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Progress Report

QUANTITATIVE ANALYSIS OF ACRYLIC COPOLYMERS BY GAS CHROMATOGRAPHY

by

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ABSTRACT

A modified chromatographic procedure has been developed for the quantitative determination of the constituents of acrylic copolymers. The sample is degraded on a hot wire coil located within the sample valve of the chromatograph. The volatile pyrolysis products are chromatographed and their presence in the helium carrier gas is detected by changes of the thermal conductivity of the effluent. Copolymer composition can be determined quantitatively with a precision of ±0.5% from standard curves of the ratio of peak areas at known composition. The analysis takes only a few minutes, can be readily adapted to other copolymers and is especially useful for cross-linked, insoluble materials.

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1. INTRODUCTION

Quantitative determination of the composition of copolymers is usually a time consuming task and can often not be accomplished without breaking down the material due to the insolubility of many high molecular weight products. Physical methods such as density, refractive index and infrared spectra of the polymer or its pyrolysis products have been used with varying success for the

elucidation of the composition of some copolymers.

Gas chromatography has also been suggested recently by the authors [1] and others as a tool for the detection of copolymeric components and their identification. Quantitative application of gas chromatography for polymers has been described by Haslam, Hamilton and Jeffs [2] and the present authors [1]. Haslam et al determined poly(ethyl esters) in methyl methacrylate copolymers by converting the alkoxyl groups to the corresponding iodides with hydriodic acid in phenol. The evolved methyl and ethyl iodides were absorbed in heptane and their ratio determined from the peak heights of the chromatograms. Strassburger et al [1] pyrolyzed the sample in air and determined the composition of the copolymer directly from the chromatograms of their pyrolysis products. The results of the quantitative analysis showed that the precision was always better with materials containing high percentages of methyl methacrylate. This greater precision did not result from instrumental errors or even from preparation of the polymer since polymerization of the material in sealed test tubes did not bring about a reduction in the standard deviation. Undoubtedly, therefore, the greatest inaccuracy was due to the method of depolymerization or the mechanism thereof despite the fact that precautions were taken to conduct this procedure under identical conditions. Furthermore, the loss of some volatile constituents such as methanol or methyl or ethyl acrylate may occur even though the receiver in which the pyrolysis products are collected is cooled in an ice bath.

It was the objective of this study to develop an improved, direct quantitative determination of the composition of copolymers by chromatographic analysis of their pyrolysis products.

2. EXPERIMENTAL PROCEDURE

2.1 Polymer Preparation

Solutions (5 ml) containing varying percentages by volume of inhibitor free monomers were de-aerated with nitrogen. The test tubes were sealed, held at 60° C until the contents had solidified, and then stored at 100° C for two to three days.

2.2 Apparatus

Analyses were made using a Consolidated Electrodynamics Corp. Chromatograph, type X-26-201 with dionyl phthalate as the liquid phase and size-graded ground firebrick as the solid support. The columns were prepared according to the procedure described by Dimbat, Porter and Stross [3]. In order to alleviate the shortcomings of the previously used pyrolysis procedure [1] the sample introduction system was modified to avoid possible loss of volatile constituents of the pyrolysis and to keep the experimental conditions as constant as possible. The system is similar to that suggested by Max Tryon of the Rubber Section, National Bureau of Standards. The ends of a nichrome No. 30 wire coil were connected to a variable transformer by means of which the temperature of the coil could be adjusted. The total resistance of the wire was 7 ohms. The copper wire leads were inserted into a standard taper Teflon plug which fitted into a tapered female glass joint sealed into the inlet system.

2.3 Operating Procedure

A polymer sample (10 to 15 mg) was placed in the nichrome coil which was heated by the passage of an electric current. A regulated flow of helium gas passed over the filament and carried the vapors directly into the heated column of the chromatograph. Details of the operating procedure are given in Table 1.

3. RESULTS AND DISCUSSION

Three typical methyl methacrylate copolymer systems containing known amounts of ethyl methacrylate, ethyl acrylate and ethylene dimethacrylate were selected to evaluate the reliability and precision of the analytical procedure.

