

## Coated wire ion-selective electrodes and their application to environmental problems

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**Abstract** - Coated wire electrodes (CWE) are shown to be simple, rugged, rapid, and reliable sensors for a variety of cation and anions, both inorganic and organic ions from a range of 0.1M to  $1 \times 10^{-6}$ M. They have been applied to analytical problems of environmental nature such as NOX in ambient air, anionic detergents in water, as well as a wide variety of drugs of abuse and pharmaceutical nitrogen compounds. The utility of solvent extraction principles in understanding electrode selectivity and the relevance of polarographic studies of ion transfer between an organic/aqueous interface to ion-selective electrode processes is discussed.

The ion-selective electrode (ISE) approach to trace analysis is advantageous because of the speed and ease of ISE procedures in which little is required. Further, ISEs possess wide dynamic ranges, and are relatively low in cost. These characteristics have inevitably led to sensors for several ionic species, and the list of available electrodes has grown substantially over the past several decades. In many cases, the traditional barrel configuration has been utilized. However, the large size of this type of ISE along somewhat cumbersome to use and unnecessarily expensive.

Coated wire electrodes (CWEs) refer to a type of ion-selective electrode (ISE) in which an electroactive species is incorporated in a thin polymeric film coated directly on a metallic conductor. Although this definition is broad enough to include those instances when the electroactive species is heterogeneously dispersed in the polymeric matrix, both the earliest and the majority of CWEs involve dissolved electroactive species. The CWE devices are so simple and inexpensive that they can be made by students and used even in an introductory laboratory course in analytical chemistry. They are capable of such extreme miniaturization that they should find application in biomedical and clinical, as well as in environmental research.

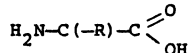
The inspiration for the discovery of CWEs came from the work of Hirata and Date [Talanta, **17**, 883 (1970)], who imbedded a copper wire in a polyvinyl chloride (PVC) disk in which a thick slurry of finely divided cuprous sulfide had been incorporated. The resulting device functioned very well as a sulfide ion ISE. What distinguished this electrode from earlier polymer-matrix-based ISEs is the bold elimination of an internal reference solution. Our research team, its curiosity piqued by the Hirata and Date work, attempted to make ISEs by the simple expedient of coating a platinum wire that was attached to the central conductor of a coaxial cable, with a mixture of PVC solution in cyclohexanone containing an electroactive species and, when the resulting film was air dried, tightly wrapping the remainder of the exposed wire with a paraffin film. These "coated wire electrodes" were very well behaved and gave reproducible and reliable (potential-log a) response curves over a wide concentration range (0.1-0.00001 M). Although some fundamental studies designed to elucidate the mechanism of the CWEs have been conducted, their behavior cannot yet be considered to be fully understood. Nevertheless, CWEs have been prepared for a wide variety of ions and they have wide application in general, clinical, environmental and industrial analysis.

This sensor, having response characteristics equal to and occasionally better than conventional types, is only 1-2 mm in diameter (further size reduction can be easily achieved), can be used at any angle, and costs only a few pennies to make. Indeed, they can be considered "disposable", though with proper handling lifetimes of over six months have been realized. During the course of CWE investigations here, the list of analyte species has been lengthened to include not only most common inorganic ions of interest, but also organic species which are anionic or cationic under appropriate solution conditions (Table 1).

TABLE 1. COATED WIRE ELECTRODES

Lipophilic Cation-basedHalide:  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CNS}^-$ Oxyanion:  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ Organic Anion:  $\text{RCOO}^-$ ,  $\text{RSO}_3^-$ 

Amino Acid:

Neutral Carrier-Based $\text{K}^+$  - ValinomycinDinonylnaphthalenesulfonate-Based

Quaternary Ammonium Ions

Drugs of Abuse, e.g., phencyclidine,  
methylamphetamine, methadone $\beta$ -Adrenergic Drugs  
e.g., acebutalolCa-Blockers  
e.g., VerapamilPhenothiazines  
e.g., chlorpromazine

