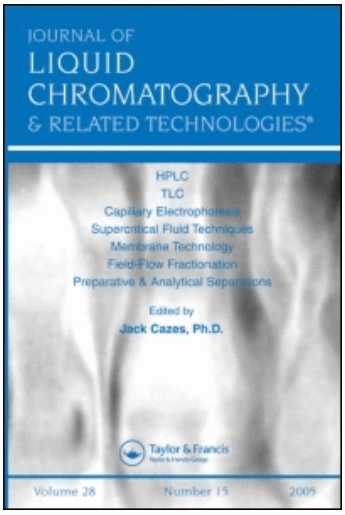

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

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To cite this Article Worstell, J. H. , Daniel, S. R. , Strand, G. O. and Frauenhoff, G. R.(1981) 'Quantitative Separation of Tetralin Hydroperoxide from Its Decomposition Products by High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 4: 3, 539 — 547
To link to this Article: DOI: 10.1080/01483918108059953
URL: http://dx.doi.org/10.1080/01483918108059953

JOURNAL OF LIQUID CHROMATOGRAPHY, 4(3), 539-547 (1981)

QUANTITATIVE SEPARATION OF TETRALIN HYDROPEROXIDE FROM ITS DECOMPOSITION PRODUCTS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

A method for the separation and analysis of tetralin hydroperoxide and its decomposition products by high pressure liquid chromatography has been developed. Elution with a single, mixed solvent from a μ-Porasil column was employed. Constant response factors (internal standard method) over large concentration ranges and reproducible retention parameters are reported.

INTRODUCTION

The analysis of mixtures resulting from autoxidation of hydrocarbons has proved to be a formidable problem for both research and process chemists. Several instrumental and wet chemical techniques have been employed to determine the composition of autoxidation mixtures (1,2). Most current methods require that the hydroperoxide of the autoxidation mixture be determined first with subsequent destruction into its decomposition products by some stoichiometric process. The decomposition products are then determined quantitatively and the amount contributed from the stoichiometric decomposition of the hydroperoxide is then subtracted to yield the concentration of the decomposition products in the system at the time the oxidation process was stopped (3).

Iodometric titrations of the total peroxide content of a solution are numerous (2). However, double bonds, if present, may interfere with the iodometric titration for peroxides (4,5). Various colorimetric techniques have also been published, but these methods tend to be as subject to interferences as the iodometric titrations (2). They also tend to have poor accuracy and precision (1,2,6,7,8). Gas chromatographic techniques are available for the determination of hydroperoxides, but the procedures are technically difficult (2). They generally require glass injection ports and low injection port and column temperatures to prevent decomposition of the hydroperoxide (9,10,11,12).

Swern, Clements, and Luong (13) obtained the NMR spectra for several pure hydroperoxides and determined that the method could not be used for quantitative work when the acidic character of the hydroperoxide proton was not significantly different from that of the protons in its decomposition products. Ward and Mair (14) were able to obtain reproducible quantitative data for a mixture of organic peroxides, hydroperoxides, and alcohols. However, neither group studied a mixture of the hydroperoxide with all its decomposition and reaction products.

High performance liquid chromatography (HPLC) affords several advantages over the above methods. First, by a judicious choice of column packing and solvent composition, a hydroperoxide and all its decomposition products can be analytically separated. Secondly, the method is applicable to thermally unstable or nonvolatile compounds. Van Tilborg (15) demonstrated the usefulness of gradient elution HPLC in separating mixtures of hydroperoxides and in separating ethylbenzene hydroperoxide from its decomposition products. HPLC has been used to determine benzoyl peroxide levels in dermatological gels and lotions (16). Deelder, et al., (17) placed a reactor column immediately after a silica gel column and measured the amount of cyclohexyl hydroperoxide in a mixture of peroxides by a colorimetric technique. The hydroperoxides were separated on the silica gel column and then reacted with sodium iodide in 2-propanol in the reactor column. The reaction produced

I^-_3 which was monitored at 362 nm. This technique is difficult and the second column in the system tends to broaden the bands of the chromatogram significantly.

The method reported here permits simultaneous determination of tetralin, tetralin hydroperoxide, tetralol, and tetralone using a single column and a single, mixed solvent.

