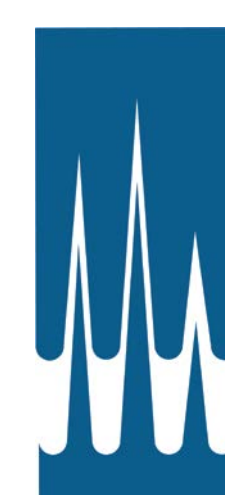




CHROMATOGRAPHIC SEPARATIONS OF ANALYTICALLY CHALLENGING FLAME RETARDANTS USING SUPERCRITICAL FLUID CHROMATOGRAPHY



Riddell N^{1,2}, McCrindle R³, McAlees A¹, Klein J¹, Chittim B¹, van Bavel B²

Introduction

The incorporation of flame retardants (FRs) into commercial products has been a common practice since the first official FR patent was filed by Obadiah Wyld in 1735.¹ Unfortunately, some of the currently used FRs have proven to be analytically challenging. For this reason, the assembly of data for risk assessments has been sluggish. For example, the derivatives of Tetrabromobisphenol-A (TBBPA) were included in a recent European Food Safety Authority (efsa) review on Brominated Flame Retardants (BFRs) in food and feed, but a lack of occurrence data meant that a risk assessment on these compounds could not be completed.² It is very difficult to achieve acceptable chromatography of the TBBPA derivatives using gas chromatography (GC) because these compounds are thermally labile and are prone to degradation. Separation methods utilizing liquid chromatography have been reported³, but the use of packed column supercritical fluid chromatography (pSFC) may also provide a viable alternative since the temperature required to maintain carbon dioxide in its supercritical state (31°C) at a pressure of 1100 psi is well below that which a compound would experience during a typical GC analysis.⁴

The unique properties of supercritical fluids may also facilitate the simultaneous analysis of related FRs that previously required multiple analytical techniques. For example, phosphorus-based flame retardants (PFRs) are receiving notable attention in Europe and East Asia⁵ and, due to the wide range of applications for which they are utilized, their formulations tend to be application specific with each formulation consisting of different resins, hardeners, and fire retardants. PFRs can be incorporated into polymers through blending (as additive flame retardants) or via chemical reactions (as reactive flame retardants).⁶ Additive PFRs are commonly used in combination with each other and triphenyl phosphate (TPP) to increase their overall effectiveness while reducing the required loading⁵, but little is known about the environmental fate of these compounds⁷ and a comprehensive analytical method has yet to be proposed.

In this study, we investigated the chromatographic separation of four tetrabromobisphenol derivatives and three phosphorus-based flame retardants (Figure 1):

Tetrabromobisphenol A-bisallylether (**TBBPA-AE**)

Tetrabromobisphenol A-bis(2,3-dibromopropylether) (**TBBPA-DBPE**)

Tetrabromobisphenol A-bis(2-bromoallylether) (**TBBPA-BAE**)

Tetrabromobisphenol A-bishydroxyethylether (**TBBPA-EtOH**)

Resorcinol bis(diphenyl phosphate) (**RDP**)

Bisphenol A bis(diphenyl phosphate) (**BDP**)

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (**DOPO**)

