LA-UR-21-30911

Title: Gel Permeation Chromatography Methods for Stockpile Relevant PBXs

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Intended for: Report

Issued: 2021-11-02

Gel Permeation Chromatography Methods for Stockpile Relevant PBXs

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Abstract

In order to accurately characterize chemical changes to the binder in plastic-bonded explosives (PBXs) it is important to develop new gel permeation chromatography (GPC) methodologies as well as update previous methods. Herein we present new and updated GPC methodology for Viton A, Kraton G, and Oxy 461. The methods developed were specifically designed for Malvern OMNISEC with a Mixed C column, but minor modifications could be made to these methods to make applicable to other instrumentation.

Experimental

GPC analysis was performed on a Malvern OMNISEC (Westborough, MA, USA) equipped with quad detection: refractive index (RI), UV/Vis photodiode array (PDA), multi-angle light scattering, and viscometer. A sample injection volume of 100 µL was used with a mobile phase flow rate of 1 mL/min. For all analyses, two serially coupled PLGel Mixed C columns (Agilent Technologies, Palo Alto, CA, USA) were implemented; between each mobile phase change, the columns were allowed to equilibrate for approximately 1 week until a stable baseline from all detectors was achieved. Prior to analysis, samples were filtered with a 25 mm diameter Whatman Puradisc 25TF filter (GE Healthcare, Marlborough, MA, USA) containing a 0.45 µm PTFE membrane in a polypropylene housing. A goal of this study was to identify the solvent producing adequate detection signal at the lowest possible concentration. In order to achieve this, a wide range of concentrations (1.5, 3.0, and 5.0 mg/mL) of each polymer were tested in each solvent.

Results and Discussion

For GPC analyses, it is preferred to dissolve a polymer in the same solvent as the mobile phase as this mitigates refractive index (RI) differences between the two solvents and prevents misinterpreting the solvent RI as part of the polymer signal. Because of this, all of our GPC efforts utilized the same solvent for sample dissolution and the mobile phase. Common GPC solvents include (but are not limited to) THF, EA, BA, toluene, DMF, and DMSO. A quick study was performed to qualitatively evaluate the dissolution of Viton A, Kraton G, and Oxy 461 in tetrahydrofuran (THF), ethyl acetate (EA), acetone, hexane, dichloromethane (DCM), and dimethylformamide (DMF) at concentrations of ~10 mg/ml. Viton A showed dissolution in THF, EA, and DMF after 30 minutes while small particles were seen in the acetone solution. After 24 hours the acetone solution still had small particles in it; however, it was elected to still evaluate Viton A in acetone. Kraton G showed dissolution in THF, DCM, and hexane after 30 minutes but not in any of the other solvents even after 24 hours. The Oxy 461 showed dissolution in all solvents except for hexane where it appeared to swell.

Figure 1A-C shows the GPC results for analysis of Viton A in THF, DMF, EA and acetone, at concentrations of 1.5, 3, and 5 mg/mL. For brevity only the refractive index (RI) data is shown as this is the detector that is most affected by the mobile phase composition. It was concluded that the optimum solvent for Viton A was THF as this produced the highest response.

