

CHROM. 14,349

## Note

### Gas chromatographic determination of methacrylamide and the other intermediates in reaction mixtures in the synthesis of methyl methacrylate from acetone cyanohydrin

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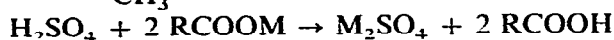
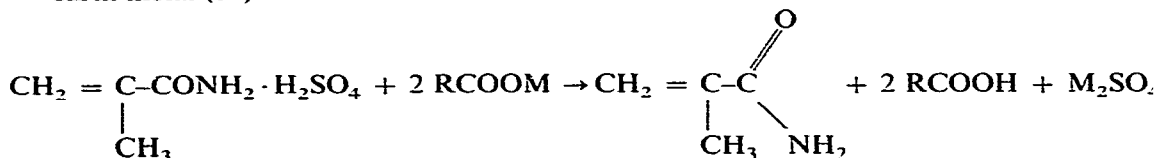
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(First received August 4th, 1981; revised manuscript received September 3rd, 1981)

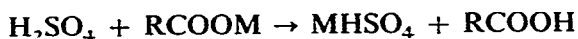
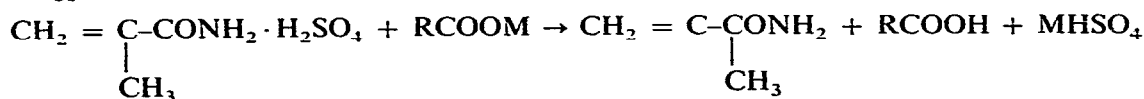
Previously described GC methods<sup>1-10</sup> for the determination of monomeric methyl methacrylate (MMA) can be applied only in the extraction and distillation stages of MMA technology. The main difficulty in the analysis of reaction mixtures is that they contain 20-40 wt.-% of sulphuric acid and methacrylamide bound as sulphate has to be freed. The problem with MMA production analyses has been solved by double-bond determinations<sup>11</sup> (determination of olefinic unsaturation by using potassium bromide-potassium bromate reagent), which is not a convenient method for the esterification stage where methacrylamide (MAA), methacrylic acid (MAK) and MMA are components of the mixture. Moreover, the determination is disturbed by oligomers that contain double bonds in their molecules.

For MMA determination a method based on hydrolysis of MAA and determination of the ammonia distilled off has been applied<sup>12</sup>. This method is relatively complex, slow and not always accurate.

The samples of reaction mixtures are pre-treated before GC determination with a reagent that binds sulphuric acid and at the same time liberates MAA. Subsequently, organic solvent is added, which dissolves the components to be determined and organic salts are separated out. Into the GC apparatus are injected only mixtures of organic compounds. Salts of alkali or alkaline earth metals with mono- and dicarboxylic acids (e.g., potassium acetate or oxalate) can be used as reagents. Sulphuric acid displaces weaker acids and liberates the sulphate of the alkali or alkaline earth metal (M):

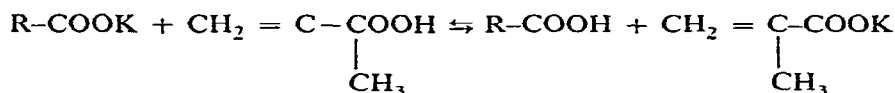


or



The most convenient solvent for the samples is dioxane, which is used in such an amount that gives concentrations of the components to be determined corresponding to the range of linearity of the detector. The inorganic salts are separated on the bottom of the vessel and the organic layer sampled for GC analysis. For the determination of MAA, MMA and methanol it is convenient to treat the samples of the reaction mixture with anhydrous potassium acetate.

In the determination of methacrylamidesulphate (MAAS), an aqueous solution of potassium acetate can be used. On the other hand, for methacrylic acid it is more convenient to treat the samples with an alkali metal salt of an acid with a lower  $pK_a$  value, e.g., potassium oxalate:



When the salt of an acid with a higher or similar  $pK_a$  value to that of MAK is used the system is equilibrated and the results are not reproducible.

This GC method has been patented<sup>13</sup>.

## EXPERIMENTAL AND RESULTS

### *Sample preparation*

To 0.3–0.35 g of reaction mixture were added 1 ml of distilled water (for MAA in MAAS) and 1 ml of the reagent (200 g of potassium acetate in 100 ml of water or 30 g potassium oxalate in 100 ml of water) and the solution was diluted with dioxane to give concentrations of the constituents to be determined corresponding to the range of linearity of the detector.

For samples from esterification that contain water, anhydrous reagents are used.

