

Comparison of Organic Components of Pre and Post Blast Smokeless Powders by HPLC



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Abstract

Black powder was once the frontrunner for use in homemade explosive devices, but now more smokeless powder substitutes are being used in place of black powder. Several components found in smokeless powders have low thermal stability, therefore high performance liquid chromatography (HPLC) can be used as an effective way of separating the different components found in a smokeless powder.

A gradient HPLC method, using a reverse phase octyl (C8) column, and UV detection can show separation of many components found in smokeless powders. The extracted smokeless powders were analyzed over a range of 210-400 nm, separating the range into five different wavelength channels.

Also, using this method a comparison can be made between pre-blast and post-blast samples taken from an explosion. Unburned and partially burned powder found among the bomb debris can be compared to samples of powder before the blast occurred. This can link the powder in the debris to the brand of powder, lot, or even a single can of powder based on morphology and specific component concentrations.

Introduction

The purpose of this research is to show how a simple gradient HPLC method can lead to the identification of several of the explosive and stabilizing components of many common smokeless powders. Also, it is the aim of this research to validate this method for the separation and identification of components in smokeless powders. Table 1 contains the components which were analyzed.

Table 1: Components Analyzed with abbreviations used and retention times (mins).¹⁻⁴

Component	RT	Component	RT
Dimethyl phthalate (DMP)	9.41	Methyl Centralite (MC)	18.65
Trinitrotoluene (TNT)	10.10	4-Nitrodiphenylamine (4N-DPA)	19.40
Nitroglycerin (NG)	11.01	Diphenylamine (DPA)	19.77
2,4-Dinitrotoluene (2,4-DNT)	11.61	2-Nitrodiphenylamine (2N-DPA)	22.19
2,6-Dinitrotoluene (2,6-DNT)	12.04	Ethyl Centralite (EC)	23.45
N-Nitrosodiphenylamine (Nn-DPA)	17.76	Dibutyl phthalate (DBP)	26.24

Also, a comparison will be made between a few of the smokeless powders before and after an explosion has occurred.

Methods and Materials

Smokeless Powder Extraction

Approximately 20 mg of each powder were placed into a capped centrifuge tube and 2.0 mL of solvent (25% butanol and 75% methanol) were added to the centrifuge tube. The solution was then vortexed for approximately 10 seconds and placed in an ultra sonic bath (1 hour). When ready for analysis, the extracted solutions were placed directly into standard GC vials with internal standard and methanol.

Standard Preparation

The standards were prepared using AccuStandard (New Haven, CT) Standards in methanol (S-9387-R3). The standard solution was initially diluted by 10:1 (MeOH:Standard). The diluted solution was then added to methanol to achieve the desired concentration. The standard solutions had concentrations of 150 µg, 112 µg, 75.0 µg, 37.5 µg, 20.0 µg, 15.0 µg, and 7.5 µg (NG 10 times the concentration of the other components). An internal standard of 2-naphthol was also added to the standards. The internal standard was prepared by dissolving 146.2 mg 2-naphthol in 100 mL of ethanol. The standard solutions, internal standard, and methanol were added to standard GC vials for analysis on the HPLC.

High Performance Liquid Chromatography

The smokeless powders were analyzed using a Varian ProStar/Dynamax System (#230 pump, #410 autosampler, and #330 DAD detector). The system was controlled by the Varian Star LC Workstation (ver. 5.52).

Peak areas from three subsequent injections were averaged then compared to the average peak area for the internal standard to generate peak ratios. The calibration curves generated using the internal standard method were then used to determine the concentration of each component present.

Table 2: HPLC experimental conditions.

Solvent Gradient	36 vol% MeOH/H ₂ O at 0 minutes to 80 vol% MeOH/H ₂ O at 25 minutes, hold for 11 minutes, Flow rate 1.0 mL/min
Column	Restek Pinnacle II C8, 150 x 4.66 mm, 5 µm particle
Detector	Wavelength Channels: 210 nm, 220-240 nm, 240-260 nm, 280-300 nm, and 390-400 nm

Post-Blast Sample Preparation

Small pipe bombs were made using 4 smokeless powders, which had already been analyzed. Approximately 40 g of powder were added to each pipe. The pipe bombs were 3/4" x 8" PVC pipe and were ignited with an electric match. The pipe bombs were detonated at the Eastern Kentucky University fire and explosive test facility.



