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Note

Chromatography of monomers

VII*. Determination of residual ethyl acrylate and methyl methacrylate in polymer emulsion: effect of precipitated copolymer

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Knowledge of the amounts of residual monomers in emulsions of synthetic polymers is of great importance in the establishment of experimental conditions for polymerization and in the control of odour. The latter may be considered of the highest importance when trace components can give rise to an health hazard.

The simplest chromatographic method available for residual monomer analysis in polymer emulsions is direct injection[1]. More labour intensive but very effective are head-space analysis[2,3] and isolation of the residual monomers by extractive distillation[4,5]. The precipitation of polymers from their organic solutions by addition of an appropriate solvent and the examination of the residual monomers in the supernatant liquor by gas chromatography has been reported[6-8].

This work describes a sample preparation for GC determination of residual monomers in acrylic emulsions involving simultaneous precipitation of the polymer by addition of concentrated acids and extraction of free monomers by a water-immiscible solvent. The method eliminates the problems connected with the direct injection of the aqueous polymer emulsion sample into the instrument and avoids the possibility of depolymerization in the injection port, without the considerable loss in sensitivity. Moreover, the method is easy to handle and does not require special laboratory equipment.

However, the analysis of free monomers in aqueous polymer emulsions may be subject to considerable errors, since there is always some uncertainty as to the extent to which the trace components being analysed are sorbed by the polymers. Similar problems are associated with the addition of an internal standard to such a sample. Moreover, large amounts of water together with various unknown compounds are present in the sample and their effects must be considered.

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The method described is an adaptation of previously used precipitation techniques[6-8] to aqueous polymer emulsion analysis. It is shown that the concentrations of both the residual monomer and the added internal standard in the extracting solvent are time dependent. By considering the sorption of the internal standard by the precipitated polymer, a method of calculation is proposed which improves upon the accuracy of the determination of residual ethyl acrylate and methyl methacrylate.

EXPERIMENTAL

Apparatus

The gas chromatograph CHROM 4 (Laboratorní přístroje, Prague, Czechoslovakia) together with a flame ionization detector was used. A glass column (4.2 m × 3.5 mm I.D.) containing 15% Apiezon L on acid-washed Chromosorb W (60–80 mesh) was employed under following conditions: nitrogen carrier gas flow-rate, *ca.* 30 ml/min; column temperature, 80°C; injector temperature, 250°C; chart speed, 0.3 cm/min.

Reagents

Butyl acetate (Lachema, Brno, Czechoslovakia), employed as the internal standard, was diluted in tetrachloroethylene (Chema, Pardubice, Czechoslovakia) to obtain a standard solution of concentration of 0.0319 g/ml. For its addition, 10-μl and 100-μl precision syringes (Hamilton, Bonaduz, Switzerland) were used.

Procedure

A *ca.* 1-g emulsion sample was precipitated with *ca.* 4 ml of tetrachloroethylene containing 0.4 g of concentrated analytical grade hydrochloric acid. A 1-μl sample of the organic layer was injected into the instrument and the monomers were eluted at an attenuation producing peaks of reasonable size. The peak areas of the monomers and the internal standard were measured by a computing integrator Autolab System IV (Spectra-Physics, Mountain View, CA, U.S.A.) and their ratios were calculated. The amounts of the monomers were calculated from a calibration plot of the ratio of the amounts of the monomer and internal standard against their peak area ratio.

The calibration was performed by using standard solutions of both monomers and butyl acetate in tetrachloroethylene at various mass ratios. The plots were shown to be linear over a mass ratio range from 0.25 to 2.50. Thus they can be described by equations with slope, Y-intercept and correlation coefficient of -0.015, 1.192, 0.99991 for ethyl acrylate and 0.069, 1.130, 0.9999, respectively, for methyl methacrylate.

RESULTS AND DISCUSSION

For the simultaneous polymer precipitation and extraction of the residual monomers from aqueous acrylic polymer emulsions, various commonly available water-immiscible solvents such as diethyl ether, benzene, toluene and tetrachloroethylene can generally be recommended. The precipitation can often be improved by the addition of small amount of concentrated hydrochloric or phosphoric acid. Be-

fore the analysis the sample is allowed to stand, usually for 24 h, and after the addition of the internal standard the organic extract is injected into the instrument.