The first electrode of this type was based on the Ca ion-didecylphosphate/dioctylphenyl phosphonate system [ref. 1]. An effective Ca ion selective CWE resulted when a 6:1 mixture of 5% PVC in cyclohexanone and 0.1 M Ca didecylphosphate in dioctylphenylphosphonate was dried on the end of a platinum wire. Favorable comparison of this electrode response characteristics against the commercial counterpart encouraged further studies with other membrane components. The Ca ion electrode response relied upon the complexation of aqueous Ca ion by didecylphosphate dispersed in the organic, or membrane, phases. In a similar manner, incorporation of methyltricaprylammonium (Aliquat 336S) salts in polymer membranes produced CWEs for their respective anions [ref. 2]. A 60%(V/V) solution of Aliquat 336S in decanol was first converted to the desired anionic form via shaking with 1 M aqueous solution of the appropriate sodium salt. A 10:1 mixture of PVC in cyclohexanone and this decanol solution was then used to coat copper wires by repeated dipping and drying until a small bead completely encapsulated their tips.

As an indication of the applicability of CWEs to environmental problems, several illustrative examples may be cited.

Determination of NOX [ref. 4]: Even low levels of NOX, such as are found in ambient air, can be determined by collecting a suitable volume of air in a gas-washing bottle containing 2% hydrogen peroxide, treating the resulting solution with manganese dioxide to destroy the excess peroxide, and determining the nitrate potentiometrically. The method is capable of good precision and compares well (1-3 relative %) with such accepted methods as the spectrophotometric xylenol procedure. The method can be used in the presence of at least a 40-fold excess of either sulfur dioxide or trioxide. With minor modifications, the method could be used for nitrates in atmospheric particulate matter.

Determination of Anionic Detergents [ref. 3]: Detergents of the alkyl sulfate and alkyl-sulfonate types can be reliably determined in the concentration range of about 0.001 to 0.00001 M by direct potentiometry. The CWE based on lauryl benzyl sulfonate responds almost as well to lauryl sulfonate (selectivity coefficient = 0.81), and somewhat better to lauryl sulfate (selectivity coefficient = 1.36), but at levels of 0.0001 to 0.00001 M, the electrode will give a satisfactorily approximate estimation of total anionic detergent present.

Assay of Phenobarbital: Since phenobarbital (5-ethyl-5-phenylbarbituric acid) is lipophilic, an ion pair complex of its anion and Aliquat 336S can be effectively used in a CWE for its estimation. A linear response to a PVC-based CWE was obtained in the concentration range 0.1-0.00001 M phenobarbital with solutions buffered at pH 9.6 so that only the anion species is present. Interference from nitrate (selectivity coefficient = 0.2) or chloride (selectivity coefficient = 0.1) is manageable. Use of the electrode permits a rapid and convenient method for phenobarbital assay in tablet preparations. In contrast to the 4 hr required for assay by the USP method with which it compares favorably in precision and accuracy, the potentiometric assay can be accomplished in under 20 min, thus making it practical to perform the CWE procedure on single tablets, should information about tablet-to-tablet variation be desired.

Determination of Potassium [refs. 14,15]: A CWE version of the valinomycin-based electrode, prepared using a PVC matrix in di-n-decylphthalate as plasticizer, functioned well in the concentration ranges from 0.1 to 0.00001 M potassium ion, and could be used in the pH range from 2 to 10. Such an electrode can be readily used for the determination of potassium in a wide variety of materials ranging from whole blood to sea water. Aside from Rb and Cs ions, whose selectivity coefficient values are 2.5 and 0.44, respectively, most cations do not appreciably interfere (except for Cu and Zn ions).

Occasionally, the electroactive species is not commercially available, as might be the case when one is developing new electrode systems. A simple means of preparing the material used for anion responsive electrodes is the extraction exchange using the readily available salt of the large cation. For example, the chloride of the large quaternary ion, Aliquat 336S (Henkel Corporation: Kankakee, Illinois) can be exchanged by the desired anion by successive extractions of an *n*-decanol solution of Aliquat 336S (10 vol% or more) with the portions of a concentrated aqueous solution of the sodium salt of the desired anion, until the final portion gives a negative test for chloride ion [ref. 2]. The number of extractions necessary for total exchange of chloride ion by the anion of interest will depend on the relative extractability of the corresponding ion pair. An alternative to using the sodium salt would be appropriate if the silver salt is reasonably soluble; then the formation of the insoluble AgCl facilitates the exchange considerably. In such a case, centrifugation is a convenient way to obtain a clear decanol solution.

