DETERMINATION OF RESIDUAL STYRENE IN POLYSTYRENE USING MICROELECTRODES.

M. D. Geraldo and M. I. Montenegro
Centro de Química Pura e Aplicada da Universidade do Minho
Largo do Paço, 4719 Braga Codex, Portugal.

It is well known, nowadays, that safety of food is a matter of particular importance both to the consumer and the food industry. Plastic packaging protects the quality of food in terms of nutritional, sensoric and microbial state of the product. On the other hand, however, there is migration of ingredients of packaging to food as a result of the interaction between both. In the case of plastic articles these ingredients are mainly additives, which are necessary for obtaining the required technical properties, and residual monomers [1].

In this programme of work it is planned to investigate the possibility of making direct determinations of migration components in food, using microelectrodes.

During the last decade many researchers have shown that the unique properties of microelectrodes make them suitable for a large variety of analytical applications, specially in complex media where conventional electrochemistry has to be ruled out [2]. For example, it has been shown possible to determine directly antioxidants in lubricating oils [3], and Williams *et al* [4] used gold microband electrodes to determine directly ascorbic acid in foodstuffs such as fruit, syrups and sauces.

Additives and residual monomers in foodstuffs, after contact with plastic packaging, are usually in very low concentrations so that their quantification is more difficult than in the plastic itself. Therefore, the best approach is to develop, firstly, procedures which unable the determination of additives in the polymer itself and in this work we report preliminary results of a microelectrode method of analysis of residual styrene in polystyrene.

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Figure 1 shows an i-E curve recorded at a 4 µm radius carbon fiber electrode, for styrene (2×10^{-3} moldm^{-3}) in DMF containing 0.1 moldm^{-3} Bu_4NBF_4 and at 50 mVs^{-1}. A sigmoidal shaped wave is observed with a half wave potential at -2.65 V *vs* Pt-QRE. This is a very negative value, close to the reduction of the medium.

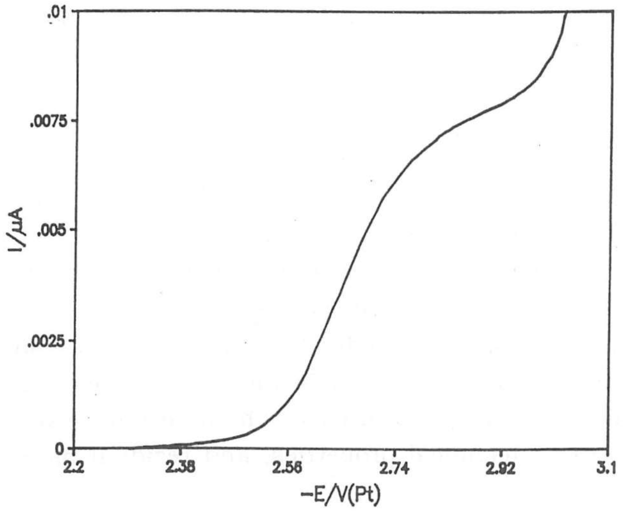

Figure 1 - i-E curve for the reduction of styrene (2×10^{-3} moldm^{-3}) in DMF containing 0.1 moldm^{-3} Bu_4NBF_4 at a carbon microelectrode.

Similar waves were recorded, in the same conditions, for different styrene concentrations and a linear relationship between limiting current and concentration was observed, as predicted by the equation,

$$i_l = 4\, n\, F\, D\, c\, r$$

where i_l is the limiting current, r the electrode radius, c the concentration an D the diffusion coefficient. A diffusion coefficient of 2×10^{-5} cm^{2}s^{-1} was estimated.

The very negative $E_{1/2}$ value for styrene and its proximity to the medium reduction potential, makes the determination of the limiting current quite difficult. It was decided, therefore, to employ the single potentiostatic method (**figure 2**), where the potential is stepped to a value in the plateau region of the i-E curve and the current is measured when it reaches a steady state value (t=60s).

