electrochemical detector

In the section on "electrodes under controlled hydrodynamic conditions" several types of electrodes suitable for continuous flow analysis have been described. Flow-through electrodes (or better flow-through cells) in the form of tubular electrodes were mentioned in the references indicated. They have been constructed from platinum and other metals but mainly from different kinds of carbon. They present several advantages and also some disadvantages. The disadvantages are related to the complicated design of the system or to the difficulty of renewal and cleaning. This latter is associated with the configuration of the electrode as well as the type of material used. Porous systems, for example are very difficult to clean. At the start of this project there was an intention to construct a type of flow-through cell using the novel voltammetric material being developed.

On the basis of the progress achieved so far in the development of new types of electrodes and after preliminary observations of the way those cells work it was decided to develop a new version of electrochemical detector of simple and versatile design. This prototype electrochemical detector is shown in Fig. 37. The shape of this detector permits its use for many different investigations and the simplicity of the system makes the renewal of the electrode surface after poisoning or damage very straightforward. The development of this cell is still in the preliminary stages even though the tests performed so far confirm the assumption that the shape of this cell provides laminar flow which, coupled with the outstanding performance of the electrode surface used, produces a signal with high sensitivity and high reproducibility. An indication of the type of signal obtained is shown in Fig. 38. This test was performed with a 10^{-3} M potassium iodide solution in 0.18M sulphuric acid solution as the carrier stream. A sensitivity of 0.02mA was employed with a flow-rate of 7.1mlmin^{-1} at +0.7V. The current