Figure 1: A unexploded pipe bomb with an electric match in a 5 gallon bucket (left), and a 55 gallon barrel used to contain the explosion in a safe environment (right).

Approximately 10 mg of each powder were placed into a capped centrifuge tube and 1.0 mL of solvent (25% butanol and 75% methanol) was added to the centrifuge tube. The solution was then vortexed for approximately 10 seconds and placed in an ultra sonic bath (1 hour). The extracted solution was placed in the freezer to avoid evaporation until analyzed on the HPLC. When ready for analysis, the extracted solutions were placed directly into standard GC vials with internal standard and methanol.

Results

The method was validated using reference samples generously supplied by MacCrehan and NIST. The samples were analyzed and the determined values were compared to literature values. The amount of NG found in the reference materials can be found below.

Table 3: Experimental and Literature Values for % of NG in Reference Materials with uncertainties

Material	Avg. Results	Literature
1928-1	41.3 ± 1.9%	30.0 ± 0.4% ³
1928-2	26.7 ± 1.0%	19.9 ± 0.2% ³
NIST RM 8107	16.5 ± 6.0 %	13.0 ± 0.1% ⁴

All compounds listed in Table 1 could be quantitatively analyzed except for DBP. Calibration curves formed from the standards were used to determine the percent of each component in each smokeless powder. 68 double based and 46 single based powders were analyzed. The double based powders were separated into groups based on the amount of NG present found in Table 4.

Table 4: Number of double based powders with low, moderate, and high percentages of NG.

% Range of Nitroglycerin	Number of Samples
Low (<15%)	33
Moderate (15-30%)	31
High (> 30%)	4

