CONCLUSION

There were no important differences in terms of the parameters evaluated for the PVC electrodes assembled from the nine PVC materials. Nonetheless, the Breon IIIEP PVC will remain our first choice simply because it is readily available in large amounts. Even the best of the alternative acrylate polymers, namely poly(2-methylpropyl methacrylate), provides an inferior sensor matrix for the organophosphate-based liquid ion-exchanger calcium cocktail used.

REFERENCES

1. Moody,G.J., Oke,R. and Thomas,J.D.R., Analyst, 1970, 95, 910.
2. Moody,G.J. and Thomas,J.D.R., in "Chemical Sensors", (Ed. Edmonds,T.E.), Blackie (London), 1987.
3. Hassan,S.K.A.G., Moody,G.J. and Thomas,J.D.R., Analyst, 1980, 105, 147.
4. Schäfer,O.F., Anal.Chim.Acta, 1976, 87, 495.
5. Hiiro,K., Kawahara,A. and Tanaka,T., Anal.Chim.Acta, 1979, 110, 321.
6. LeBlanc,O.H. and Grubb,W.T., Anal.Chem., 1976, 48, 1658.
7. Fiedler,U. and Růžička,J., Anal.Chim.Acta, 1973, 67, 179.
8. Moody,G.J., Saad,B. and Thomas,J.D.R., Analyst, 1987, 112, 1143.
9. Moody,G.J. and Thomas,J.D.R., Unpublished work.
10. Lakshminarayanaih,N., J.Memb.Science, 1981, 8, 255.

ADSORPTIVE STRIPPING VOLTAMMETRY: A VERSATILE TECHNIQUE FOR ENVIRONMENTAL AND CLINICAL STUDIES

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Electroactive organic compounds that adsorb strongly on mercury can be determined at very low concentrations by adsorptive stripping voltammetry at a hanging mercury drop electrode[1]. The compound is accumulated from a reproducibly stirred solution by adsorption at a newly-formed mercury drop for a suitable fixed time before being determined in quiescent solution by means of a potential sweep method. The technique is being used increasingly for the determination of drug compounds, and also for the determination of reducible metal ions after adsorption as chelate complexes[1].

The present increasing interest in adsorptive stripping voltammetry has been made possible by the introduction of modern static mercury drop electrode stands, such as the PAR 303 and the Metrohm 646 and 663, which allow virtually instantaneous automatic production and renewal of hanging mercury drop electrodes. The use of a microprocessor-controlled

polarographic/voltammetric analyser allows the adsorptive stripping experiment to be automated readily.

In our own work sixteen food and two cosmetic synthetic colouring matters were shown to adsorb strongly on a hanging mercury drop electrode and to be amenable to determination by differential pulse adsorptive stripping voltammetry[2]. When a two-minute accumulation time was used the increase in sensitivity over differential pulse polarography at a dropping mercury electrode was between nine- and one hundred-fold depending on the colouring matter determined. Using longer accumulation times 1×10^{-10}M concentrations of some food colours could be determined. The addition of tetraphenylphosphonium chloride shifts the reduction potentials of some colouring matters to more negative values and can decrease or increase the size of the peaks obtained. This makes it a useful reagent for partially identifying individual colouring matters even when they are present at very low concentrations. Procedures for applying the method to the determination and partial identification of colouring matters in tablet coatings and in a lipstick have been developed. The need to dilute more concentrated sample solutions has the advantage of eliminating matrix effects which are sometimes apparent when differential pulse

polarography is applied without dilution.

In his paper on the adsorptive stripping tensammetric determination of monensin Kalvoda[3] has given a simple method of distinguishing whether a reductive or tensammetric process is occuring during the potential sweep. If immediately after the sweep, a second sweep is made from the same starting potential, in the case of a reductive process the peak virtually disappears (if the reduction is irreversible), whereas for a tensammetric process only a slight loss of accumulated material occurs.

It is also important to distinguish between different mechanisms by which accumulation occurs. The term 'adsorptive stripping voltammetry' has been applied to methods in which accumulation occurs by adsorption. Accumulation can occur by oxidation of mercury and formation of mercury salts. No accepted terminology has been introduced so far, but to be unambiguous both the method of accumulation and the method of stripping should be indicated. Kalvoda has shown that catecholamines can be accumulated as mercury salts[4]. In the same issue of The Analyst Ordieres et al have accumulated 5-fluorouracil as a mercury salt[5] whereas Wang et al have accumulated it at a more negative potential by adsorption[6].

In a recent communication from this laboratory the possibilities and advantages of using derivatisation techniques in conjunction with

adsorptive stripping voltammetry was pointed out. A method of determining aromatic amines by differential pulse adsorptive stripping voltammetry after diazotisation and coupling with 1-naphthol to form an azo dye was developed[7].

Work has commenced in our laboratories on the labelling of large molecules for adsorptive stripping voltammetric determination in immunological methods. Bovine serum albumin labelled with fluorescein isothiocyanate or rhodamine B isothiocyanate can be determined by differential pulse adsorptive stripping voltammetry at a hanging mercury drop electrode. In both cases, in addition to the stripping peak given by the dye moiety on the label, a stripping peak is given also by the reduction of mercury(II) sulphide produced during accumulation by oxidation of mercury in the presence of the thiocarbamoyl moiety. Indeed bovine serum albumin labelled with unsubstituted phenyl isothiocyanate gives the mercury(II) sulphide stripping peak. The labelling molecules themselves give differential pulse adsorptive stripping voltammetric peaks due to the dye (where present) and isothiocyanate moieties and the excess of these compounds would have to be removed after labelling albumin for use in any immunoassay developed. Some loss of signal was observed on adding antisera to labelled albumin, but this could be due to

competitive adsorption and studies are continuing.

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REFERENCES

1. Wang, J., American Laboratory, October 1985, 68.
2. Fogg, A.G., Barros, A.A., and Cabral, J.O., Analyst, 1986, 111, 831.
3. Kalvoda, R., J. Electoanal. Chem., 1984, 180, 307.
4. Kalvoda, R., J. Electoanal. Chem., 1986, 214, 191.
5. Ordieres, A.J.M., Gutierrez, M.J.G., Garcia, A.C., Blanco, P.T., and Smyth, W.F., Analyst, 1987, 112, 243.
6. Wang, J., Lin, M.S., and Villa, V., Analyst, 1987, 112, 247.
7. Fogg, A.G., and Lewis, J.M., Analyst, 1986, 111, 1443.