A similar approach can be used to prepare the electroactive species for cation-responsive electrodes. Calcium ion can be extracted by di(2-ethylhexyl)phosphoric acid (DEHPA) in decanol at elevated pH values. Alternatively, the calcium chelate can be prepared by treating the DEHPA solution with an excess of CaO. It is not always necessary to obtain the electroactive species to be used prior to its incorporation into the polymeric matrix. For example, in cation-selective electrodes based on dinonylnaphthalene sulfonic acid (DNNS), the acid itself is dissolved in a PVC solution, the film electrode formed, and then converted to the desired cation form by immersing it in the appropriate cation salt solution [9]. This approach is, in effect, the method of activating "neutral-carrier" CWES. The neutral carrier is dissolved in the polymeric matrix and the resulting film electrode is conditioned by immersing it in the appropriate salt solution.

A relatively wide variety of polymeric matrices have been found utilizable in CWE construction, including polyvinyl chloride (PVC), polymethyl methacrylate (PMM), and epoxy. In order to introduce the electroactive species into epoxy, a suitable weight of the salt was mixed with the curing agent and this, in turn, was combined with the epoxy resin. A metallic wire was dipped into the resulting mixture to form a small bead, which completed its polymerization in place. The addition of the electroactive species, e.g., Aliquat 336S perchlorate, generally retarded the epoxy polymerization time, but 3-4 hr was adequate in all cases for completion of this step.

In the cases of polymers like PVC and PMM, for which suitable solvents were available, the polymer solution was mixed with the electroactive species, either neat or in solution, and the film was formed on the metallic substrate by evaporation. For example, PVC can be dissolved in solvents such as tetrahydrofuran (THF) or cyclohexanone, PMM is soluble in methyl acetate or trichloroethylene, and polystyrene is soluble (4 wt%) in chloroform.

In order for the polymer film to behave properly in those CWES and similar ISEs which are based on liquid membrane principles, i.e., those in which the electroactive species is molecularly dispersed or dissolved rather than present in finely divided solid particles, the polymer film must have some attributes of a liquid phase. In particular, the temperatures at which the electrode is employed should be higher than the glass transition temperature of the polymer.

The glass transition temperature of an amorphous polymer is the relatively well-defined temperature at which the rigid "glassy solid" material becomes a viscoelastic fluid. The most pronounced changes in the behavior of amorphous polymers occur at the glass transition temperature, at which significant increases in conductivity and dielectric constant are most relevant. The glass transition temperatures of unplasticized polymers increase with the average molecular weight of the polymer, as well as with the specific nature of the polymer. For commercial grades of unplasticized polyvinyl chloride (PVC), the glass transition temperature is about 80°C. Below this temperature, the electrical conductivity of PVC is about  $10^{-10}$  mho/cm, and its dielectric constant is about 3; above this temperature, these values increase to about  $10^{-9}$  mho/cm and 15, respectively.

Plasticizers, as their name implies, are polymer additives whose purpose is to render the polymer more plastic, i.e., more viscoelastic at ambient temperatures. A wide variety of organic compounds, most frequently aromatic esters such as the phthalates, have been employed as plasticizers. If enough plasticizer is incorporated, it will lower the glass transition temperature to under room temperature. Properly plasticized films are necessary for proper CWE and other polymer-film ISE behavior. This was intuitively accepted early on, but Carmack first clearly demonstrated this correlation [ref. 22].

Consideration of the role of plasticizers is most critical for neutral carrier CWES, where, because of the high cost of valinomycin and other carriers, only minimal amounts are used. As a result, plasticizers such as didecylphthalate are required. In contrast, with anion selective electrodes based on the higher molecular weight quaternary ammonium salts such as Aliquat 336, the electroactive species comprises a major component in the film and thus provides sufficient plasticizer action so that no additional plasticizer is needed.