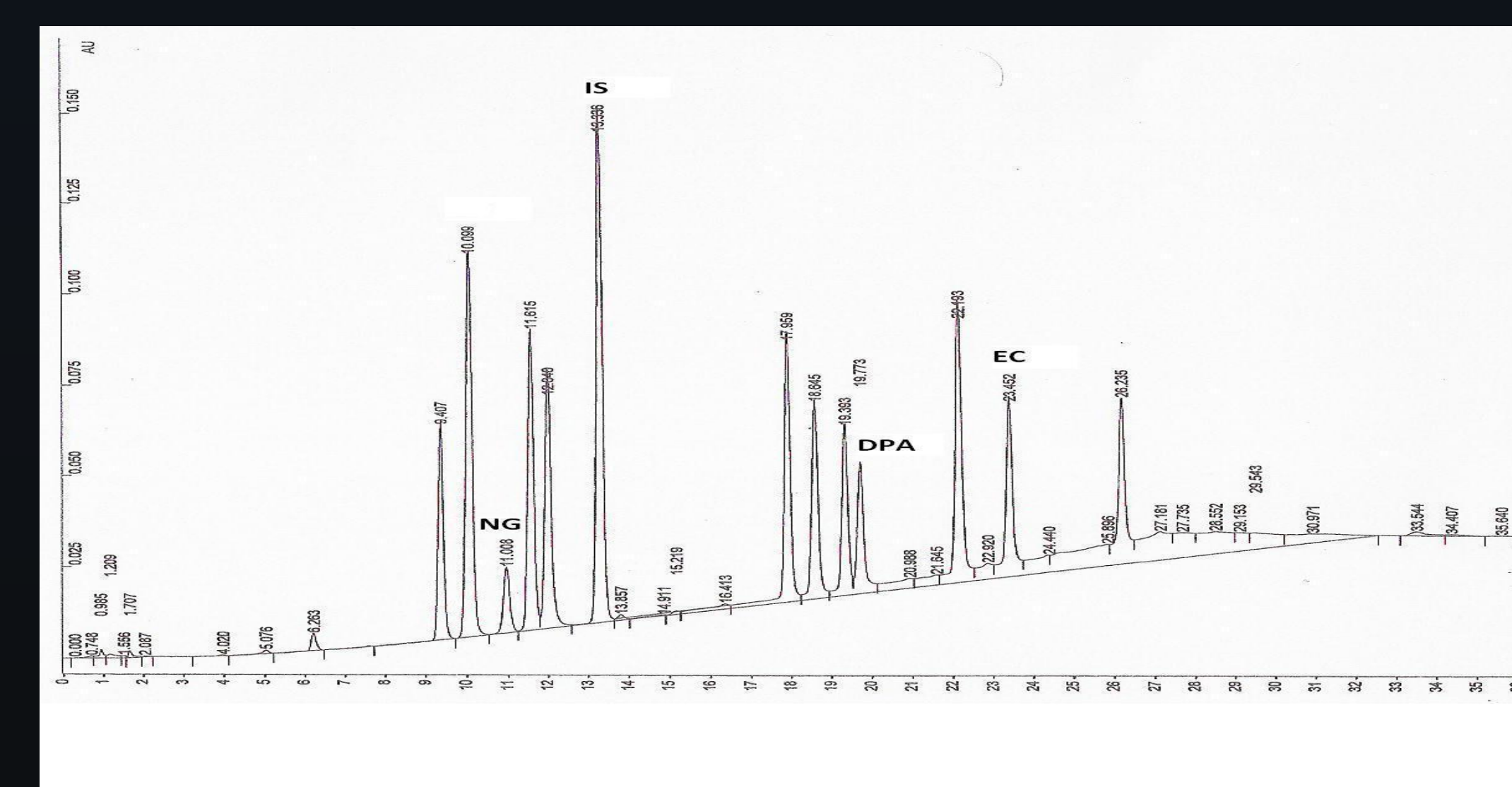


Figure 2: Representative Chromatogram of Standard Mix showing NG, internal standard, DPA, and EC (220-240 nm). Good baseline separation for all components tested.