The disadvantage of precipitation techniques is the rather limited choice of suitable precipitants, so the components being analysed very often have to measured in the tail of the peak due to the solvent. However, by use of tetrachloroethylene, in the present assay on the non-polar Apiezon L stationary phase, both monomers were eluted before the solvent with good separation (Fig. 1).
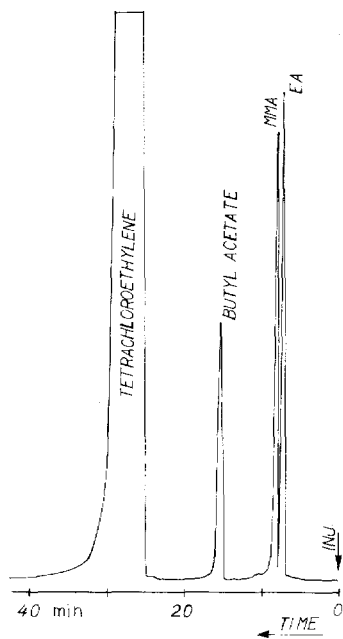

Fig. 1. Chromatogram of ethyl acrylate (EA), methyl methacrylate (MMA) and butyl acetate (internal standard) in a tetrachloroethylene layer on Apiezon L (4.2 m × 0.35 cm I.D.) glass column at 80°C.

Upon addition of hydrochloric acid acidified tetrachloroethylene, the ethyl acrylate–methyl methacrylate copolymer is immediately precipitated from aqueous emulsion. Moreover, after standing for almost 10 days, no dissolution of the precipitate was apparent. From the chromatogram, low-boiling alcohols attributable to ester hydrolysis were not present.

The described procedure can be used for routine applications with sufficient reproducibility. However, there is the possibility that adsorption and/or absorption by the precipitated polymer may affect the quantitation of the residual monomers. In order to investigate this, immediately after precipitation of the polymer emulsion a known amount of butyl acetate as the internal standard was added to the sample and the detector response to the both the monomers and internal standard was measured (Table I). From the observed response to ethyl acrylate, it is seen that the amount of residual monomer in the organic layer of the sample increases with the time of extraction. On the other hand, the response to the internal standard slightly

TABLE I

DETECTOR RESPONSES TO BUTYL ACETATE (INTERNAL STANDARD) AND ETHYL AC-
RYLATE IN THE TETRACHLOROETHYLENE LAYER

Extraction time (h)	Peak area		Peak area ratio, monomer/internal standard
	Butyl acetate	Ethyl acrylate	
2	577 775	225 767	0.391
3	572 270	274 670	0.480
4	568 678	291 616	0.513
24	507 590	362 105	0.713
25	504 271	364 703	0.723

decreases over a 25-h period from the time of sample preparation including butyl
acetate addition. Consequently, the peak area ratio for the monomer and internal
standard increases and the amount of the residual monomer seems to increase (Fig.
2).

The experiments were repeated several times under the same conditions with
various times. From regression analysis, the time dependence of the amount of the
internal standard added to the sample, relative to the initial value 1.000, can be
described by the equation $k = 0.990 - 0.00242t$, where t is time from the addition
of the internal standard to the sample. Hence k can be considered as a factor for
correction of the actual amount of internal standard in the tetrachloroethylene layer
of the sample. These butyl acetate data resulted in a correlation coefficient of 0.9955,
indicating a high degree of linearity for 40 determinations over 4 days (Fig. 3).

The utility of the correction factor, k, for improvement of the accuracy of the
residual monomer assay was tested as follows. Weighed amounts of ethyl acrylate
and methyl methacrylate were added to *ca.* 1 g of the polymer emulsion previously
analysed, employing the sample preparation procedure described, and then reana-
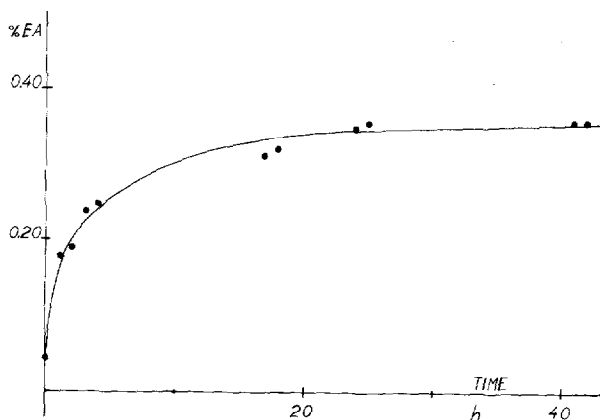

