DETERMINATION OF CONTAMINANTS IN PLASTICS FOR PACKAGING

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Plastic packaging is widely used in several fields but a severe control of the amount of contaminants, for example, residual monomers, is essential. Hence, it is important to determine the concentration of these substances since they alter the polymer mechanical properties and they present a risk for human health[1].

In this work styrene determinations in ABS (copolymer of acrylonitrile, butadiene and styrene) and in polystyrene were performed, using an electrochemical method. The objective was to develop a method for the determination of the residual monomer that offered advantages over the method proposed by the standard procedure. In the latter case the monomer is determined by gas-liquid chromatography[2,3] (GLC) after sample preparation which consists in the precipitation of the polymer.

In the electrochemical procedure the polymer is simply dissolved in an appropriate solvent, followed by the addition of an electrolyte and a voltammetric method is used for the quantification of the monomer.

Figure 1 shows cyclic and square wave voltammograms at a vitreous carbon electrode (radius = 0.13 cm) of a sample of ABS (Cycolac TCA 10000, Natural) dissolved in N,N-dimethylformamide (DMF) containing 0.1 mol dm^{-3} of Bu$_4$NBF$_4$. Both voltammograms show two peaks but we were

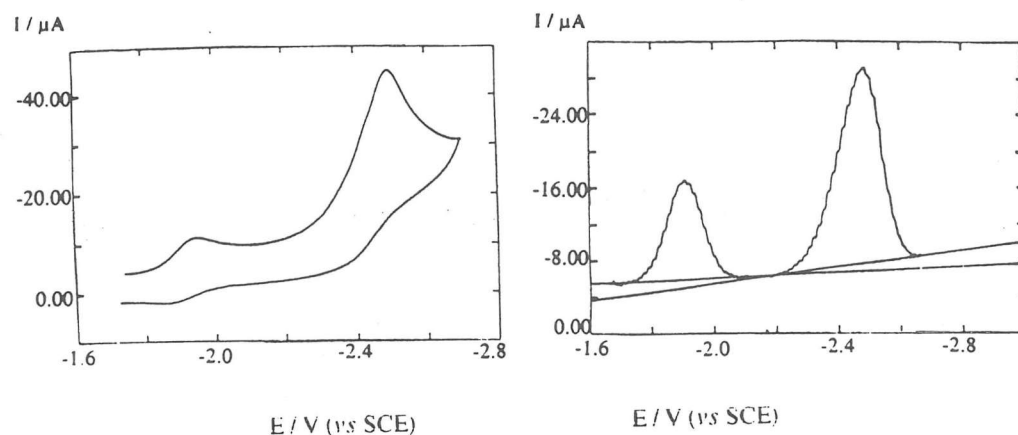only able to identify the second one, at a potential close to -2.50 V *vs* SCE, as been styrene.

Figure 1   a) Cyclic voltammogram of 1.2 g of ABS dissolved in 100 cm³ of DMF containing 0.1 mol dm⁻³ of Bu₄NBF₄ at a vitreous carbon electrode of radius 0.13 cm, v = 100 mVs⁻¹.

b) Square wave voltammogram of the solution in a) with E_{SW} = 4 mV, ΔE_S = 10 mV, f = 200 Hz.

Table 1 shows the percentage of styrene obtained and shows that cyclic voltammetry (CV) gives a higher value than the square wave voltammetry (SWV).

Table 1- Values of styrene percentage in ABS and in polystyrene by voltammetric methods (CV; LSV (linear sweep voltammetry); SQW).

Technique	% Styrene	
Polymer	ABS (CYCOLAC)	Polystyrene (BASF)
CV	1.59 ± 0.08	-
LSV	-	0.053 ± 0.004
SWV	0.87 ± 0.27	0.026 ± 0.004

GLC analysis gives a value closer to the value obtained by SWV and, hence, the higher value obtained by CV is probably due to the difficulty in drawing the baseline. On the other hand, it is well known that for analytical purposes, SWV is preferable to CV, since it is a differential technique which improves selectivity.

According to table 1 the value obtained was 0.87% which is well above 0.1%, the maximum value allowed in food packaging application.