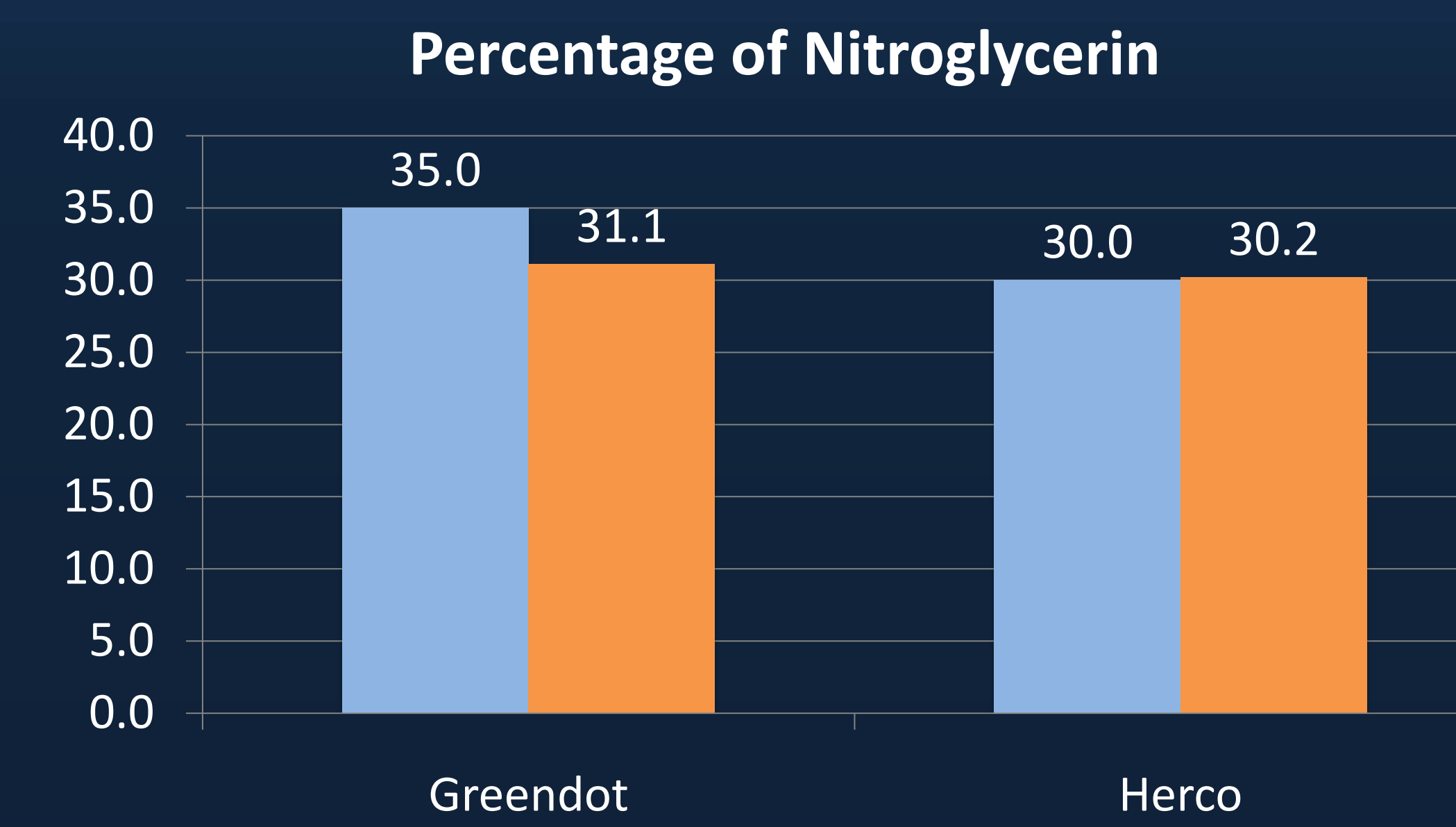


Figure 3: Percentage of NG found in Pre (Blue) and Post (Orange) Blast samples for the two double based powders tested.