EXPERIMENTAL

Compound Synthesis and Purification

Tetralin hydroperoxide was prepared by the method of Knight and Swern (18). The melting point was 56°C. The reported melting point was 55.7° - 56°C.

Tetralone (95% purity) and n-dodecane were purchased from Aldrich Chemical Company (Milwaukee, Wis.). Tetralone was distilled under N_2. n-Dodecane was washed with concentrated H_2SO_4 until the acid layer was colorless. The n-dodecane was then distilled. Purity of both was determined on a Varian Model 3700 gas chromatograph equipped with a 6 ft by 1/8 inch o.d. copper column packed with 3% Carbowax 20M supported on Teflon.

Tetralol was prepared by reduction of tetralone with $LiAlH_4$ in THF. The resulting product was a 55/45 tetralol/tetralone mixture based on the 7.90 ppm tetralone peak and the 8.04 ppm tetralol peak in the proton NMR. Tetralone was removed by precipitation of the semicarbazone from ethanol. After ethanol evaporation, the product exhibited no carbonyl band in the IR, and was used without further purification.

Apparatus

A Waters Associates liquid chromatograph fitted with a Model 6000 constant flow pump, a μ-Porasil column, a Model U6K syringe-loading sample injector and a Model 440 UV detector was used. The sample absorbance was monitored at 254 nm. A Waters Associates Model R401 refractometer was coupled to the UV detector effluent port so that nonabsorbing compounds could be determined.

Methods

Samples of tetralin, tetralin hydroperoxide, tetralone, and tetralol were individually dissolved in 10 mls of n-dodecane. A 2.5 microliter capacity Hamilton syringe was used to inject 0.2 microliter of the sample into the injection loop. Response factors were then determined for each individual component by varying the concentration of the component in the n-dodecane solvent. A 0.2 microliter sample of a mixture of the above components was also run.

Chromatographic grade isooctane, acetonitrile and chloroform were distilled and the stabilizer (0.75% ethanol) was removed from the chloroform by treatment with activated silica gel. The mobile phase was prepared to contain 65% (v/v) isooctane, 34.3% (v/v) chloroform, and 0.7% (v/v) acetonitrile. The flow rate was 2.0 mL/min (1500 psi).

Mobile phase was recycled via batch distillation. A volume of isooctane (least volatile component) equal to that of the pot residuum was added to the distillate. Minor addition of isooctane or acetonitrile was then made as needed to reproduce tetralol retention time.

RESULTS AND DISCUSSION

n-Dodecane was used as the internal standard. It does not absorb significantly at 254 nm and therefore does not interfere with the determination of the peaks for the tetralin derivatives.

TABLE 1
Slopes and Regression Coefficients for Response Factors

Compound	Slope $\frac{\text{moles}/\ell}{\text{area}}$	r
Tetralin	0.32	0.999
Tetralone	0.042	0.999
Tetralin Hydroxide	0.027	0.999
Tetralol	0.064	0.999

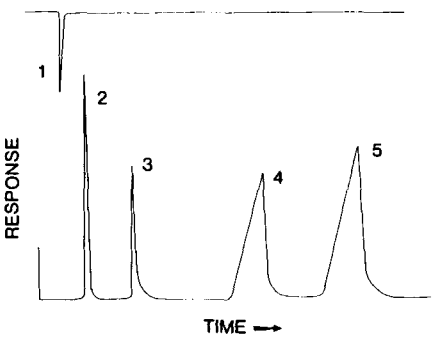

FIGURE 1: Refractive index liquid chromatogram of n-dodecane (above) and UV absorbance liquid chromatogram of tetralin autoxidation products (below). Peak identities: (1) n-dodecane, (2) tetralin, (3) tetralone, (4) tetralin hydroperoxide, (5) tetralol. Column: Waters Associates μ-Porasil.

The n-dodecane content was determined using the refractive index (RI) detector (upper trace in Figure 1). The UV detector responses were thus standardized based on the RI response for dodecane. Response factors are reported in Table 1.

The chromatogram for separation of the tetralin derivatives is shown in Figure 1 and the retention times are given in Table 2.