### *GC determination of MAA*

Analyses were carried out on a Chrom 41 apparatus equipped with a flame-ionization detector (FID) and a stainless-steel column (1.2 m × 3 mm I.D.) packed with 5% (w/w) of PEGA on Chezasorb support (0.1–0.5 mm). The following conditions were used: column temperature 160°C (isothermal); injector temperature, 250°C; carrier gas, nitrogen at a flow-rate of ca. 0.03 l/min; hydrogen flow-rate, 0.03 l/min; air flow-rate, 0.6 l/min; injection volume, 1 μl. For all analyses of reaction mixtures a small stainless-steel conical screen was inserted into the injection chamber, the dimensions being adapted to the length of the injection syringe needle. Dioxane and acetic acid eluted immediately and the retention times of MAK and MAA were 45 and 180 sec. respectively (Fig. 1); the standard deviation was 0.58% (w/w) and the relative standard deviation was 1.89%; the sensitivity of the amplifier was 1:1000.

### *GC determination of MAK*

The samples were treated as for the MAA determination and separately for MAA and MAK. The following conditions were used: column temperature, 130°C; injector temperature, 180°C; other conditions as given above. Dioxane and acetic

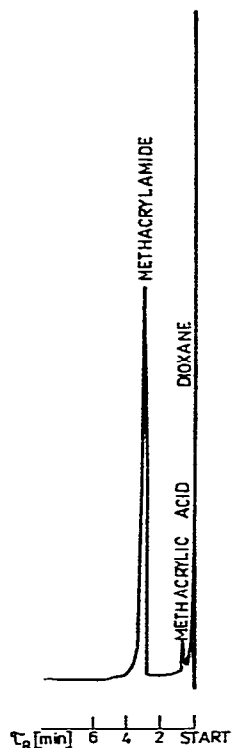


Fig. 1. GC determination of MAA.

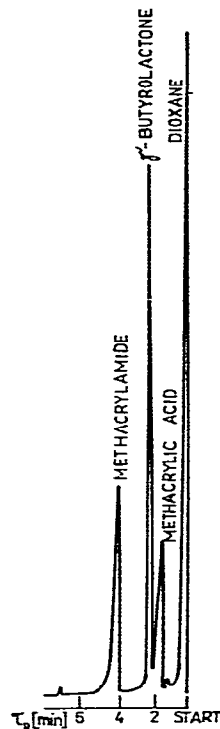


Fig. 2. GC determination of MAK.

acid eluted immediately and the retention times of MAK and MAA were 110 and 250 sec, respectively (Fig. 2); the standard deviation was 0.47% (w/w) and the relative standard deviation was 3.02%.

#### GC determination of MMA and methanol

Samples were treated as for MAA (see above). A CHROM 5 gas chromatograph with an FID was used; the column (3.7 m  $\times$  3 mm I.D.) was packed with 10% (w/w) of Carbowax 20M plus 1% (w/w) of sodium hydroxide on Chromaton NAW (0.2  $\times$  0.25 mm) support. The following conditions were used: column temperature, 100°C; injector temperature, 150°C (modification of injector as described above); carrier gas, nitrogen at a flow-rate of *ca.* 0.04 l/min; hydrogen flow-rate, 0.04 l/min; air flow-rate, 0.6 l/min; injection volume, 1  $\mu$ l. The retention times were as follows: methanol, 108 sec; MMA, 168 sec; impurity from dioxane, 144 sec; dioxane, 240 sec (Fig. 3). The standard deviations were 0.26% (w/w) for methanol and 0.658% (w/w) for MMA; the relative standard deviations were 3.78% and 2.22%, respectively.

For all analyses the method of direct calibration was employed.

#### CONCLUSION

A simple, rapid and accurate method for the determination of the main inter-

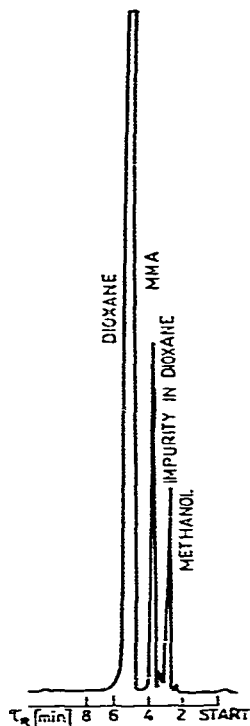


Fig. 3. GC determination of MMA and methanol.

mediate components in the synthesis of MMA from acetone cyanohydrin has been developed. The method involves pre-treatment of samples and makes possible the GC analysis of organic compounds in the presence of inorganic acids. The method can be employed directly in production plants for inter-stage control.

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