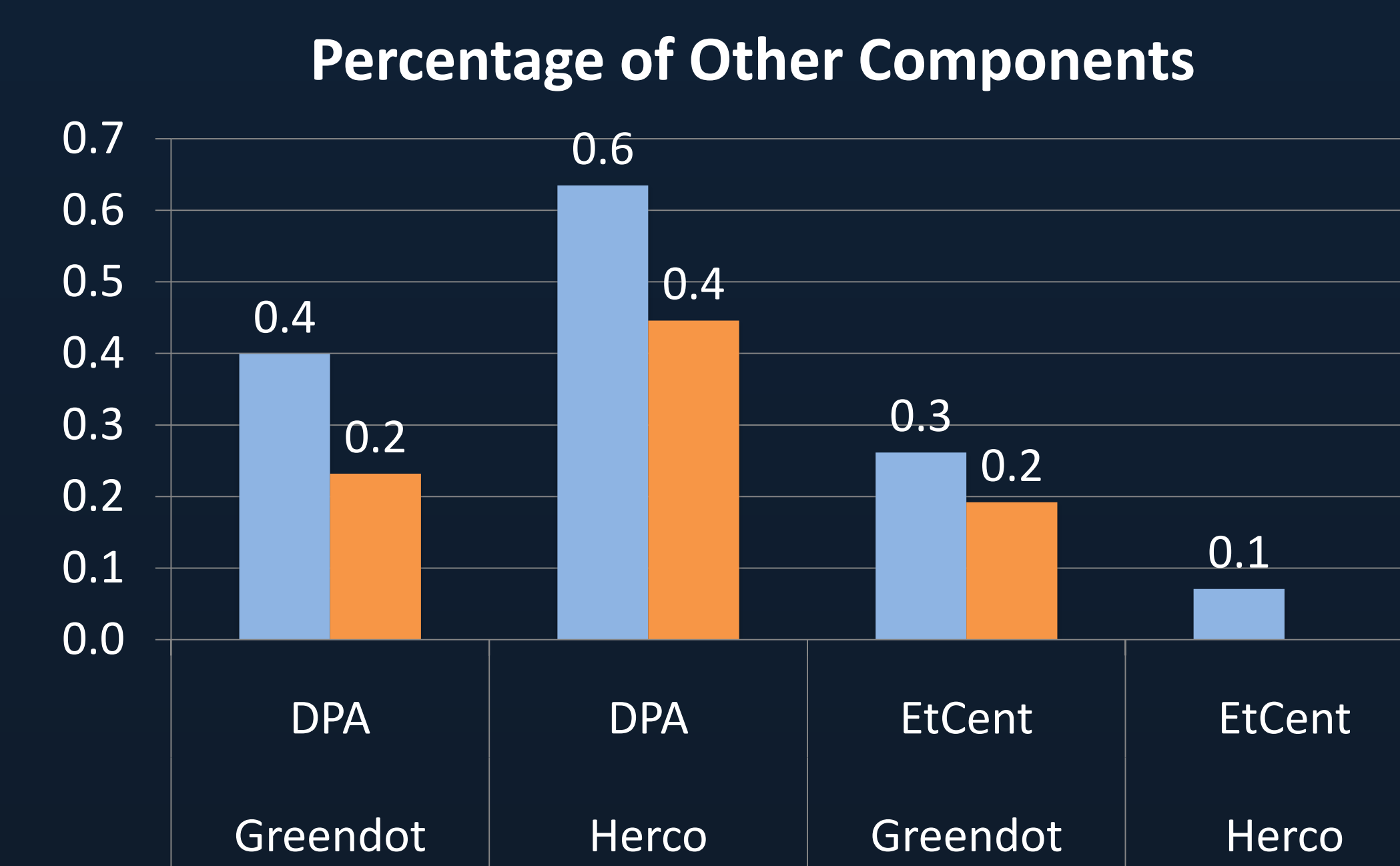


Figure 4: Percentage of other components found in Pre (Blue) and Post (Orange) Blast samples for the two double based powders.