TABLE 2
Retention Times for Separation of Autoxidation Products (in mins)

Tetralin	Tetralone	Tetralin Hydroperoxide	Tetralol
1.70	4.06	10.15	13.22
1.65	4.02	10.13	13.20
1.84	4.15	10.18	13.25
1.66	4.02	10.13	13.18
1.64	4.06	10.03	13.15
1.66	4.10	10.05	13.13
1.66	4.05	10.03	13.10
1.63	4.05	10.03	13.36
1.64	4.00	10.03	13.05
1.63	4.03	10.13	13.03
1.67	4.05		13.06
1.63	4.04		13.05
1.65	4.05		13.01

The data for tetralin, tetralone, and tetralol represent runs performed every 24 hours for a 168 hour period. The mobile phase was batch distilled 7 times during this period and readjusted after each distillation. The data for tetralin hydroperoxide were gathered over a 12 hour period with only one batch distillation of the mobile phase. This short time period was used due to the rapid decomposition in solution of tetralin hydroperoxide into tetralone and tetralol (3).

The data of Table 1 demonstrate the reproducibility of the method despite rather inexact control of mobile phase composition. Retention times are rather insensitive to the isooctane/chloroform ratio and strongly dependent upon the acetonitrile content. The variation of retention times with acetonitrile concentration in a nominally 65% (v/v) isooctane mobile phase is shown in Figure 2. The influence of CH_3CN is even greater when the isooctane/chloroform ratio is greater. At these levels (< 1%), the acetonitrile does not greatly alter the bulk solvent properties of the mobile phase. The observed effects are consistent with diminuation of the analyte distribution coefficients due to analyte/CH_3CN competition for adsorption (19) Manipulation of the CH_3CN concentration represents a convenient, rapid method of adjustment of retention times and resolution factors. We have found similar behavior with analytes containing a variety of functional groups.

The resolution between the tetralin and tetralone peaks and the tetralone and tetralin hydroperoxide peaks is 1.8 and 4.0, respectively. Baseline resolution also occurs between the tetralin hydroperoxide and tetralol peaks (R_s = 1.8).

The method is designed for the separation of a hydroperoxide from its parent compound and decomposition products, not for separation of two hydroperoxides. However, this method is now being studied for the analysis of autoxidation products in complex hydrocarbon mixtures. Use of the UV absorbance detector restricts application to those systems containing appropriate chromaphores. The detection limit for tetralin hydroperoxide was found to be 7×10^{-10} g.

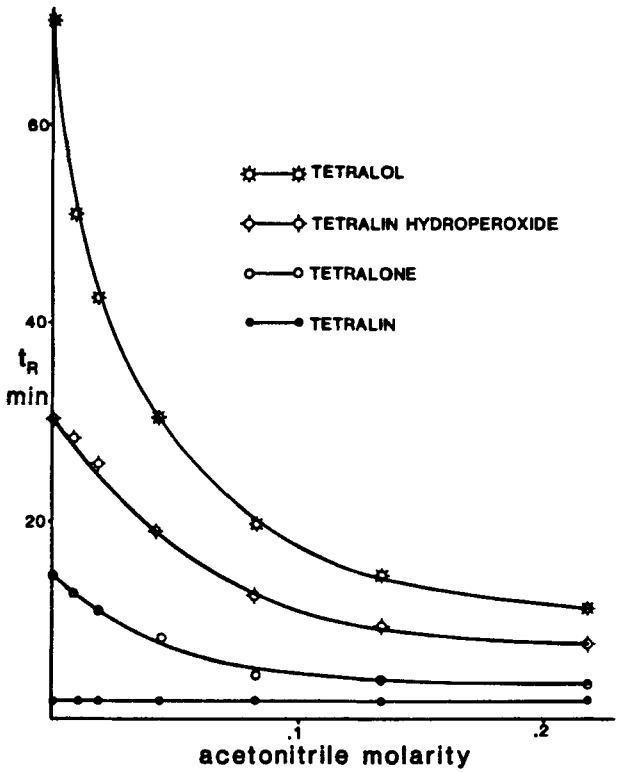

FIGURE 2: Effect of acetonitrile concentration in a 65/35 (v/v) isooctane-chloroform mobile phase on retention times.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of this work by the National Aeronautics and Space Administration under grant NSG-3122.

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