Materials and Methods

Samples of RDP, BDP, and DOPO were provided by Susanne L. Waaijers (IBED, University of Amsterdam) and were characterized through a combination of LC/UV, LC/MS/MS, GC/MS, NMR (¹H and ³¹P NMR), and preparatory thin-layer chromatography (prep-TLC) experiments. All LC/UV experiments were conducted using a Waters Prep LC 4000 System coupled to a Waters 2487 Dual λ Absorbance detector using a μ Bondapak C₁₈ column (10 μ m, 3.9 x 300 mm). LC/MS/MS experiments were conducted on a Waters Acquity UPLC coupled to a Micromass Quattro micro API MS using an Acquity UPLC BEH Shield RP₁₈ column (1.7 μ m, 2.1 x 100 mm). All GC/MS experiments were conducted on a Agilent 7890A (HRGC)/5975C (LRMS) using a 15m DB-5HT column (0.25 mm id, 0.1 μ m film thickness) or a Shimadzu GCMS-QP2010 using a 30m DB-5 column (0.25 mm id, 0.25 μ m film thickness). All injections were done in splitless mode and a full scan range of 50-1000 amu was collected in positive ion electron impact mode (EI+). NMR experiments were run on a 400 MHz Bruker instrument using CD₂Cl₂ (CDN Isotopes) or CDCl₃ (CDN Isotopes) as the solvent. Prep-TLC separations were conducted using custom plates prepared in-house. SFC experiments were conducted using a Waters Acquity UltraPerformance Convergence Chromatography (UPC²) system (carbon dioxide with a methanol cosolvent). UV detection was accomplished using an in-line Acquity UPC² PDA detector (225 nm) and full scan MS data (100-1400 amu) were collected on a Micromass Quattro micro API MS (ionization modes: positive and negative ESI with a make-up solvent of 50:50 methanol:isopropanol).

Results

The technical formulations of RDP and BDP were found to contain multiple oligomers. Rigorous characterization resulted in the determination of the following compositions: RDP contained 8% of TPP, 75% of the RDP monomer, 15% of the RDP dimer, and 2% of the RDP trimer. BDP was determined to contain 3% of TPP, 80.5% of the BDP monomer, and 16.5% of the BDP dimer. The components of the technical mixtures of RDP and BDP were easily separable using reverse phase liquid chromatography (LC) with common C₁₈ stationary phases, however accurate representations of the technical composition of DOPO was not possible by LC or GC. DOPO can exist in multiple interconvertable forms and liquid chromatography resulted in the detection of open, closed, and mixed species (all of which had very poor peak shape), but each species was observed in different runs under very specific conditions. It has been reported that commercial DOPO usually contains appreciable amounts (~30%) of the hydrated "open-chain" phenolic phosphinic acid, this was confirmed by ¹H NMR (see Figure 2); two sets of signals were observed that could be assigned to the open and closed forms. Integration indicated that the technical product contains 65% of the closed form and 35% of the open form of DOPO. GCMS analysis of the same technical mixture resulted in only one observable peak. The thermally sensitive open form of DOPO appears to close when exposed to various injector port temperatures (e.g. 250°C and 120°C). This technique would be useful for determining "total DOPO" in a sample, but would not be able to provide information regarding the relative amounts of open and closed DOPO in environmental samples.