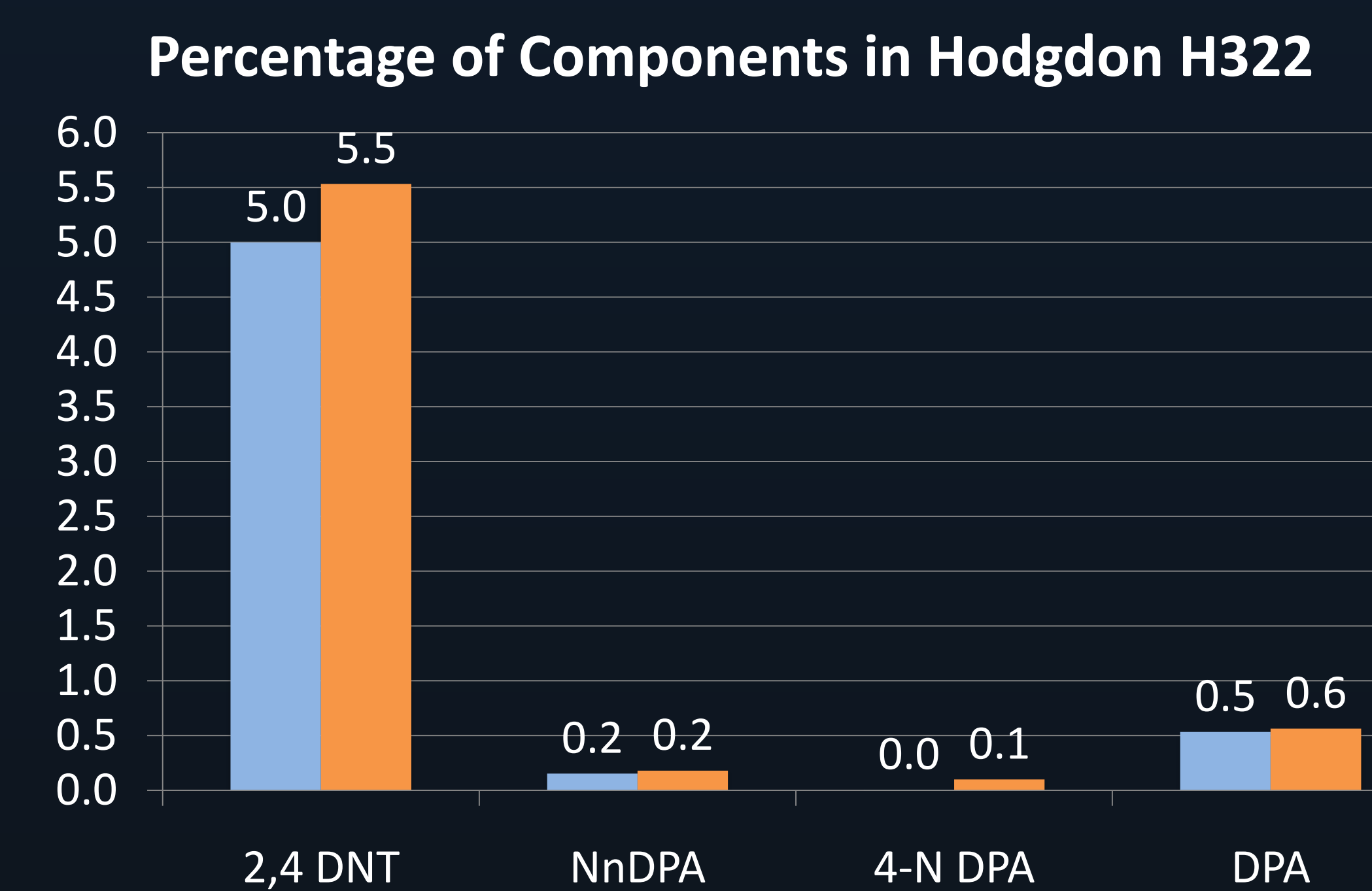


Figure 5: Percentage of components in Hodgdon H322 Powder in Pre (Blue) and Post (Orange) Blast samples.