A number of techniques have been used in the construction of coated wire electrodes. Originally, a platinum wire, soldered to the central conductor of coaxial cable wire, was used as the metallic substrate. Subsequently, it was found that the simpler procedure of applying the film to the copper central conductor directly was entirely equivalent, except for a significant shift in the  $E^0$  of the electrode. Quite a number of metals have since been tested and, with the interesting exception of the value of  $E^0$ , which was a function of the metal, the electrode behavior was the same. The effect of the nature of the metal used as the conducting substrate on the  $E^0$  of the CWE might be useful to shift response curves to more convenient potential ranges.

In many cases, the selectivities of the CWEs were significantly better than the conventional, "barrel-type" counterparts [ref. 2]. This, along with absence of the traditional internal reference electrode, raised fundamental questions surrounding the charge conduction mechanism occurring in the membrane and at the polymer-substrate interface. Calculation of activation energies from the temperature dependence of conduction suggested that an electronic mechanism was operative, such as that observed in organic semiconductors [ref. 6]. Later studies of the pressure dependence of conduction gave strong evidence for ionic conduction because much larger activation volumes than could be expected from an electronic mechanism were obtained [refs. 7,8]. As such, the existence of some redox couple at the substrate-polymer interface probably functions as an internal reference. This hypothesis is further reinforced when one considers that conditional standard potentials shift by significant and reproducible amounts from one type of metal substrate to another.

Our attention next turned to the development of cation selective electrodes in order to develop methods for protonated alkylammonium ions. Initial studies in this area were aimed at improving selectivity among similarly charged cations by utilizing a mobile exchange site, facilitating membrane response to changing counter ions [ref. 9]. These membranes were comprised of dinonylnaphthalene sulfonic acid (DNNS), a lipophilic anionic extractant, dissolved in a PVC membrane plasticized with dioctylphthalate. Extremely high selectivity was observed for alkylammonium ions over common inorganic ions. Among organic species, selectivity increased regularly with the number of carbon atoms of the interferents tested. This indicated great promise for sensors of pharmaceutical interest, since many such compounds are high molecular weight protonated amines in the physiologic pH range. Currently, DNNS based CWEs are made by dissolving the amine of interest in a 5% PVC in tetrahydrofuran (THF) which is also 0.5% in DNNS and 4.5% in plasticizer, usually dioctylphthalate. This solution is then used to coat the end of a copper wire which is elsewhere insulated with non-plasticized PVC. Following conditioning in a 0.001 to 0.0001 M solution of the analyte, the electrodes are ready for use. CWEs are available [ref. 9-12] for drugs of abuse, such as phencyclidine (PCP), cocaine, methylamphetamine, and methadone, as well as  $\beta$ -adrenergic and calcium blockers for cardiac treatment, such as propranolol, protriptyline, acebutalol, lidoflazine, verapamil, diltiazem, and nicardipine, as well as psychotherapeutic agents, such as the phenothiazines (e.g., chlorpromazine).

Electrode selectivity is described by the "selectivity coefficient", which is calculated from EMF responses of the electrodes samples in the presence and in the absence of an interfering ion using the following relationship:

$$E = E^0 + \frac{59.2}{n} (a_i + K_{i,j} a_j^{n/z_j})$$

where

$$K_{i,j} = \text{selectivity coefficient}$$

$n$  and  $z$  are charges of the primary and interfering ions, respectively, and  $a$  is the ion activity. Experimentally, computer-generated solutions of specific ratios of the activities of the primary and interfering ions are made, followed by correction of the "new" activity of ion "i" due to addition of ion "j".

Systematic selectivity studies of both cation- and anion-responsive CWEs reveal the importance of solvent extraction parameters. Using tributylammonium as a primary ion, log [selectivity coefficient] values were determined for various substituted alkylammonium ions [refs. 10,11]. As was the case for Aliquat-based electrodes for organic species [ref. 2], selectivity improved considerably with increasing molecular weight. These observations are closely related to analyte extractability. From solvent extraction studies and from calculated extraction constants [ref. 13], close one-to-one correspondence is observed between the extraction constants and electrode selectivity coefficients. Hence, one can see the utility in considering solvent extraction parameters in predicting electrode selectivity behavior.