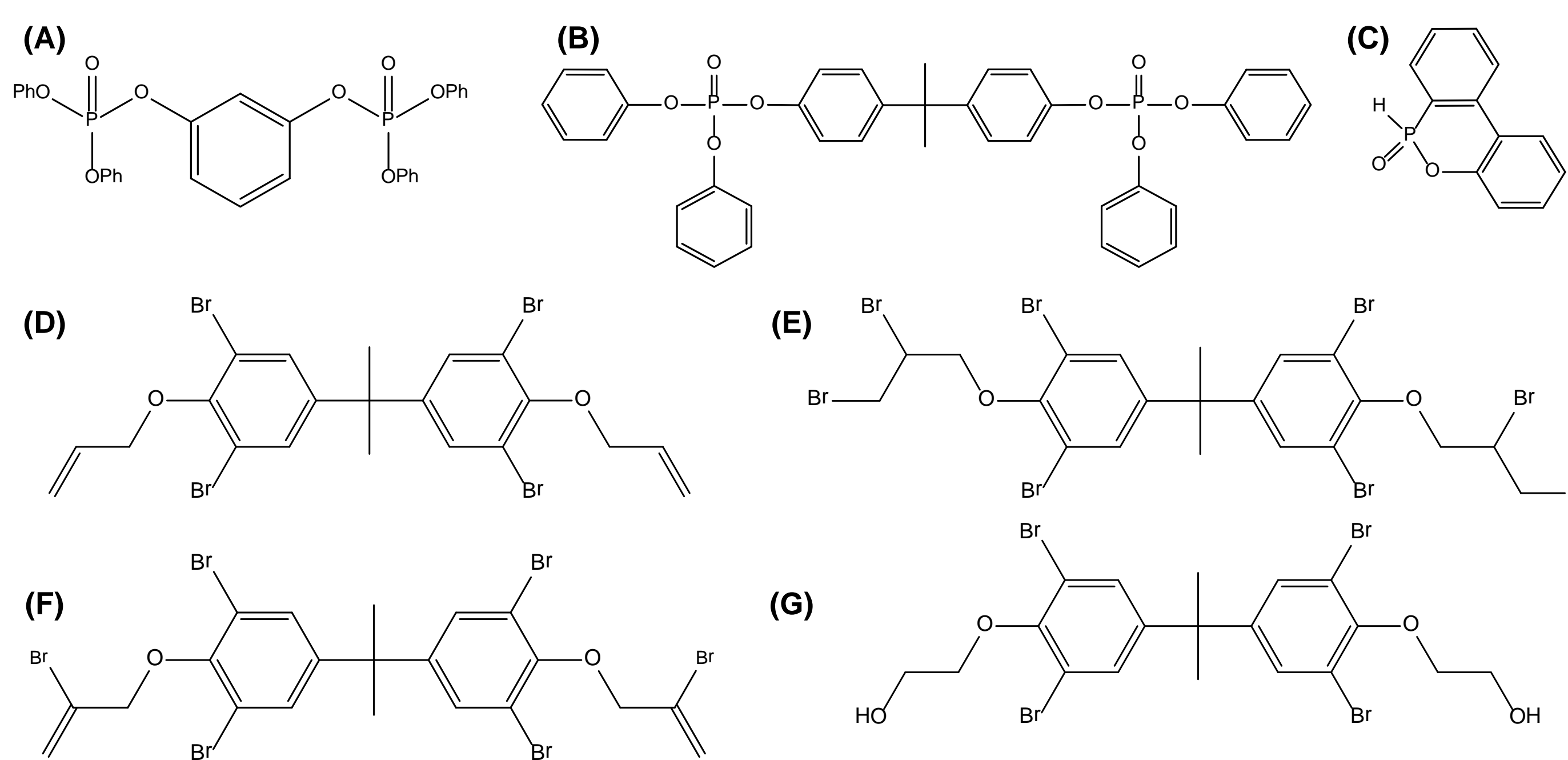


Figure 1: Structures of the compounds under investigation: (A) RDP, (B) BDP, (C) DOPO, (D) TBBPA-AE, (E) TBBPA-DBPE, (F) TBBPA-BAE, and (G) TBBPA-EtOH.