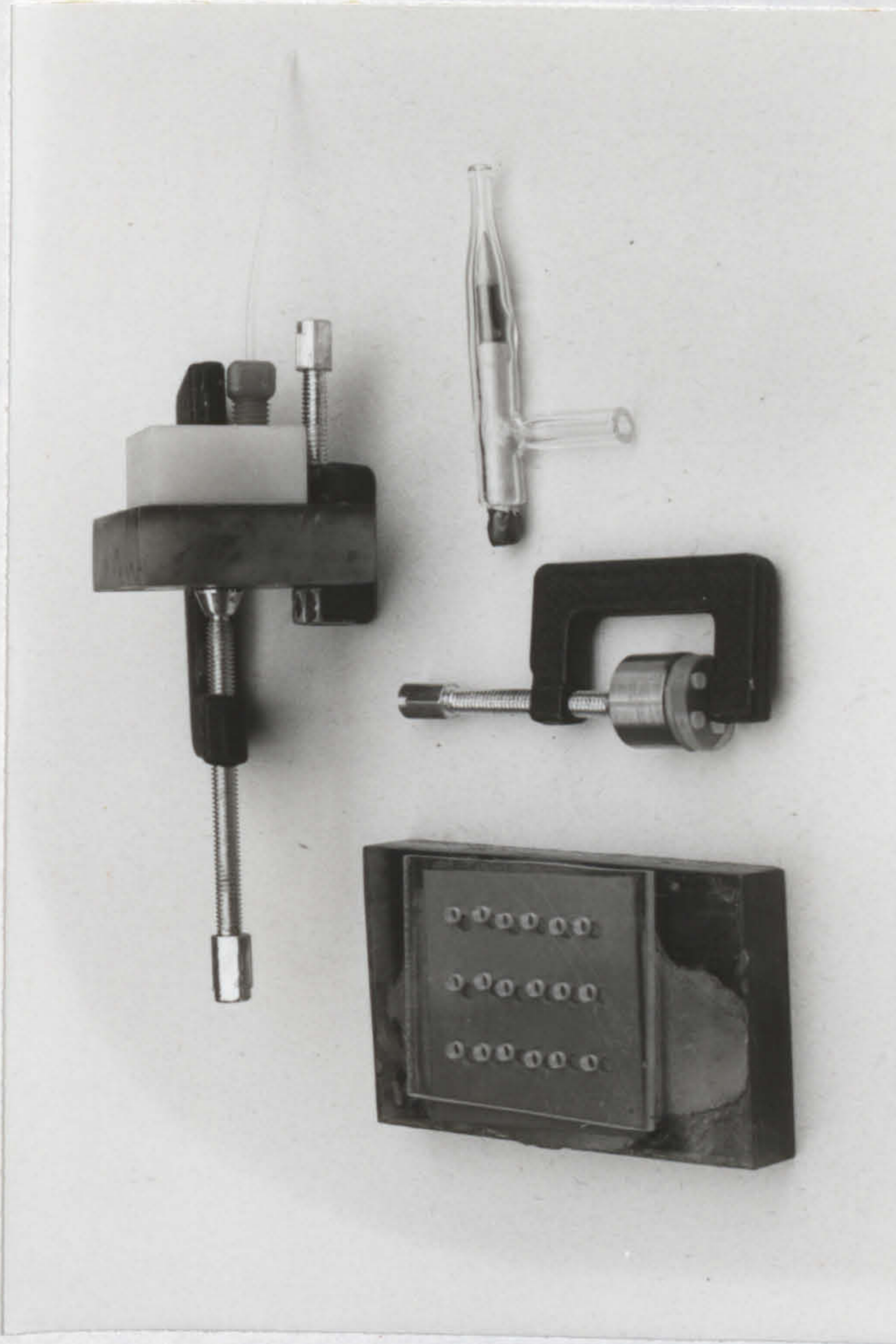


Fig. 37 Prototype Microcell and Electrochemical Detector

Top: thin-layer type of ECD.

Bottom (left to right): microcell (nylon support),

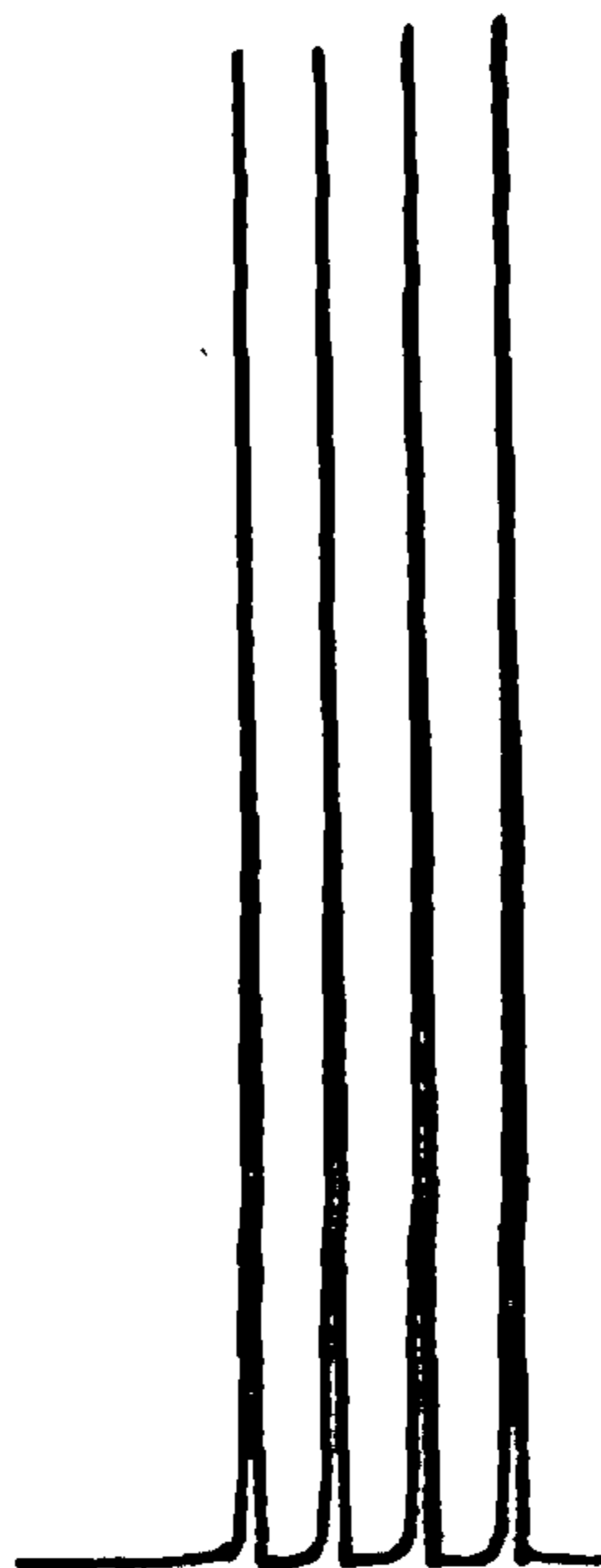
microcell (metal support) and conical ECD.

cell is believed to be a suitable model for the development of multi-voltammetric and multi-ion-selective electrode analyzers.

