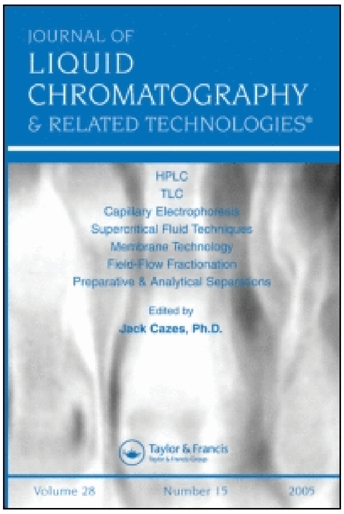

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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Timothy J. Mann[a]
[a] Union Carbide Corporation, Hahnville, Louisiana

To cite this Article Mann, Timothy J.(1980) 'High Performance Liquid Chromatographic Analysis of Polymerization Inhibitors in Acrylic Monomers', Journal of Liquid Chromatography & Related Technologies, 3: 2, 219 — 227

To link to this Article: DOI: 10.1080/01483918008060166

URL: http://dx.doi.org/10.1080/01483918008060166

JOURNAL OF LIQUID CHROMATOGRAPHY, 3(2), 219-227 (1980)

HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC ANALYSIS OF POLYMERIZATION INHIBITORS IN ACRYLIC MONOMERS

Timothy J. Mann
Union Carbide Corporation
P. O. Box 50
Hahnville, Louisiana 70057

ABSTRACT

High performance liquid chromatographic methods are described which provide for the quantitative determination of p-hydroquinone in acrolein and p-monomethyl ether of hydroquinone in the ethyl, n-butyl, iso-butyl, and 2-ethylhexyl esters of acrylic acid. The procedures are fast, precise, and applicable to industrial process analyses.

INTRODUCTION

Acrolein (2-Propenal), acrylic acid (2-propenoic acid) and its esters are the smallest compounds to possess both an ethylenic bond and a carbonyl group, and hence, are quite reactive and prone to polymerization. To supress undesirable polymerization during manufacture, storage, and transportation, polymerization inhibitors are added to the monomers.

Most commercial manufacturers use p-hydroquinone (HQ) as the inhibitor for acrolein and p-monomethyl ether of hydroquinone (MMHQ) for the acrylic esters. (HQ and MMHQ are used throughout the acrylics industry to denote 1,4-dihydroxybenzene and 1-hydroxy -4 methoxybenzene, respectively. In view of the industrial acceptance of this nomenclature, these designations will be used throughout this paper.) Typical inhibitor concentrations for HQ in acrolein are 0.100-0.250% by wt., while the concentration for MMHQ in acrylic esters normally ranges from 10-60 ppm.

The industry acceptable colorimeteric procedure for MMHQ in the ethyl, n-butyl, iso-butyl, and 2-ethylhexyl acrylic esters is known to be susceptible in interference from several compounds. The herein presented high performance liquid chromatographic (HPLC) procedure is believed to be more specific for the inhibitor species. Likewise, the spectrophotometric method for HQ in acrolein is susceptible to interference. It is also a rather lengthy procedure requiring approximately forty-five minutes to complete. In contrast the HPLC method takes less than ten minutes.

These methods were developed for use in an industrial process laboratory. They employ neat sample injections, isocratic solvent systems, ambient temperatures, and the same analytical column. This allows both methods to be performed on one moderately-priced HPLC system.

MATERIALS

Equipment

Analyses were performed on Waters ALC/GPC 201 liquid chromatograph (Waters Associates, Milford, Mass.) equipped with U6K injector and 6000 A model pump. The detector employed was a Varian Vari-Chrom (Varian, Palo Alto, Ca.), the output of which was attenuated with a 100:1 resistor pad to provide compatability with a Linear Model 261 recorder (Linear Instruments, Irving, Ca.) operating on a range of 0-1 mv and a chart speed of 20cm/hr.

Separations were made on a 4.6 mm I.D. x 250 mm column packed with LiChrosorb RP-2, 10 μ particle diameter, supplied by Brownlee Labs (Santa Clara, Ca.). All solvents and samples were filtered by means of the Waters Solvent Clarification kit and the Waters Sample Clarification kit, respectively.

Chemicals

The 2,2,4-trimethylpentane was supplied by Burdick and Jackson Laboratories (Muskegon, Michigan) and the chloroform (inhibited with 0.75% ethanol) by Mallinckrodt (St. Louis, Missouri). Both were spectroquality. The methanol was commercial grade supplied by Union Carbide Corporation. (Texas City, Texas)

METHODS

HQ In Acrolein

A ternary solvent system of 20% 2,2,4-trimethylpentane, 79.20% chloroform, and 0.80% methanol (v/v percent) was used at a flow rate of 2.0 ml/min.. The analytical wavelength employed was 292 nm with a 16 nm bandwidth and an absorbance range of 0.5 AUFS. Samples were injected neat with injection volume varying between 5 and 10 µl according to the anticipated concentration range.