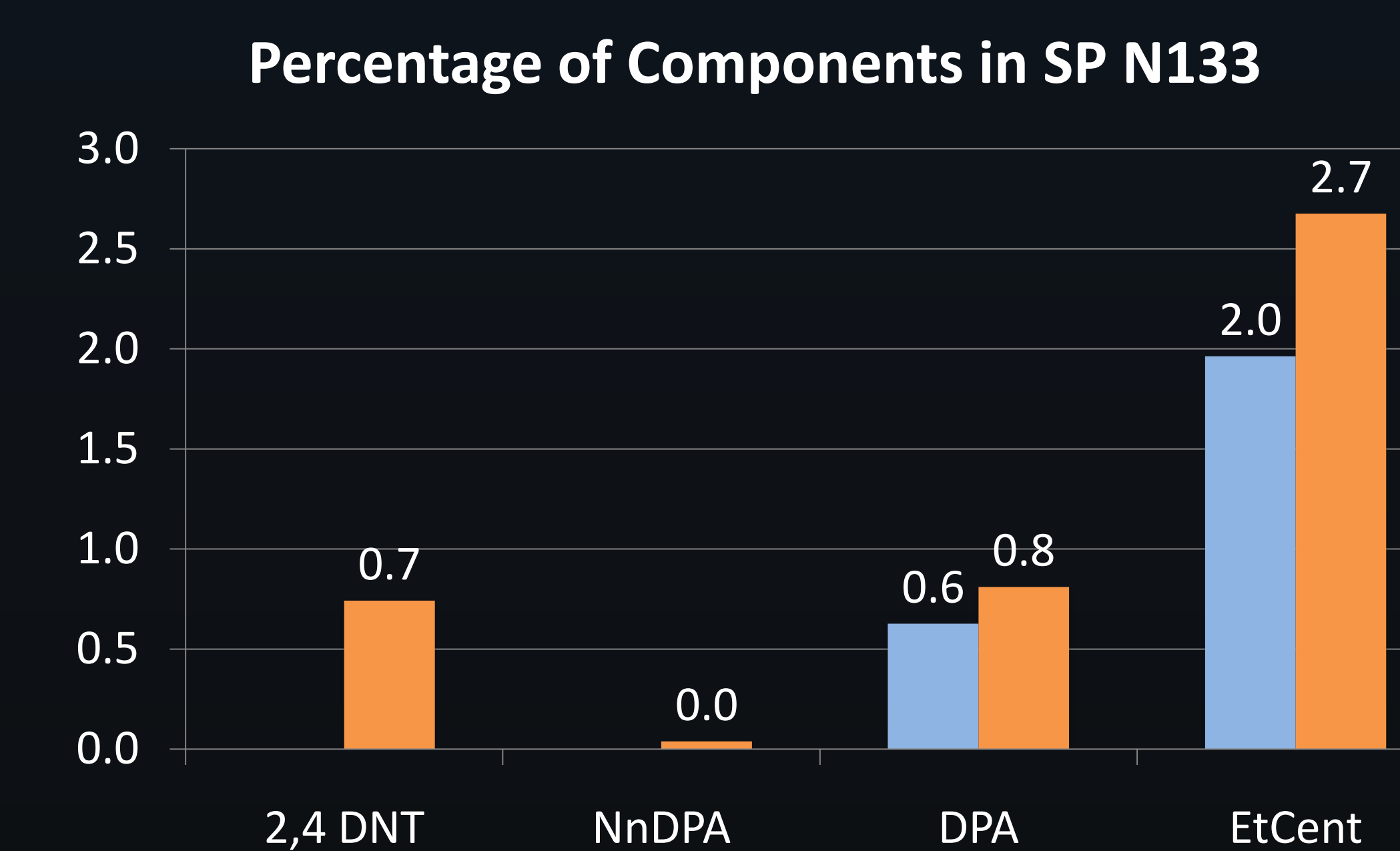


Figure 6: Percentage of components in SP N133 Powder in Pre (Blue) and Post (Orange) Blast samples.

Discussion

The results show that geometric isomers, such as 2,4-DNT and 2,6-DNT, can be fairly well separated. In the double-based powders the four most common components were NG, DPA, Nn-DPA, and EC. The major components of the single-based powders were 2,4-DNT, Nn-DPA, and DPA. The percentage of DBP could not be calculated because the standards would not produce consistent results. The percent relative standard deviation of the DBP samples ranged from 10% to over 100%.

This simple HPLC method was also used to compare pre-blast and post-blast samples to see if a match could be made after an explosion has taken place. The Greendot powder showed the major components of NG, DPA, and EC, which were all present before and after the blast occurred in approximately the same percentage. The post-blast sample showed some of the minor components being present but all were in a concentration of less than 0.1% of the powder. This could be due to some of the powder being partially burned rather than not burned at all. Also, the 2,4-DNT present in the Greendot could be due to contamination from a single-based sample because it was only present in one out of the three post-blast samples. The Herco powder showed similar results to the Greendot; the two major components of NG and DPA were present in both samples in approximately the same percentage. The Hodgdon H322 showed the best results when comparing the pre-blast to post-blast samples. All the components, whether major or minor, that were present in the pre-blast sample were also present in the post-blast sample in almost exactly the same percentage. Smokeless powder N133 also showed a similar match between the pre-blast and post-blast samples for the major components of DPA and EC.

Conclusion

The results of this research show that by using a simple extraction procedure followed by a reverse phase gradient HPLC method, several of the explosive and stabilizing components of smokeless powders can be analyzed. Also, this research shows that this same method can be used to compare pre-blast and post-blast samples in explosive debris. By using the internal standard method, a percentage of the original powder can be determined.

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