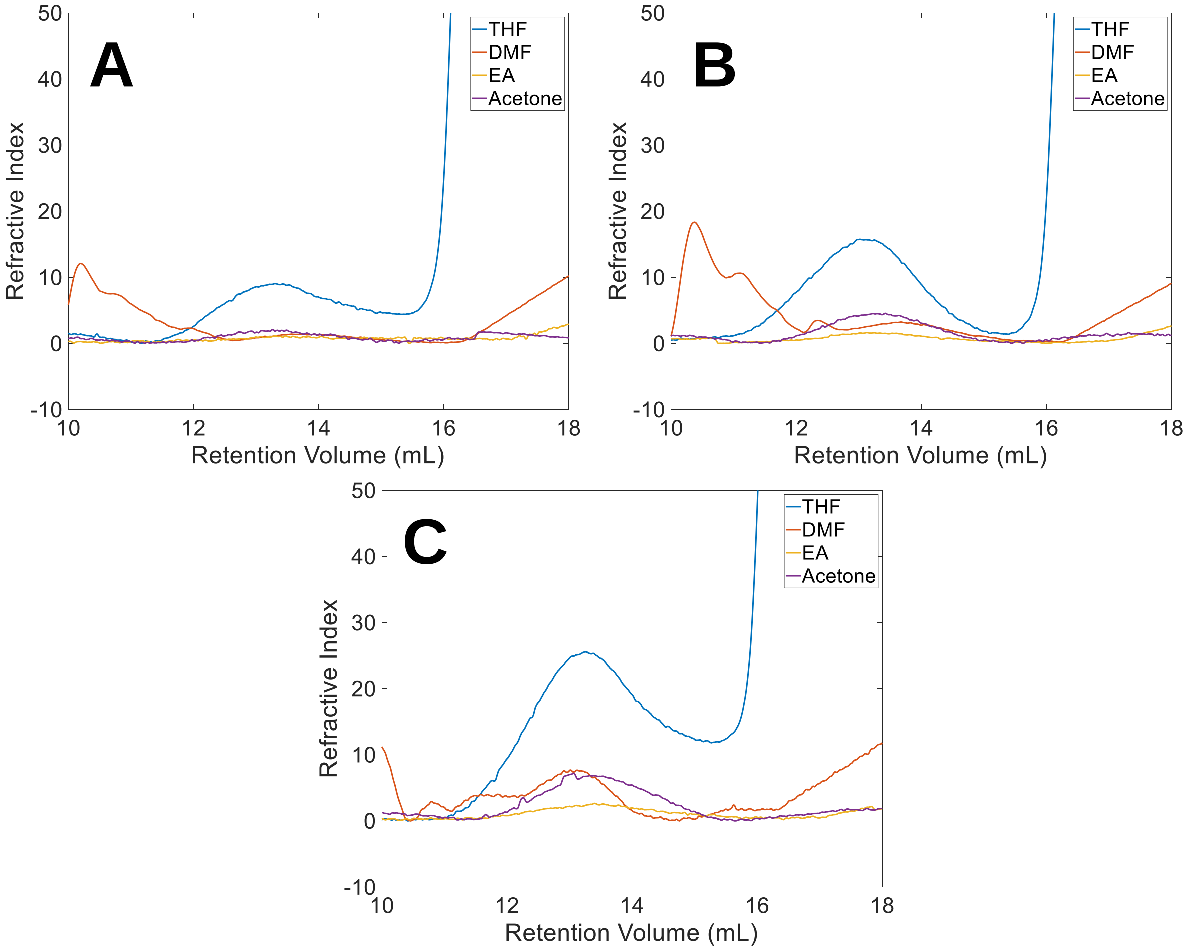

Figure 1. GPC results for analysis of Viton A at concentrations of 1.5 (**A**), 3.0 (**B**), and 5.0 mg/mL (**C**) in THF, DMF, EA, and Acetone.

Figure 2A shows the GPC results for analysis of Kraton G in THF at concentrations of 1.5, 3, and 5 mg/mL. For brevity only the refractive index (RI) data is shown as this is the detector that is most affected by the mobile phase composition. While Kraton was also soluble in DCM and hexane it was decided not to pursue these options unless the THF did not perform as well. DCM was not selected as chlorinated solvents are harsh to handle as well there disposal is not as optimum as THF. Hexane was not pursued due to simplicity of changing the instrument from polar solvents to non-polar solvents which requires extended equilibrium times.

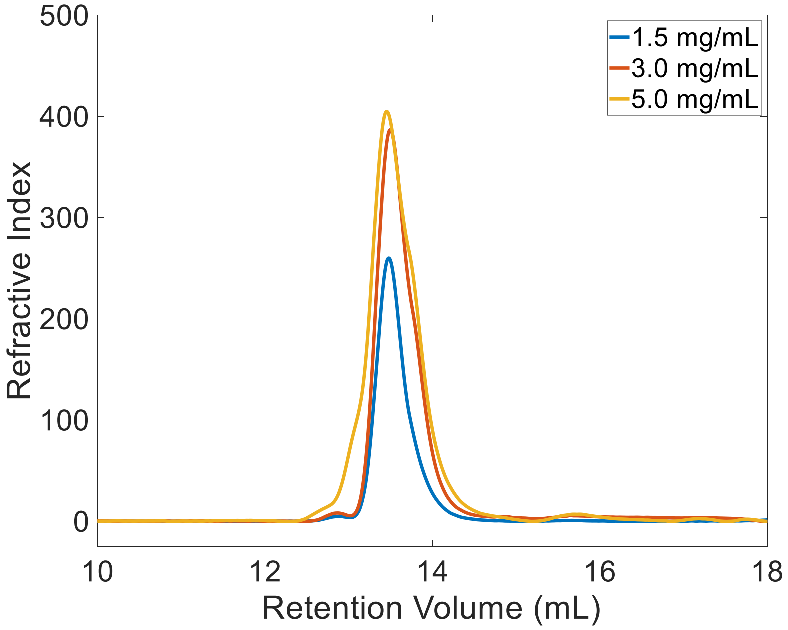

Figure 2. GPC results for analysis of Kraton G in THF at concentrations of 1.5, 3.0, and 5.0 mg/mL.