Figure 2 shows the corresponding square wave voltammograms using standard addition method.
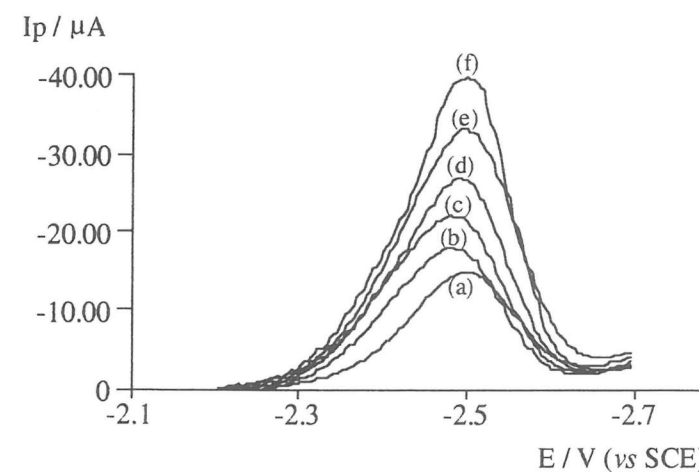

Figure 2 - Square wave voltammograms for the styrene reduction in 0.5 g of ABS dissolved in 100 cm³ of DMF containing 0.1 mol dm⁻³ of Bu₄NBF₄ at a vitreous carbon electrode, E_{SW} = 4 mV, ΔE_S = 10 mV, f = 200 Hz, using the standard addition method. Moles added to 10 cm³ of sample solution: (a) 0; (b) 1.8 µmol; (c) 3.6 µmol; (d) 5.4 µmol; (e) 7.2 µmol; (f) 9.0 µmol.

The determination of styrene in polystyrene involved, however, another difficulty since this polymer is not easily soluble in DMF or other appropriate solvent for electrochemical studies. Instead, it is easily soluble in aromatic hydrocarbons such as toluene which has a low dielectric constant. However,

the use of microelectrodes allows the electrochemical determination of styrene in toluene containing a small percentage of DMF in order to dissolve the supporting electrolyte, and in a previous work[4], a mixture of toluene / DMF (90/10) was used for the styrene determination using SWV and a gold microdisc of 6 μm of radius. Also in this case the GLC analysis provides a value of styrene percentage which is in good agreement with that obtained by SWV.

The above results, seem to indicate that this method for styrene determination can be easily applied to other copolymers. Depending upon the solvent used for the polymer dissolution, micro or conventional sized electrodes may be used.

The electrochemical method offers several advantages over chromatography since it does not require sample preparation, it is quicker to register a voltammogram than a chromatogram and the equipment is cheaper.

References:

1- R. Ashby, I. Cooper, D. Shorten, and P. Tice, "Food Packaging Migration and Legislation", Pira International, Surrey, 1992.

2- P. Shapras and G.C. Claver, Anal. Chem., 36, 1964, 2283.

3- Portuguese Standard Procedure NP 3993 or ISO 2561.

4- M.D. Geraldo, M.I. Montenegro, and D. Pletcher, Talanta, in press.

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BATCH INJECTION ANALYSIS WITH STRIPPING VOLTAMMETRY

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ABSTRACT

Batch injection analysis in conjunction with preconcentration by anodic stripping voltammetry and adsorptive stripping voltammetry has been investigated and optimised. Mercury films are pre-formed *in situ* within the cell on glassy carbon substrates by injection of 100μl electrolyte containing mercury ions. Increased electrolysis efficiency in the stripping experiment is obtained by continuing preconcentration after injection of ≤100μl of the metal-ion-containing analyte. Detection limits are in the nanomolar range. This procedure should find widespread application to all types of stripping voltammetry.

INTRODUCTION

In batch injection analysis (BIA) a small sample of analyte (generally ≤100μl) is injected directly into an appropriate detection zone. The technique thus has characteristics of flow injection analysis (FIA) with very low dispersion and, during the injection period, of continuous flow analysis. Particular advantages can be gained by using motorised electronic micropipettes for the injection resulting in high accuracy and reproducibility, and the possibility of performing sequential injections at small time intervals.

For electrochemical amperometric and voltammetric detection, the sample is injected directly over the centre of a disc electrode immersed in electrolyte solution. The hydrodynamics during injection is thus of the wall-jet type which has been demonstrated [1], and which is almost without memory effects. Point-by point voltammetric curves can be registered from successive injections at different potentials, and cyclic and square wave voltammograms can be registered during injection enabling the determination of thermodynamic and kinetic parameters as well as of concentration from the same experiment [2].