Because CWEs are responsive solely to ions and not neutral species, the pH profile of the potential response of a CWE for an anion that has proton affinity, e.g., acetate or leucine anion, can be interpreted as the change of the activity of the anion with pH. This would make it possible to calculate the corresponding pK. The procedure is exactly analogous to calculating pK values using a pH-responsive electrode. Similarly, solubility products constants and complex formation constants are accessible.

Another equilibrium parameter, one applicable to colloid-forming species, that can be obtained using the CWE is the critical micelle concentration (CMC). In a study of anionic detergent solutions [ref. 3], a sharp break was found in the otherwise linear calibration curve of, say, a lauryl sulfate CWE which occurred at precisely the CMC. The electrode responds to only the monomer because the micelle concentration in moles/liter is close to zero. This represents a much more rapid method for reliable CMC determination than the study of interfacial tension as a function of concentration.

More recently, we have begun to study ion transport mechanisms involved in electrochemical and other processes. In recent years, the study of the faradaic ion transfer across an aqueous/immiscible organic solvent interface has been developed and recognized as a powerful tool for the investigation of liquid-liquid (L-L) interfacial phenomena [ref. 16]. This method possesses basic features which are quite similar to the classical electrochemical system in which a solid electrode/solution (S-L) interface is employed. When these interfaces are externally polarized, ion transfer takes place predominantly at the L-L interface because both liquid phases are ion-permeable, while electron transfer predominates at the S-L interface because of high electron conductivity of the solid electrode phase. Electrochemical study of the aqueous/organic interface can provide a model for biological membranes as previously pointed out by Koryta et al. [ref. 16]. The advantage of using such systems over an artificial membrane system is that one can isolate the information on interfacial phenomena, because mass transfer in the liquid phase is simple diffusion, which may not be the case in the membrane system. Employing this technique, Koryta and Samec's group investigated the facilitated transfer of ions (alkali and alkaline earth ions and protons) by such neutral carriers as valinomycin, crown ethers, and nonactin present in the organic phase [refs. 17,18]. Through these studies, they arrived at a transport mechanism of potassium-valinomycin complex ion, concluding that complex formation (and dissociation) occurs in the organic phase following phase transfer of the hydrated potassium ion and a surface reaction between aqueous potassium ion and the carrier molecule in the organic phase.

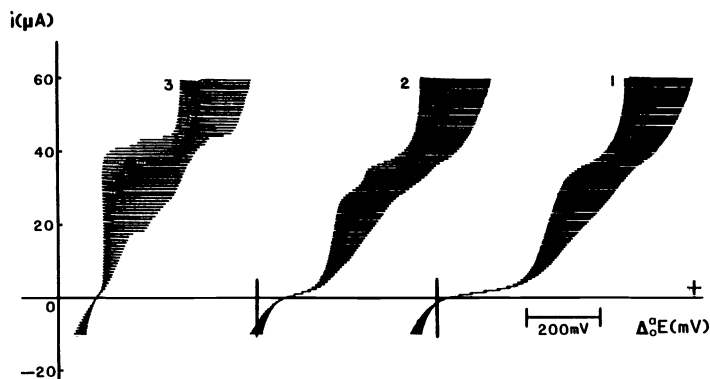
On the other hand, our work [ref. 19] on the analogous ion transfers involved in metal chelate solvent extraction systems, i.e., where metal ions are transported (extracted) into the organic phase in the presence of neutral carrier extractants, complex formation was demonstrated to occur in the aqueous phase following the transport of the carrier from the organic to the aqueous phase, even with carriers having low aqueous solubility.

The reaction mechanism of the potassium ion transfer from aqueous to nitrobenzene phases, which is facilitated by valinomycin present in the organic phase, was elucidated by polarography at the ascending water electrode and chronopotentiometry at the stationary water electrode. The complex ion is formed in the aqueous phase reaction between potassium ion and valinomycin that migrated from the organic phase. The accumulation of the complex ion in the aqueous phase is controlled by the diffusion of valinomycin from the bulk organic phase to the water-nitrobenzene interface.