MMHQ In Acrylic Esters

A solvent system composed of 60% 2,2,4-trimethylpentane and 40% chloroform (v/v percent) was used at a flow rate of 1.5 ml/min.. A detector wavelength of 292 nm with a 16 nm bandwidth and an absorbance range of 0.01 AUFS was used. A 10 µl neat injection was used for the normal concentration range of 0-30 ppm. Higher concentration were analyzed by diluting the sample with an appropriate amount of the chromatographic solvent to keep the MMHQ peak within the range of the calibration curve.

DISCUSSION

The colorimetric procedure for the determination of MMHQ in acrylic esters involves the reaction of MMHQ with nitrous acid from aqueous sodium nitrite. The reaction results in an equilibrating nitroso derivative (see figure 1) which is measured spectrophotometrically. While the procedure has adequate sensitivity, it lacks specificity, as several compounds have been shown to interfere. It's precision and accuracy can also be affected by instability of the sodium nitrite solution.

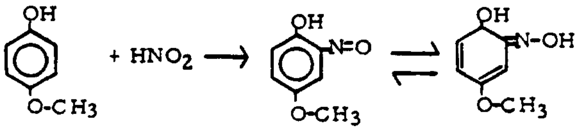

FIGURE 1: Reaction of MMHQ and Nitrous acid

The spectrophotometric determination of HQ in acrolein entails the vacuum evaporation of the acrolein and subsequent uptake of the residue in methanol. This solution is then analyzed spectrometrically to determine the HQ content. This method is susceptible to various interferences, although they are not believed normally to be a problem. The chief disadvantage of this method, therefore, is the analysis time.

While little data have been accumulated on the specificity of the described HPLC procedures, the author has encountered no problems in this respect. Both methods exhibit good linearity and, by nature of the chromatographic process, are believed to be more specific for the inhibitor species.

As stated earlier, acrylics are prone to polymerization. Polymerization may be induced by UV radiation which results in a polymer film on the detector cell lens. Reductions in sensitivity have been noticed after long periods of operation. This requires cleaning the cell with 1:1 nitric acid. The cleaning frequency in our laboratory has been about six weeks, or after approximately 1000 analyses. Sensitivities return to their original range after cleaning the cell. Polymerization of the acrylate in the UV cell may be avoided by deflecting the UV beam away from the cell during the passage of the monomer. This technique has been sucessfully used in the analysis of polymerization inhibitors in tetraethyleneglycol dimethacrylate.(1)

RESULTS

MMHQ In Acrylic Esters

A typical analysis of MMHQ in the acrylic esters is shown in Figure 2. The four acrylic esters elute together near the column void volume. The MMHQ elutes with good peak symmetery and resolution.

Calibration is achieved through analysis of solutions of known MMHQ concentrations in an acrylic ester. To facilitate standard preparation, the acrylic ester is scrubbed with a sodium hydroxide solution to remove MMHQ. When preparing the standards

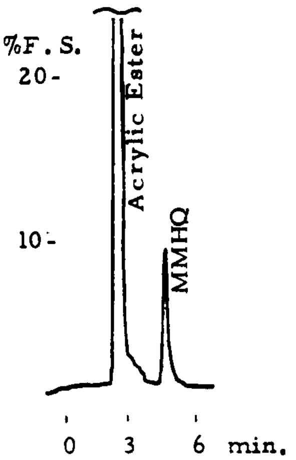

FIGURE 2: Typical chromatogram of MMHQ in acrylic esters

it must be remembered that MMHQ is an antioxident and will diminish in purity during storage. Therefore, fresh MMHQ should be used for calibration. Figure 3 illustrates a typical calibration curve.

Quantitation is achieved by the peak height method. Chart divisions are used for peak measurements and yield at 0.5 ppm/chart division response, which is quite adequate. A density correction factor, based on the ratio of the density of the ester to be analyzed and the density of the ester used for calibration, is employed to quantitate the different esters.

To compare the HPLC procedure with the colorimetric method discussed earlier, a sample was analyzed ten times by each method. This testing resulted in an average difference between the two methods of 0.28 ppm at the 14.5 ppm level. The standard deviations observed were 0.76 for the colorimetric method and 0.31 for the HPLC method.

HQ In Acrolein

Figure 4, represents a typical HQ in acrolein analysis by HPLC. Resolution is seen to be very good, as is the peak shape. Acrolein dimer elutes between acrolein and HQ and could interfere

