Journal of Chromatography, 596 (1992) 290–293
Elsevier Science Publishers B.V., Amsterdam

CHROM. 24 043

Short Communication

Determination of topanol antioxidants in methacrylates using capillary gas–liquid chromatography

Ian D. Smith* and David G. Waters

SmithKline Beecham Pharmaceuticals, Old Powder Mills, Leigh, Tonbridge, Kent TN11 9AN (UK)

(First received September 6th, 1991; revised manuscript received January 24th, 1992)

ABSTRACT

This paper presents a method to identify and determine topanol A and topanol O antioxidants in methylmethacrylate and 11-bromoundecylmethacrylate. The method is both simple and rapid. Analysis is performed on a 10 m × 0.53 mm I.D. HP-1 capillary gas chromatography column with a temperature gradient and a high carrier gas flow-rate (16.5 ml/min). Quantitation is by internal standardisation. Validation of the method is described for both topanols at concentrations of approximately 50 ppm in methylmethacrylate and 250 ppm in 11-bromoundecylmethacrylate.

INTRODUCTION

Methylmethacrylate is supplied with an antioxidant to inhibit spontaneous polymerisation. The antioxidant, either topanol A (2-*tert.*-butyl-4,6-dimethylphenol) or topanol O (2,6-di-*tert.*-butyl-4-methylphenol), has been added at a concentration of approximately 50 ppm. Methylmethacrylate is used in the preparaton of a cross-linked polymethacrylate and the antioxidant is carried into the intermediate product (11-bromoundecylmethacrylate) and concentrated approximately 5-fold to about 250 ppm. The structures of the analytes are shown in Fig. 1.

It was necessary to be able to identify which of the two topanols had been added, and to determine the concentration in methylmethacrylate and 11-bromoundecyl-methacrylate.

A number of methods have been reported in the literature, with a variety of sample matrices and by a number of techniques. These include the analysis of BHT (butylated hydroxytoluene, or topanol O) in transformer oil by high-performance liquid chromatography (HPLC) [1], derivatisation followed by packed-column gas chromatography (GC) and HPLC [2], determination in soaps [3] and in soybean oil [4] by packed-column GC, and in chewing gum by capillary-column GC [5]. However, none of these were suitable for the required analysis, so a new method was developed. It was decided to use 2,4,6-tri-*tert.*-butyl phenol (see Fig. 1) as internal standard to improve the precision of analysis, and to employ a wide-bore capillary GC column to take advantage of the well-known high sample capacity and good efficiency.

EXPERIMENTAL

Chemicals

2,6-Di-*tert.*-butyl-4-methylphenol (99%), 2-*tert.*-

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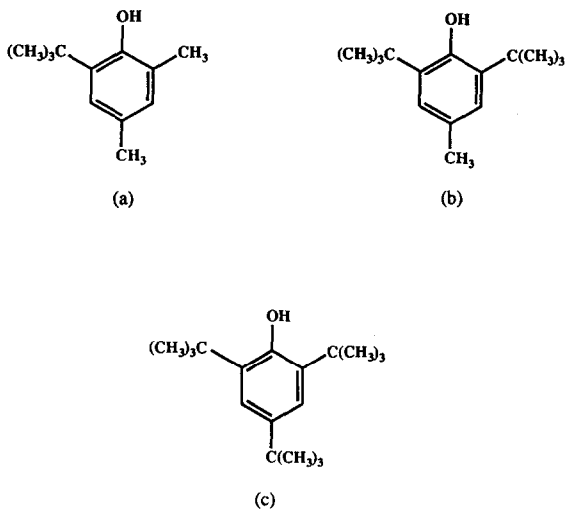

Fig. 1. Structures of (a) topanol A, (b) topanol O and (c) the internal standard.

butyl-4,6-dimethylphenol (99%), and 2,4,6-tri-*tert.*-butylphenol (97%) were all supplied by Aldrich. Dichloromethane was HPLC grade, supplied by Romil.

Instruments

GC analysis was performed on a Varian Model 3400 gas chromatograph, equipped with a Varian Model 8035 autosampler, a Varian Model 1093 septum programmable injector used in on-column mode and a flame ionisation detector. The GC column was a Hewlett-Packard HP-1 (methyl silicone), 10 m × 0.53 mm I.D., 2.65 μm film thickness. The injector temperature was 250°C, the detector temperature 260°C. The oven temperature programme was slightly different for the two sample matrices. For methylmethacrylate samples, it was 70°C for 3 min, then up to 150°C at 15°C/min, and held at 150°C for 12 min. For 11-bromoundecylmethacrylate samples, it was 70°C for 3 min, then up to 150°C at 15°C/min, and held at 150°C for 5 min, then up to 250°C at 30°C/min and held at 250°C for 5 min as a purge step to ensure the complete elution of all the sample components. The carrier gas was helium, at a flow-rate of 16.5 ml/min (measured at 70°C by a bubble flow meter). The injection volume was 0.3 μl.