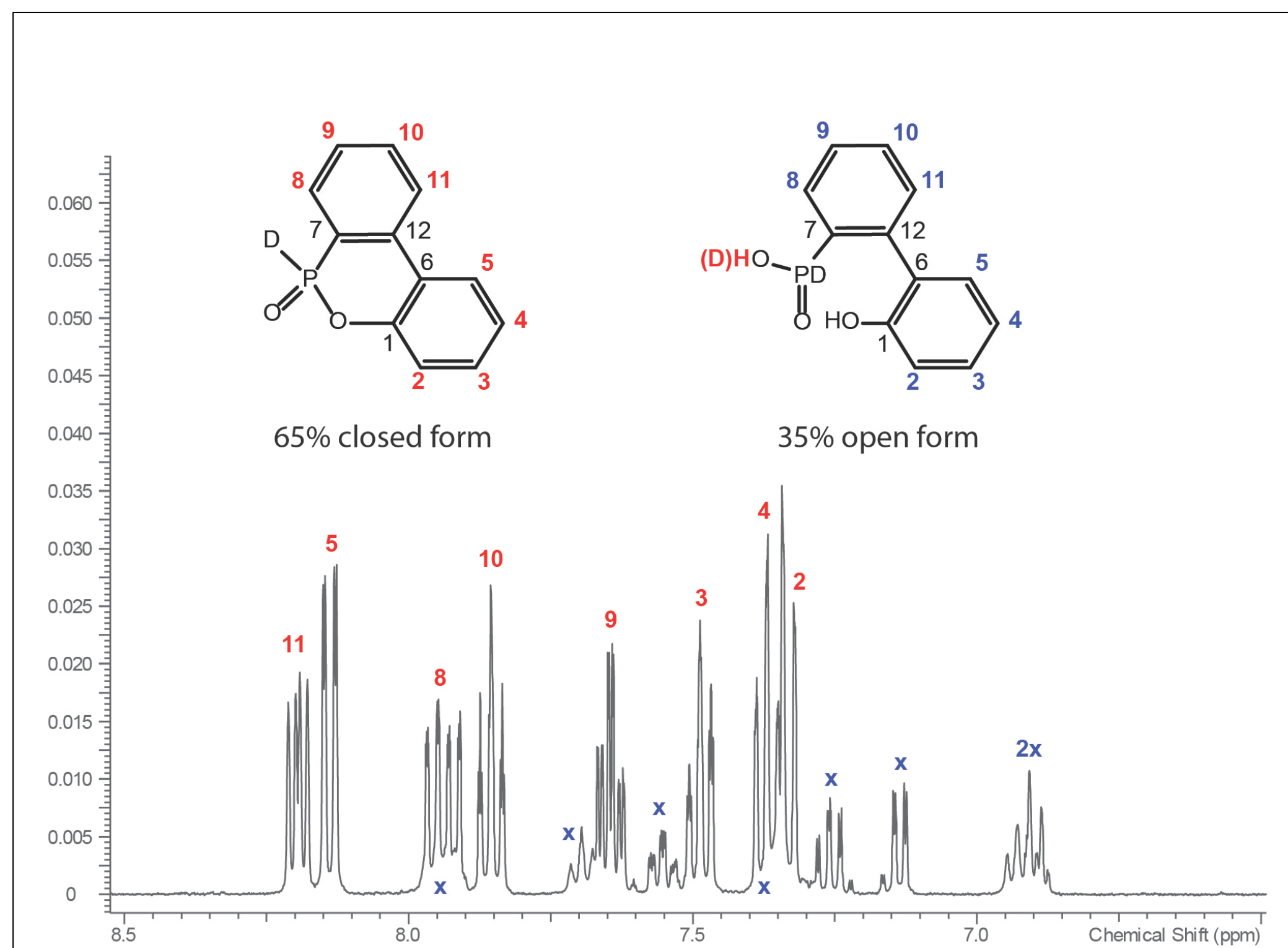


Figure 2: ¹H NMR of technical DOPO in CD₃OD. Proton assignments have been indicated using a colour co-ordinated system (red = signals associated with the closed form, blue = signals associated with the open form).