Figure 3A-C shows the GPC results for analysis of Oxy 461 in THF, EA, and acetone at concentrations of 1.5, 3, and 5 mg/mL. Again for brevity only the refractive index (RI) data is shown as this is the detector that is most affected by the mobile phase composition.

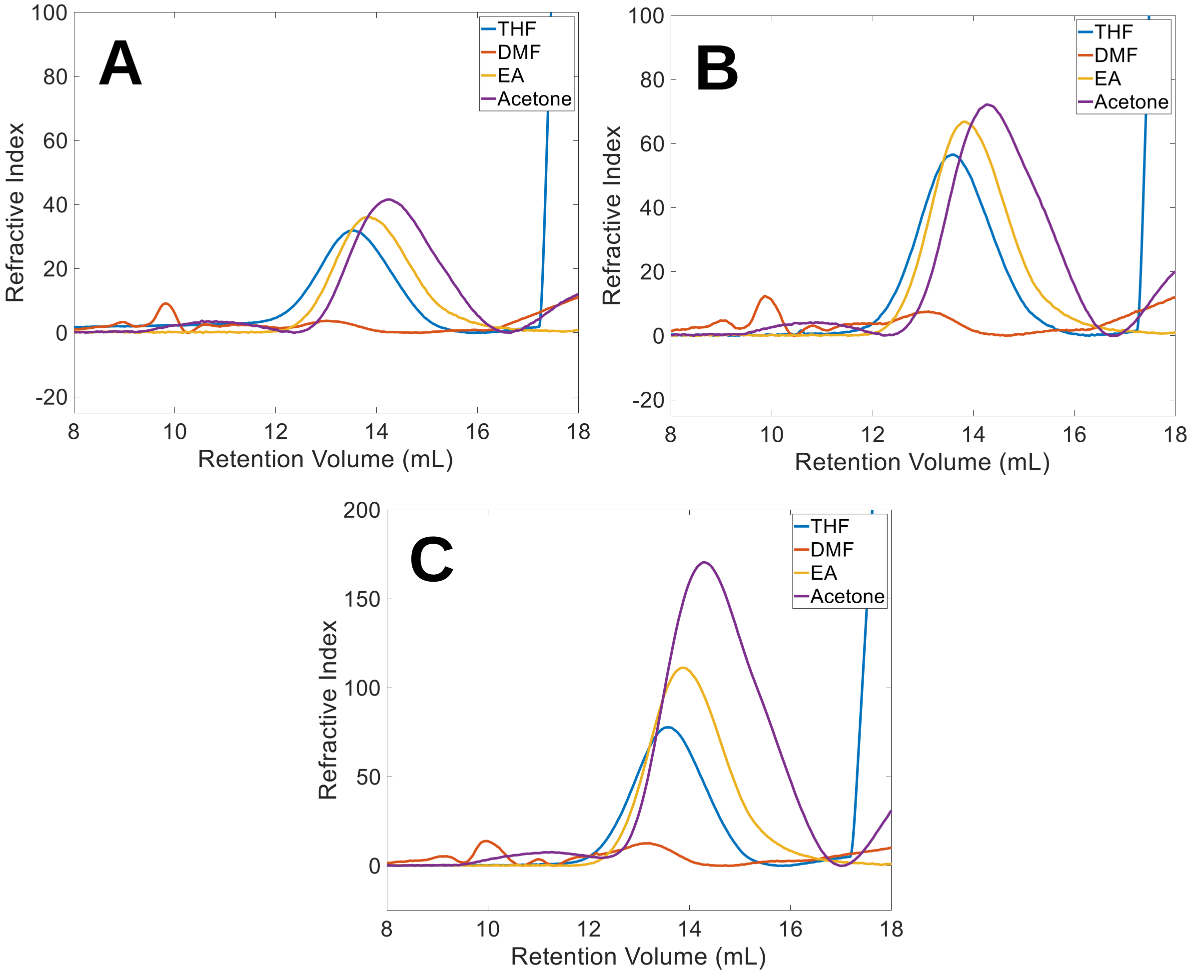

Figure 3. GPC results for analysis of Oxy 461 at concentrations of 1.5 (**A**), 3.0 (**B**), and 5.0 mg/mL (**C**) in THF, DMF, EA, and Acetone. While acetone gave the largest response, a separate broad peak appeared at 11 minutes which was not seen in the other solvents.

Based on the RI response for Oxy 461 in THF, DMF, EA, and acetone the optimum solvent for analysis is acetone. However, when acetone was used, a separate peak appeared at 11 minutes which was not seen in the other solvents. Nevertheless, all solvents results in adequate detector response with the exception of DMF. Thus while acetone may be the best solvent, THF or EA would also be acceptable.