Fig. 38

FIA of 10^{-3} M KI in 0.18M H_2SO_4 as carrier stream; four injections of $100\mu l$ detected with the ECD depicted in Fig.37. Flow-rate of $7.1mlmin^{-1}$; 0.02mA full scale (100mm) and potential of +0.7V.

Instruments used: PAR 174A Polarographic Analyzer and LINSEIS L650 Recorder.



Ion-selective electrodes

The construction, classification and application of ion-selective electrodes (p.23) and epoxy-based ion-selective electrodes (p. 58) have been reviewed in this work.

The voltammetric graphite-loaded epoxy-based electrodes developed in the course of this work proved to be highly satisfactory for several applications.

The extension of the coating and curing technique proposed as the basis for the construction of these electrodes has been applied successfully to other different ends such as the reclamation of used and faulty glassy carbon

electrodes, the construction of microcells, the coating of fibres and the preparation of a new device for continuous flow voltammetric detection. Therefore it was logical to extend these applications to the construction of potentiometric sensors and the preliminary steps in this direction have been made a year ago (322). Indeed the production of such sensors was and is a fundamental aim of this study.

Because of the nature of the sensors and the outstanding behaviour of commercial types of sulphide ion-selective electrode the first investigations were directed to the preparation of a silver sulphide-loaded epoxy-based ion-selective electrode.

The determination of sulphide in many different systems, especially in effluents (323, 324) and in biological samples (325-327). The construction (328, 329), the properties (330-335) and the applications (336-338) of a silver sulphide membrane ion-selective electrode have been discussed in the literature. One interesting and inexpensive approach for the construction of a "home-made" sulphide ion-selective electrode (and other ion-selective electrodes) of the "all-solid" type was introduced by Lima and Machado (339, 340). They utilized a silver-loaded epoxy resin as the support for the application of the solid (powdered) sensor in order to obtain electrodes with similar properties to the corresponding commercial units.

In the beginning of this work, three main types of sensors were constructed: a coated wire sulphide electrode (using the multilayer coating technique described previously) a direct contact coated disc electrode (using the multilayer coating technique) and a loaded disc electrode with internal reference solution. In all cases 80% m/m silver sulphide have been mixed with the epoxy adhesive and thoroughly homogenized. In the case of the internal reference disc electrode, a 0.1M AgNO_3 solution and a silver wire were used as the internal reference system as described previously by Mascini et al (341).

The study of these electrodes produced the following preliminary results:

a) the response of the coated wire electrodes are very rapid, very stable and similar to that of the commercial electrode used for comparison (Orion 94-16).

b) the stability of the electrodes increased when the copper wire used as a support was previously coated with a graphite-loaded epoxy base and cured as usual, i.e. when the silver sulphide loaded epoxy was coated on top of graphite-loaded epoxy resin.

c) the disc electrodes (both solid contact and the internal reference solution version) had to be conditioned in 10^{-1} M sodium sulphide solution for a period of 5 to 7h before producing a stable response but after that they become very stable.