Data collection and processing was performed using a Perkin-Elmer LIMS/CLAS 2000 data system. Least-squares regression analysis and plotting of graphs were performed using Cricket Software's "CricketGraph".

Procedures

Methylmethacrylate analysis. The internal standard solution was prepared at a concentration of 0.1 mg/ml. A standard solution was prepared with concentrations of 0.005 mg/ml for both of the topanols and of the internal standard.

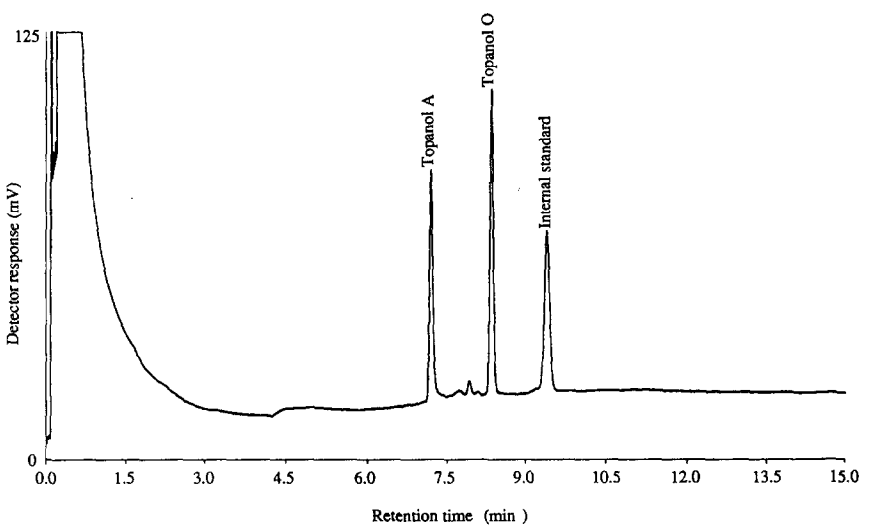

Fig. 2. Chromatogram of the 50-ppm standard solution, showing both the topanol peaks and the internal standard peak.

Sample solutions were prepared by dissolving 1 g of sample and 1.00 ml of internal standard solution in 10 ml of dichloromethane, giving a sample concentration of approximately 100 mg/ml.

Sample and working standard solutions were analysed in duplicate.

11-Bromoundecylmethylacrylate analysis. The internal standard solution was prepared at a concentration of 0.5 mg/ml. A working standard solution was prepared with concentrations of 0.025 mg/ml for both of the topanols and of the internal standard.

Sample solutions were prepared by dissolving 2 g of the sample and 1.00 ml of the internal standard solution in 20 ml of dichloromethane, giving a sample concentration of approximately 100 mg/ml.

Sample and working standard solutions were analysed in duplicate.

Calculation of results. The chromatograms were integrated and the areas of the topanol and internal standard peaks found. The concentration of topanol in the sample was determined using the conventional ratio calculation.