Poly(methyl methacrylate) degrades with the formation of monomer as the only pyrolysis product whereas other polymeric components often form a number of decomposition products as evidenced on the chromatograms by the presence of more than one peak besides the characteristic methyl methacrylate peak. Since the height of the peaks is much more affected by changes in column temperature than peak area the ratio of the peak area of the methyl methacrylate peak to the total area under the peaks is usually more reliable for the preparation of calibration curves and for the subsequent analyses of unknowns.

The standard analysis curve for methyl methacrylate - ethyl methacrylate copolymers is given in Fig. 1. This peak area ratio-composition curve is linear with a slope approximating unity over the composition range examined. Departures from the straight line

are of the order of the experimental error. The points indicate the extreme values for at least 6 analyses (three of each specimen) at each composition. The values of two standard deviations of the ratio of peak areas lie within the circles. Statistical analysis of the results indicates that there is no evidence of differences between duplicate specimens of the same composition. The standard deviation measuring the variability of single measurements is 0.48%. This value is the same over the composition range investigated. If three replicate measurements are averaged, the "true" value can be predicted with 95% confidence to be in an interval extending from 0.55% methyl methacrylate below the average to 0.55% methyl methacrylate above the average.

Similar results were obtained for the analysis of methyl methacrylate - methyl acrylate copolymers (Table 2). The peak area ratio-composition curve is again a straight line with a slope of 0.78. The deviation of the slope from unity may be due to (1) the slight overlap of the methyl methacrylate peak with another peak (2) the possible formation of small amounts of methyl methacrylate on pyrolysis of poly(methyl acrylate) and (3) the large difference in the thermal conductivity of the pyrolysis products.

Pyrolysis of methyl methacrylate-ethylene dimethacrylate (EDMA) copolymers on the hot filament gives a chromatogram with only one major peak, methyl methacrylate. Since a number of peaks are present on the chromatograms of the liquid obtained on pyrolysis in air [1] the decomposition of this copolymer differs when conducted in air and in helium carrier gas.

Apparently in the helium atmosphere a reaction takes place between depolymerized methyl methacrylate monomer and some other degradation products with the formation of a relatively non-volatile compound. The composition of methyl methacrylate-ethylene dimethacrylate copolymers can, however, be determined by pyrolysing a weighed sample on the hot filament and using the ratio of sample weight to area of the methyl methacrylate peak for obtaining the standard analysis curve (Fig. 2). This calibration curve is not linear. A quadratic function provides a reasonably good fit, showing a slope that increases with the concentration of EDMA. The equation of this quadratic is $y = 5.007 + 0.02624x + 0.001506\, x^2 \qquad (1)$

where y = weight of sample/MMA peak area

x = percent EDMA

The standard deviation characterizing the variability between triplicate determinations of the same sample is 0.06% EDMA. There is also no evidence of sample to sample variability.

Using the quadratic as a calibration line, the precision of a value read from the curve varies with the EDMA concentration; the precision increases with increasing EDMA content. For values greater than 30% EDMA, the true value can be predicted with 95% confidence within less than 2% EDMA. For values less than 30% the precision is less. However, by using a larger number of standard samples to obtain additional points for the establishment of the calibration curve a precision of ± 0.5% may be obtained.

4. CONCLUSIONS

Pryolysis of copolymers on a hot coil surrounded by carrier gas is most suitable for their quantitative analysis. Components can be determined with a precision of 0.5%. Undoubtedly, the reliability of the calibration curve can often be further improved by increasing the number of analyses of "standard polymers" in the preparation of the calibration curve.

Ease, speed and accuracy of analysis make this method advantageous for the quantitative determination of components of acrylic copolymers. It is believed that similar techniques may be readily adapted to other copolymer systems.

5. BIBLIOGRAPHY

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Table 1

OPERATIONAL CONDITIONS

1.	Column length	6 ft.
2.	Bore (in. diam.)	3/16
3.	Column material	25% (wt) ground dinonyl phthalate on fire brick mesh # 30 to 70
4.	Carrier gas	helium
5.	Flow rate	50 ml/min.
6.	Pressure head	7.5 psi
7.	Column temperature	140° C
8.	Sample quantity	10-15 mg

Table 2

ANALYSIS OF METHYL METHACRYLATE - METHYL ACRYLATE COPOLYMERS

Composition % MMA[1]	MMA Peak Area / Total Area		
	Specimen		
	1	2	3
90	0.916	0.912	0.916
80	0.856	0.854	0.854
70	0.778	0.771	0.771
60	0.687	0.678	0.675
50	0.617	0.619	0.609

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[1] MMA = methyl methacrylate.