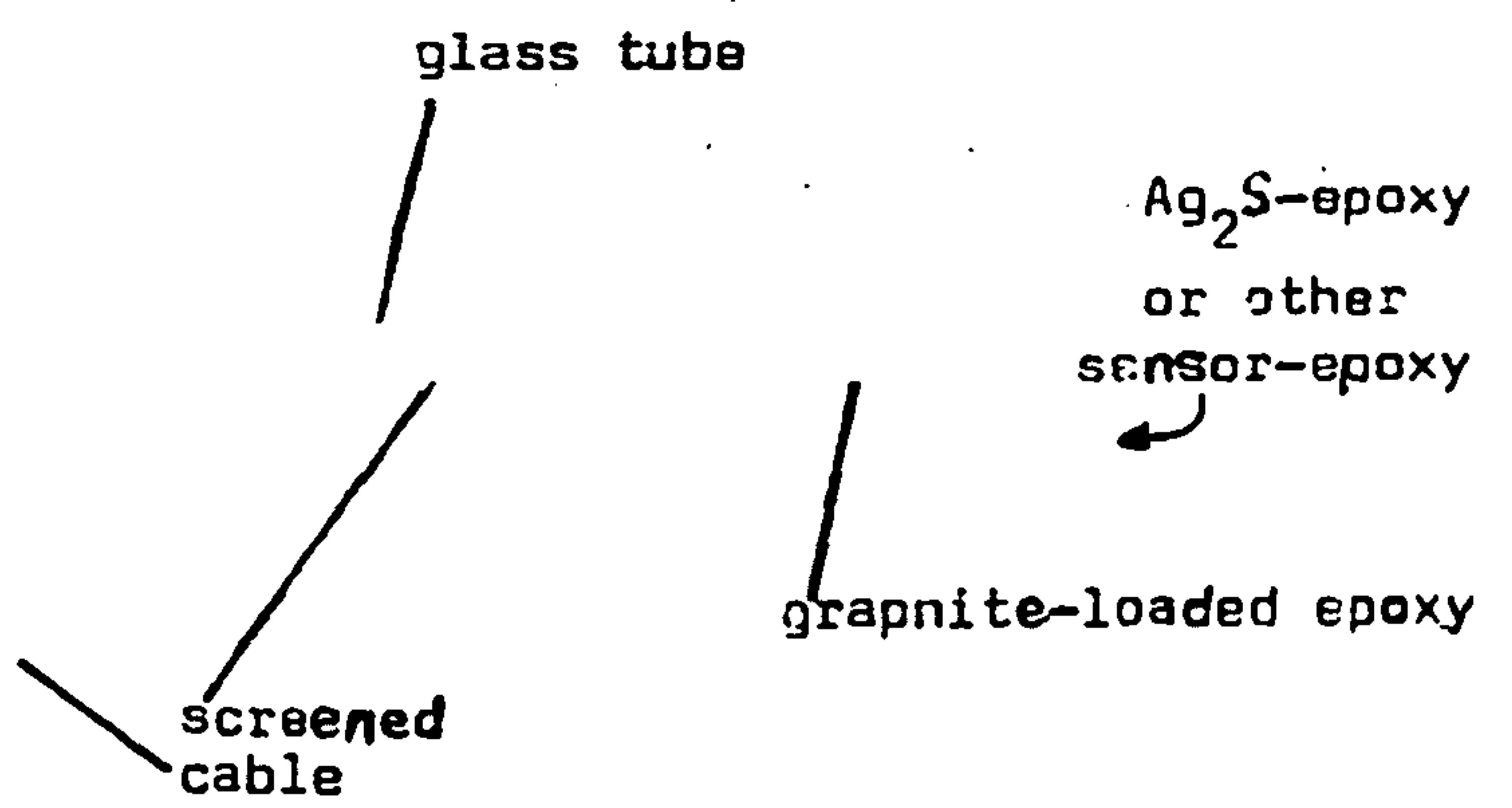
d) all these systems were observed to give stable and reproducible potential readings for at least three weeks.

e) the response from these conditioned electrodes in standard sulphide solutions in the presence of ascorbic acid (20g per liter) were similar to that obtained with the Orion 94-16 unit. In some cases the readings of potential were less negative with a difference of 30 to 130mV.

Preliminary investigations on the construction of epoxy-based ion-selective electrodes for the determination of calcium and potassium using commonly used sensor materials had only limited success. The results are reported in a recent MSc thesis (342). Since that time considerable progress has been made in improving the coating and related techniques. Further studies in the light of these findings should prove successful.

A recommended form of construction of sulphide and other types of electrodes based on the techniques described in this thesis is shown in Fig.39.

Once again here the sensor loaded epoxy is coated on to a graphite-loaded epoxy base which provides suitable electrical contact with the resulting



membrane.

Three main types of sensor have been considered for the continuation of this study: insoluble precipitates (halogenides, metal complexes and others), high temperature ceramic compounds (glasses, mixed oxides, mixed sulphides and mixed phosphates) and polymerized derivatives (polymerized amines and similar compounds via HF cross-linking action. The multilayer coating and curing technique seems to offer the necessary conditions for the firm inclusion of certain solids (as sensors for ISEs) which have been observed to be more difficult to attach or include in the case of Růžička's Selectrode^(R) (328) and in other polymeric membranes less rigid than epoxy resin. Finally the influence of plasticizers and solvent mediators and the evaluation of the potentialities of the systems developed here for the preparation of new surface modified (or chemically modified electrodes) as described previously (see p. 29) using the carbon surface or the epoxide system itself is already a matter of consideration.