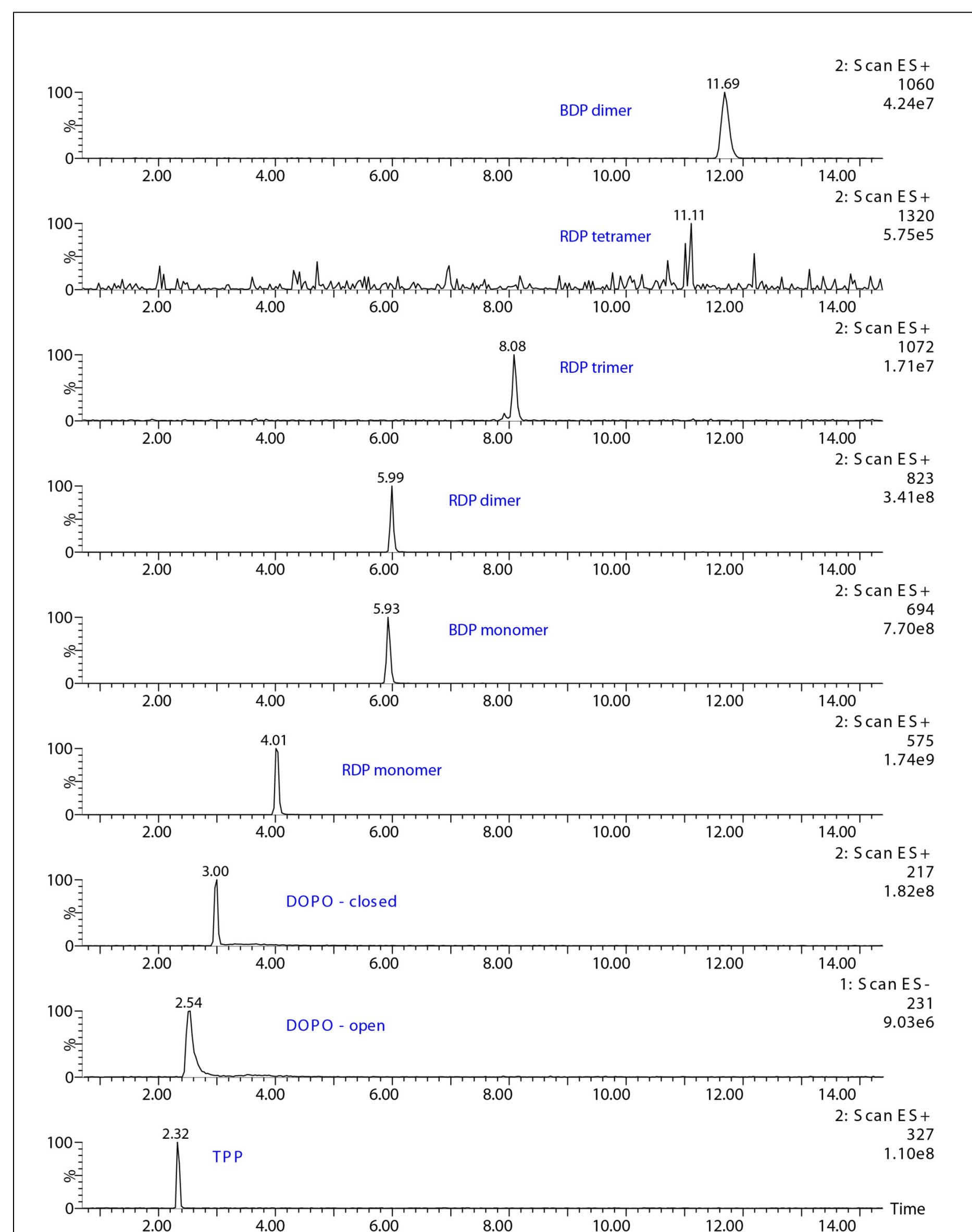


Figure 3: SFC analysis of technical RDP, BDP, and DOPO on a Restek DB Biphenyl (3 μ m, 4.6 x 150 mm) column using methanol with 10 mM NH₄OAc as the cosolvent.

