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DETERMINATION OF ANALYSIS CONDITIONS FOR THE HEADSPACE GC-MS MEASUREMENT OF RESIDUAL MONOMER CONTENTS IN LATEXES

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The increasing demand of the reduction of the residual monomer content in polymeric emulsions, used in paints, varnishes, paper and/or textile coatings, among others, is leading to the development of robust and precise analysis procedures for the quantification of the residual monomer content. The Headspace Gas Chromatography (HS-GC) technique presents a series of advantages in relation to the direct injection technique. First HS analysis protects the chromatographic columns from non volatile compounds that might degrade the performance of the stationary phase of the column or interfere with the analysis. Furthermore, HS is a way of pre-concentrating samples, particularly useful in the analysis of organic volatile compounds in air, water or solids [1] and, therefore, this technique can be up to 1000 times more sensitive than direct injection [2]. Another advantage is that the additional parameters of the HS-GC technique (equilibration temperature and thermostating time) offer greater flexibility than direct injection for the separation of analytes with close elution times [3]. Finally, when a significant number of samples has to be analyzed routinely a high level of automation is desirable in order to reduce costs and static HS-GC is the most indicated method in this aspect [1]. Nevertheless, many problems must still be solved in order to enhance the comprehension of the HS technique [4]. Those problems are related with precision, sensibility and recuperation and are governed by the same factor, the partition coefficient of the analytes in the sample, that in turn is influenced by the equilibration temperature, composition and sample properties. Also, according to Kolb [1] an inherent problem of the HS technique for the quantitative analyses is the inclusion of the matrix effect in a calibration factor. Furthermore, in the determination of the HS-GC analysis conditions the classic conflict of the chromatographic methods between resolution and sensibility, besides the analysis time, must be taken into account. Often a compromise must be found to attend satisfactorily all those criteria.

In this work optimal analysis conditions were determined in order to increase the sensibility of residual monomer (vinyl acetate, VA, and butyl acrylate, BuA) measurements by headspace gas chromatography in polymeric emulsions. All analysis were performed using a headspace sampler

interfaced with a gas chromatograph equipped with a mass spectrometer (Shimadzu). Tests were performed with two different formulations: GCMS1 (805 ppm of VA and 80 ppm of BuA) and GCMS2 (40 ppm of VA and 6 ppm of BuA), both prepared with 2.00 g of water and 0.05 g of latex (VA/BuA copolymer 85/15 wt/wt with 18.8 % of solids content and no detectable amounts of monomers). For each condition 3 identical samples were analyzed, nevertheless no sample was analyzed more than once, since although the removed aliquots are very small, they might interfere in the repeated analysis of the same sample. Due to space limitations only results for formulation GCMS1 are presented here since results for GCMS2 followed the same trends.

Figure 1a presents the effect of equilibration temperature, the intensities of the relative responses increase with increasing temperature. Despite the ebullition points of VA and BuA being, respectively, 72.6 e 148°C, temperatures above 80°C were avoided in order to minimize the evaporation of the aqueous sample matrix since for quantitative analysis it is necessary to keep constant the volume of the liquid matrix. Figure 1b shows the effect of thermostating time at 40°C, but no clear effect is observed and Figure 1c shows the decrease of the relative responses with the increase of ratio between the volumes of the liquid and gas phases in the vial (V_L/V_G). A series of analysis was also performed in order to verify the effect of the initiator concentration in the samples. No salting-out effect was observed due to variations in the initiator concentration in the range usually used in emulsion polymerizations.

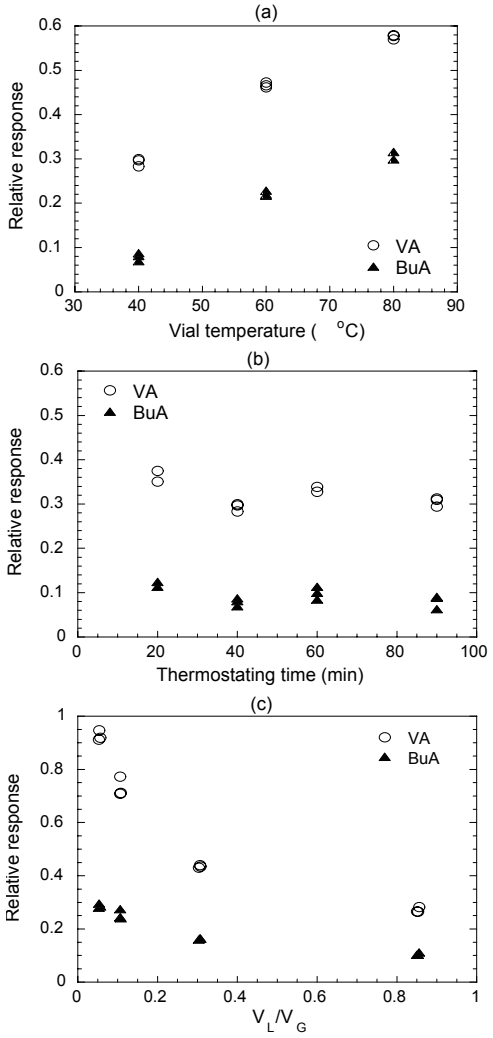

Figure 1 - Effect of analysis conditions on VA and BuA analysis - GCMS1.

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