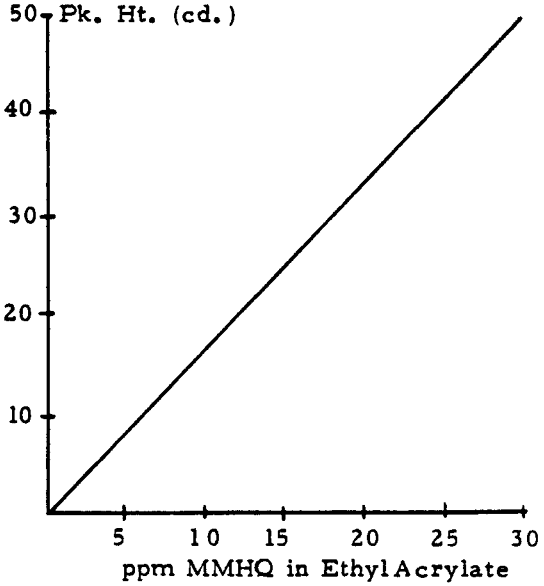

FIGURE 3: Calibration curve of MMHQ in Acrylic Esters

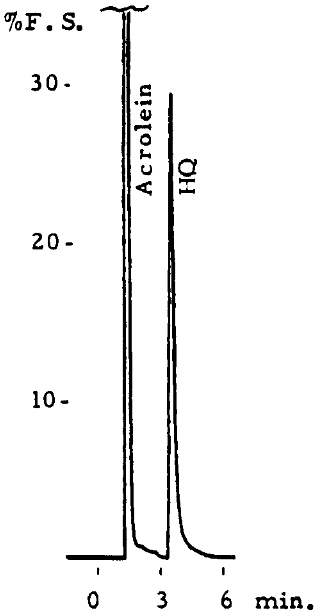

FIGURE 4: Typical chromatogram of HQ in acrolein

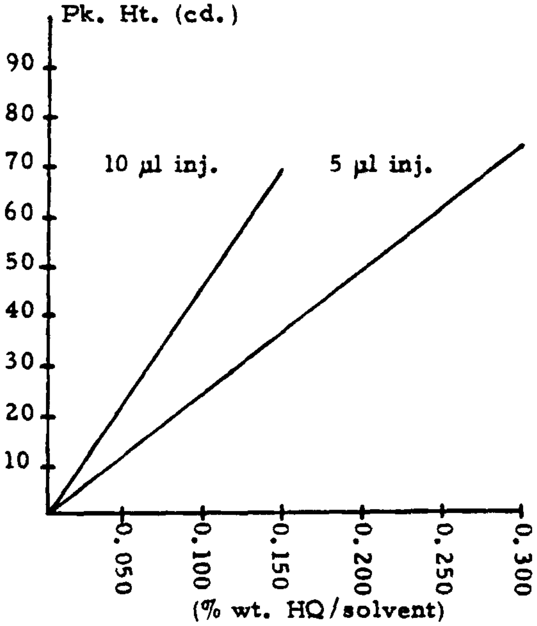

FIGURE 5: Calibration curve of HQ in the HPLC solvent

if present in high concentrations. (Acrolein dimer is also known to interfere with the spectrophotometric procedure in high concentrations, as it absorbs at the analytical wavelength.) Although the presence of dimer in the acrolein could conceivably interfere and complicate quantitation of the HPLC procedure, this problem has not presented itself when working with acrolein up to two months old.

Due to the lacrimal and polymerization properties of acrolein, its use as a calibration medium was precluded. Because of this, the chromatographic solvent was used as the standard medium. As with MMHQ, fresh HQ must be used for calibration due to its rather rapid oxidation at ambient conditions. Figure 5 illustrates typical calibration curves for HQ in solvent.

Quantitation is again done by the peak height method using chart divisions for measurements. Because the HPLC solvent was used as the calibration mixture, quantitation is somewhat complicated. Two factors must be applied to convert the weight percent

HQ in HPLC solvent in the calibration curve to weight percent HQ in acrolein.

First, we must correct for the differing densities of the solvent and acrolein. Ratioing the acrolein gravity (.844@20/20) and the HPLC solvent gravity (1.3175@20/20), we obtain a density correction factor of 0.6406.

Next, we must account for matrix effects, or the effect of acrolein on the HQ peak. The HQ band in acrolein is not broadened as severely as the HQ in the standards since it does not traverse the entire system as a free band. Thus, a sharper peak is generated in an acrolein matrix than in the standard matrix.

This factor was experimentally determined for ten samples using the average of duplicate analyses. The average factor was determined to be 1.3284 with a standard deviation of 0.0668. This factor was also confirmed by the method of additions.

Combining the density and matrix factors, we obtain a HPLC correction factor of 0.8510. Using this correction factor and the calibration curve, the per-cent HQ in Acrolein may be calculated by equation No. 1.

$$\text{HQ\% by wt./Acrolein} = (\text{concentration from calibration curve}) \times 0.8510 \qquad (1)$$

When the HPLC method was compared with the spectrophotometric procedure, the analysis of a single sample ten times by each method yielded an average difference of 0.0008% by wt. at the 0.08% by wt. level. The observed standard deviations were 0.019, for the spectrophotometric method and 0.009 for the HPLC procedure.

CONCLUSIONS

These HPLC procedures are fast and precise. In addition, their instrumental parameters and analytical simplicity allow their use by inexperienced chromatographers on a moderately priced HPLC system. Their use by an industrial laboratory should result in a reduction in the cost of determining inhibitors in acrylic compounds.

ACKNOWLEDGEMENTS

The author gratefully acknowledges the technical and administrative assistance of Messrs. W.L. Miller and H K Webb, of Union Carbide Corporation.

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