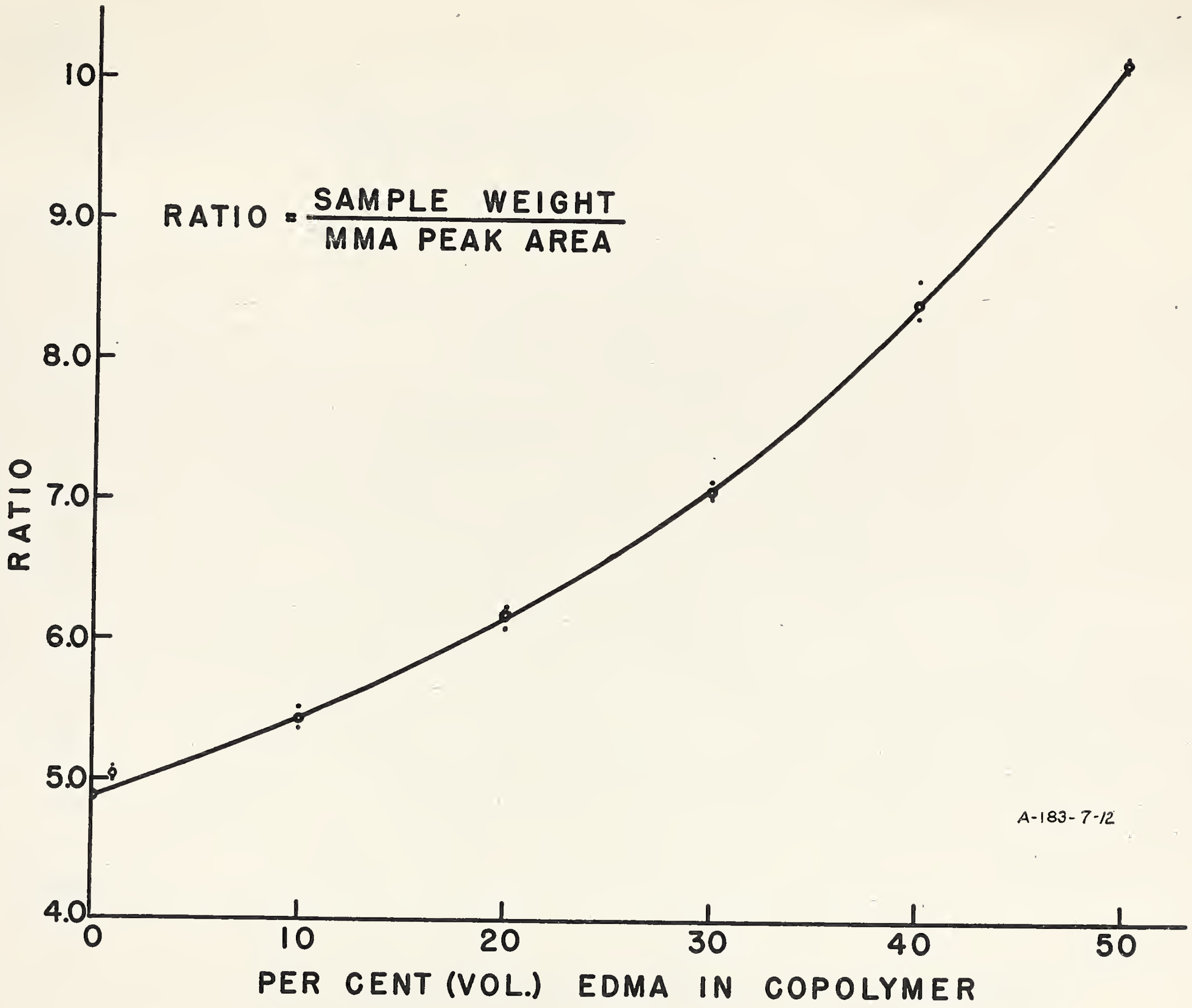

Figure 1. Standard curve for the analysis of methyl methacrylate-ethyl methacrylate copolymers.