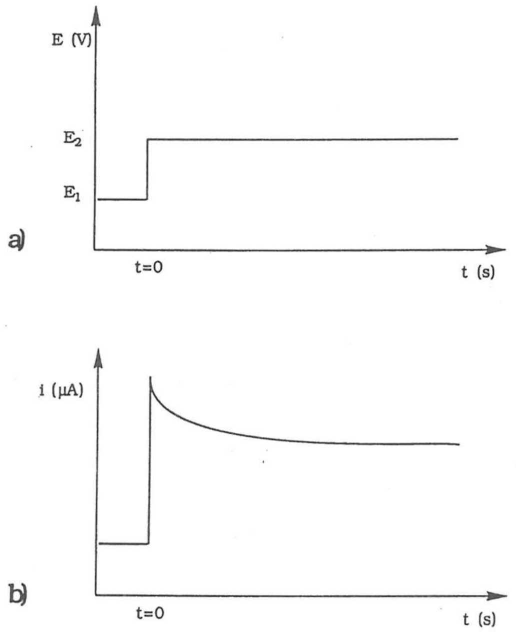

Figure 2 - a) Potencial-time profile for a single potencial step
b) i-t response for the potential step experiment

This method was applied to solutions containing different styrene concentrations and a linear relationship was obtained between limiting current and concentration.

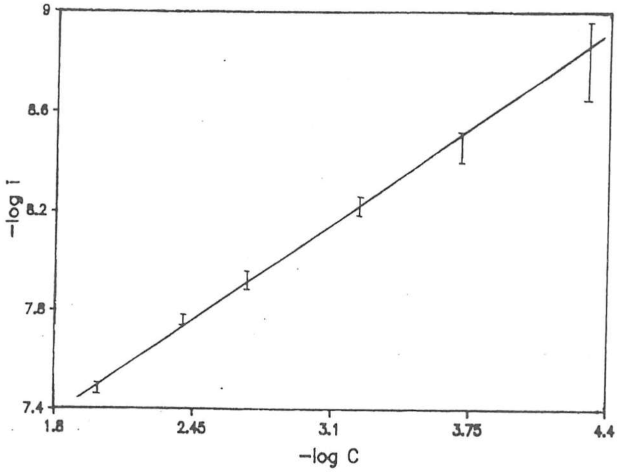

Figure 3 - Variation of i_l with concentration

Figure 3 shows the calibration curve obtained for six concentrations and for each concentration, six current transients were recorded. The error bars in the calibration curve were drawn for 95% probability.

The styrene detection limit was estimated to be 5 x 10^{-5} moldm^{-3}.

Determinations of the residual monomer in two different types of polystyrene (one of which used in yoghurt packaging), were carried out. The polymer was simply dissolved in DMF, and a voltammogram was recorded after centrifugation and addition of Bu_4NBF_4. The values of styrene found were 0.05% and 0.08%, both below 0.1% which is the maximum concentration allowed in food packaging. These results were confirmed by GLC using the internationally accepted procedure [5].

Considering that only 1/100 or 1/1000 of the additives or contaminants from packaging can migrate into food [6], it is obvious that this method is not sensitive enough for direct determinations in foodstuffs and, therefore, pulse methods should be employed in order to increase the sensitivity.

Some attempts were made to carry out direct electrochemical measurements in yoghurt and **figure 4** presents an i-E curve of liquid yoghurt at a vitreous carbon fiber, after deliberate addition of styrene. A wave appears at potentials close to those observed for a solution containing styrene in DMF and can be attributed to the reduction of this monomer.

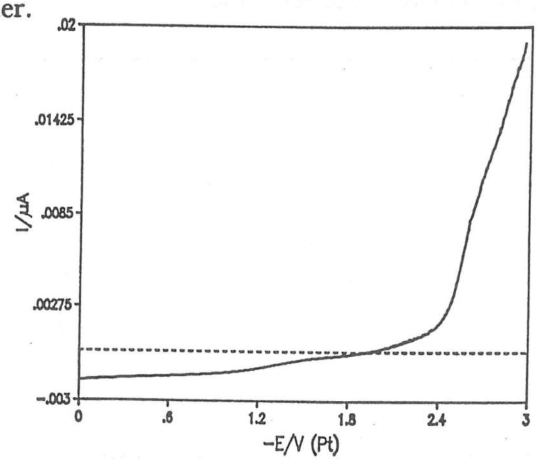

Figure 4 -i-E curve of liquid yoghurt, at a vitreous carbon fiber, after deliberate addition of styrene.

It should be emphasied that yoghurt is apparently a suprisingly convenient medium to carry out electrochemistry and it seems possible to make analytical measurements directly in this and other dairy products.

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