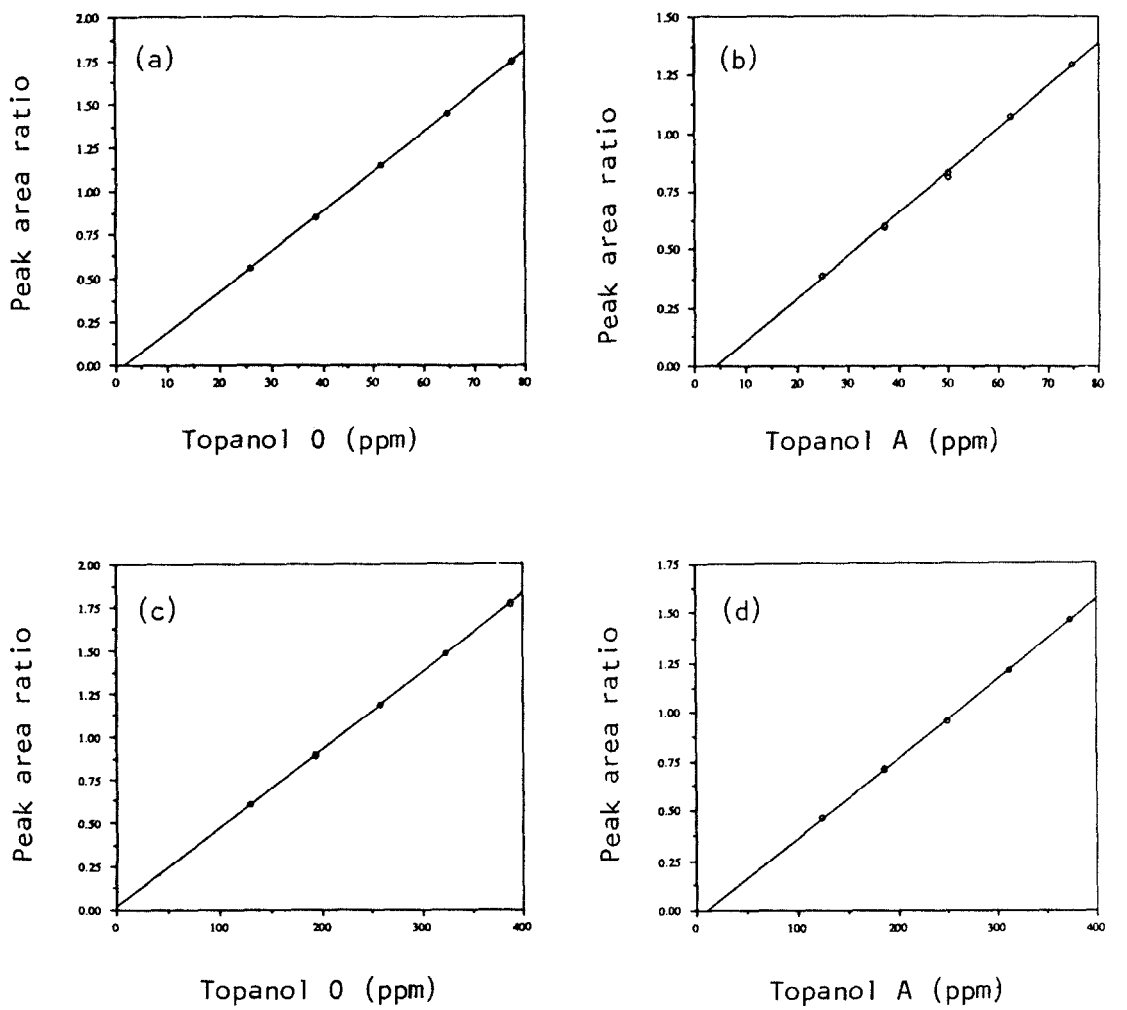

Fig. 3. Plots of the linearity of the peak area ratio against concentration for (a) topanol A and (b) topanol O over the range 25–75 ppm, and (c) topanol A and (d) topanol O over the range 125–375.

Validation experiments. The linearity of response of the method was examined by two injections at each of five concentrations over the ranges 25 to 75 ppm and 125 to 375 ppm. These ranges represent 50 to 150% of the nominal standard concentration of topanol for methylmethacrylate and 11-bromoundecylmethacrylate respectively.

The stabilities of both solutions were assessed by comparison with freshly prepared solutions after 4 and again after 7 days storage in the dark at 4°C. The sample stability was assessed by analysing a freshly prepared sample solution and then reanalysing against freshly prepared standards after 24 h storage in the dark at 4°C.

The precision of replicate injections was examined by making 10 injections of the same standard solution.

RESULTS AND DISCUSSION

The method described gave well resolved peaks with good efficiency in a total run time of less than 10 min. A chromatogram of the 50-ppm standard is shown in Fig. 2.

The peak area ratio response was found to be linear for both topanols over the concentration range examined. Plots of peak area ratio against concentration are shown in Fig. 3. The correlation coefficients (r) were all 0.999 or better.

Standard solutions were found to be stable on storage in the dark at 4°C for up to 7 days, and sample solutions for at least 24 h.

The precision of replicate injections were found to be quite acceptable for trace level assays. At 50 ppm, topanol A gave a peak area ratio relative standard deviation (R.S.D.) of 5.6%, topanol O, 4.1%. At 250 ppm the R.S.D. for topanol A was 5.8% and topanol O 3.2%. These results give confidence limits ($p = 0.05$) for topanol O of ± 1.2 ppm at 50 ppm and ± 5.0 ppm at 250 ppm.

Methylmethacrylate eluted with the solvent peak, and no other sample-related peaks have been observed in chromatograms of methylmethacrylate samples. The 11-bromoundecylmethacrylate elutes after the internal standard, and a number of sample-related peaks have been seen in chromatograms from samples of this compound. These are low-level impurities in the samples, and although they run close to the topanol O and internal standard peaks, there is no evidence of co-elution or interference. There is a minor impurity in the 2,4,6-tri-*tert.*-butylphenol, which elutes between the two analyte peaks and is well resolved from both.

CONCLUSION

The methods presented are simple and rapid, allowing both the confirmation of the identity of the antioxidant and its determination at low levels. The method has acceptable reproducibility, as shown by the relatively low R.S.D. values and is linear over the ranges examined.

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