In further pursuit of greater understanding of these highly interesting transfer processes, we extended our study to the system of potassium-dibenzo-18-crown-6 (DBC) in dichloroethane (DCE) using the ascending water electrode (AWE) in a current scan polarographic system described earlier [ref. 20]. The range of potassium ion concentrations in the aqueous phase, which was 1 M in  $MgSO_4$ , was from 0.001 M to 1.00 M. In the DCE, which was 0.01 M in tetraheptylammonium tetraphenylborate, the DBC concentration ranged from 0.0002 to 0.0006 M.

At the concentrations of KCl in the aqueous phase at or below 0.02 M, a single wave is obtained whose limiting current is directly proportional to the concentration of DBC in the DCE phase and to the square root of the height of the hydrostatic head of the aqueous electrolyte. The logarithmic analysis of this wave shows a straight line with a slope of 52 mV. The product of the applied current and the square root of the transition time was found independent of the applied current in constant current chronopotentiometry at the stationary water electrode (SWE). The square root of the transition time,  $\tau$ , increases linearly with the square root of the standing time,  $t$ , i.e., the time elapsed before the SWE system undergoes constant current electrolysis. It is clear from these results that the transfer process is diffusion-controlled and the transferring species from the aqueous phase into the organic phase is the complex ion of potassium with crown ether in accord with [ref. 19]. If the potassium ion itself were transferring, one would not expect any accumulation as represented by an increase of  $\tau$  with  $t$  at the SWE. The half wave potential of the wave shifts to less positive values with increasing potassium concentration. When the potassium concentration reaches 0.01 M or higher, however, a new series of phenomena are observed.

At 0.01 M, the half wave potential reaches a value which it maintains until the wave disappears entirely at a potassium concentration of 0.2 M. Furthermore, the limiting current of the first wave in the region  $0.04 M < C_{K^+} < 0.2 M$  exhibits a first order dependence on electrostatic head as well as an independence of DBC concentration. Starting at  $C_{K^+} = 0.04 M$ , an additional wave appears at less positive potential, which increases in height at the expense of the original one, which finally disappears at  $C_{K^+} = 0.2 M$ . The



Current Scan Polarogram at AWE  
 Aqueous phase:  $\text{MgSO}_4$ , 1M  
                   KCl (M), (1) 0.01  
                                   (2) 0.1  
                                   (3) 1  
 DCE phase: THA.TPB, 0.01 M  
               DBC, 0.4 mM

ION TRANSPORT PROCESSES OF POTASSIUM WITH DIBENZO-18-CROWN-6 ETHER

half wave potential of this second wave moves to less positive values with further increases in potassium concentration, increasing the difference of the half wave potential between the two waves. The limiting current of this wave exhibits a square root dependence on the hydrostatic head. Chronopotentiometry conducted at 1 M KCl, where only the second wave is observed, results in  $\tau$  values that are independent of  $t$ . Finally, it should be noted that the sum of the heights, i.e., limiting currents, of the two waves, remains constant throughout the entire range of potassium concentration and proportional to the crown ether concentration in DCE [ref. 21].

These findings demonstrate unequivocally that the second wave is fundamentally different from the first. The first wave at  $C_{K^+} \leq 0.01$  M displays all the characteristics of a process which involves diffusion of DBC from DCE to the aqueous phase, where it reacts with  $K^+$  to form  $K(\text{DBC})^+$ , the complex ion which transfers electrochemically across the interface. At  $C_{K^+} < 0.01$  M, the diffusing DBC reacts with  $K^+$  in the interfacial region explaining the adsorption characteristic (i.e. hydrostatic head) observed. At still higher potassium concentrations, the second wave, which may represent the electrochemical transfer of the simple potassium ion, appears. Even this process depends on the rate of diffusion of DBC to the interface from the bulk organic phase.

Such studies can provide illuminating insights into the mechanism of ion selective electrodes, solvent extraction processes, and thiomembrane mechanisms.

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