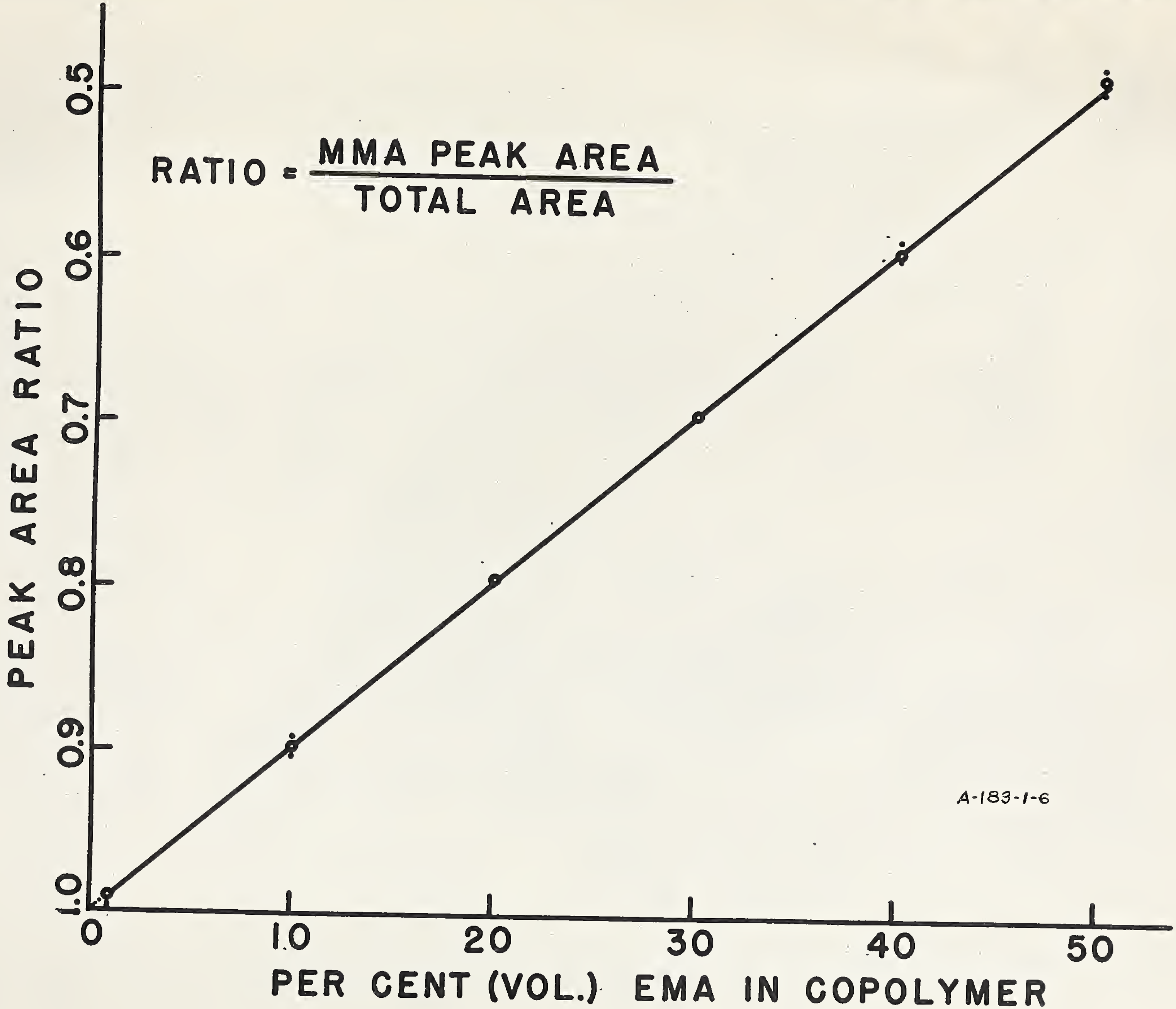

Figure 2. Standard curve for the analysis of methyl methacrylate-ethylene dimethacrylate copolymers.