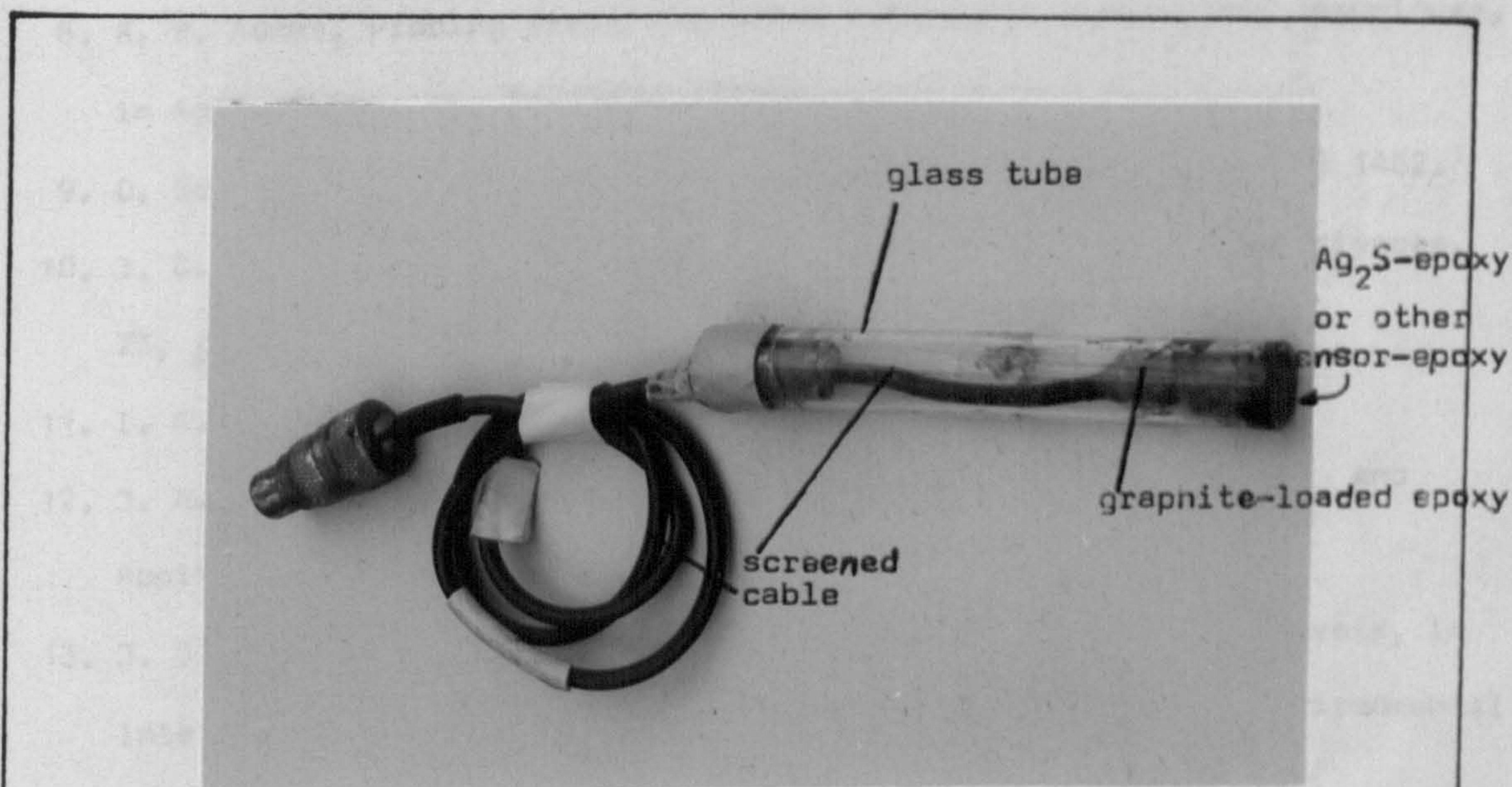


Fig. 39 Graphite-loaded Epoxy-based Ion-selective Electrodes.
(Solid Contact Type)

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