Fig. 2. Dependence of the determined amount (%, w/w) of residual ethyl acrylate (EA) on the time of
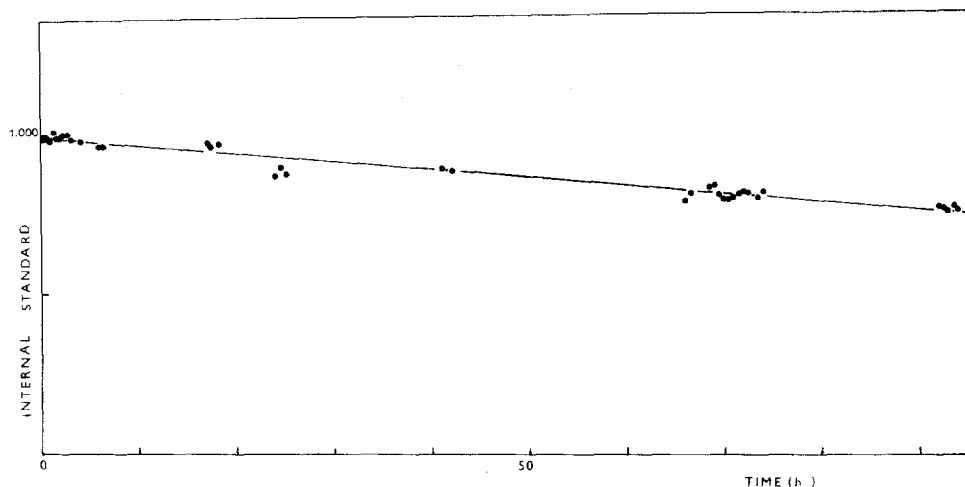extraction of the precipitated polymer.

Fig. 3. Time dependence of the amount of the internal standard in the tetrachloroethylene layer relative to the initial value of 1.000.

lysed for the total free monomers. The amounts of the total free monomers recovered were calculated employing k to eliminate time-dependent adsorption and/or absorption effects on the amount of internal standard added (Table II). When the sorption effects were considered (Method II), with the exception of two measurements, the relative experimental errors did not exceed 17%. When the factor k was omitted (Method I) the errors were considerably larger.

It may be concluded that simultaneous precipitation of polymer emulsion by hydrochloric acid and extraction by water-immiscible solvents followed by gas chro-

TABLE II

MONOMER DETERMINATIONS EXPRESSED AS CONFIDENCE LIMITS FOR $\alpha = 0.05$, WHEN THE AMOUNTS OF INTERNAL STANDARD ADDED TO THE ORGANIC LAYER OF THE SAMPLE WERE CONSIDERED TO BE UNCHANGED (METHOD I) AND WHEN SORPTION EFFECTS WERE CONSIDERED (METHOD II)

Initially present	Added	Total found (%)			
		Method I	Rel. error	Method II	Rel. error
Ethyl acrylate (%)					
0.06	0.05	0.14 ± 0.02	+27.3	0.11 ± 0.02	0.0
	0.11	0.27 ± 0.01	+58.8	0.18 ± 0.01	+5.9
	0.21	0.48 ± 0.03	+77.8	0.29 ± 0.02	+7.4
	0.53	0.92 ± 0.02	+55.9	0.51 ± 0.01	−13.5
Methyl methacrylate (%)					
0.01	0.05	0.09 ± 0.02	+50.0	0.07 ± 0.02	+16.7
	0.10	0.24 ± 0.01	+118.2	0.15 ± 0.01	+36.4
	0.20	0.45 ± 0.02	+114.3	0.27 ± 0.01	+28.6
	0.51	0.94 ± 0.02	+80.8	0.52 ± 0.01	0.0

matography seems to give a satisfactory estimate of the content of residual mono-mers. The accuracy of the assay can be considerably improved by elimination of the matrix effect.

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