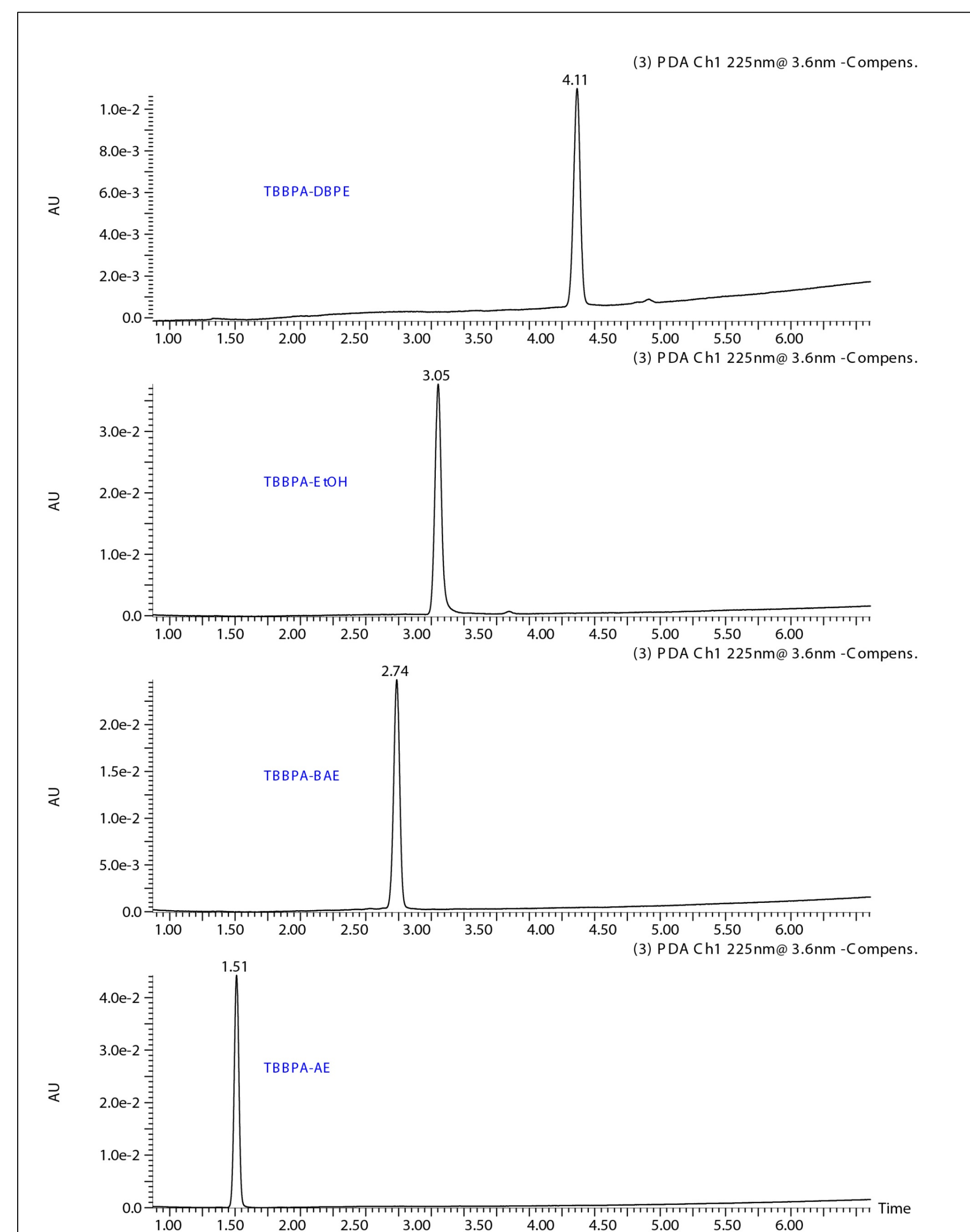


Figure 4: Separation of four derivatives of TBBPA on a Restek Pinnacle II PAH (4 μ m, 3.2 x 150 mm) column using methanol as the cosolvent.

Separation of the components of technical RDP, BDP, and DOPO (dissolved in acetonitrile) was successfully performed on a Restek DB Biphenyl column using supercritical chromatography (Figure 3). However, in order to elute the open form of DOPO it was necessary to add 10 mM of NH₄OAc to the methanol cosolvent. The addition of this additive resulted in a marked change in the retention time of the open form of DOPO; presumably by blocking some of the free silanol groups on the column.

Attempts to analyze the derivatives of TBBPA using gas chromatography resulted in additional erroneous peaks and poor peak shape (peak fronting was specifically observed which is evidence of on-column degradation). However, NMR data indicated that the standards being injected onto the GCMS system were of high purity. Attempts to optimize the GCMS parameters still did not result in acceptable results. When the same standards were analyzed using a Restek Pinnacle II PAH column on the UPC² system, excellent peak shape and purities similar to those determined by NMR were observed (Figure 4). To conclude, separations of analytically challenging flame retardants (PFRs and TBBPA derivatives) were successfully carried out using supercritical fluid chromatography.

Contact Information:

¹ Wellington Laboratories Inc., Research Division, Guelph, Ontario, N1G 3M5, Canada;

² Man-Technology-Environment (MTM) Research Center, Örebro University, Örebro 70182 Sweden;

³ Chemistry Department, University of Guelph, Guelph, ON, Canada N1G 2W1

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