Nitrocellulose-Based Propellant Analysis Technical Procedure Validation Summary

Scope: The goal of this study was to perform additional validation activities for the Explosives Unit (EU) Nitrocellulose-Based Propellant Analysis technical procedure that was previously validated under prior FBI Laboratory Quality System requirements. Therefore, only the below performance characteristics were targeted. Additional method optimization tasks were performed outside the scope of the validation performance characteristics.

- Accuracy
- Matrix Effects/Interferences (Selectivity)
- Limit of Detection
- Processed Sample Stability
- Repeatability/Ruggedness

The following powders were utilized throughout the validation:

- Ref #70 – Norma R1 – rod – diphenylamine (DPA), trinitrotoluene (TNT), ethyl centralite (EC), 2-nitroDPA, diisopentylphthalate
- Ref #218 – Hercules RL-7 – perforated disc – NG, DPA, EC, dibutylphthalate, 2-nitroDPA, 4-nitroDPA
- Ref #436 – Hercules Red Dot* – disc – NG, DPA, EC, 2-nitroDPA
- Ref #742 – Accurate 2230 – ball/flattened ball - NG, DPA, methyl centralite (MC), dibutylphthalate, 2-nitroDPA
- Ref #769 – IMR4007SSC – perforated rod – MC, EC
- Ref #827 – Vectan A0* – lamel – 2,6-dinitrotoluene (DNT), 2,4-DNT, DPA
- Blackhorn 209

*Hercules Red Dot and Vectan A0 were selected because they have different colored marker grains.

The following solvent was used throughout the validation, unless otherwise noted:

- Methylene chloride spiked with undecane at 40 ppm

All data was normalized to undecane as the internal standard. All validation tasks also included the use of Hodgdon HS-7 (Ref #365) as a positive control.

Validation Tasks:

1. Literature Review Part 1: Compounds of interest were reviewed to determine any that were missing or no longer useful. Those with an asterisk were utilized in other components in this study due to their uniqueness or importance in nitrocellulose (NC)-based propellants.

Akardite II		2,4-DNT	DPA*
Methyl centralite*	Diethyl phthalate	2,6-DNT	2-NitroDPA
Ethyl centralite*	Diisobutyl phthalate	4-Nitrotoluene	4-NitroDPA
NG*	Diisopentyl phthalate	2-Nitroresorcinol	4-NitrosoDPA
Camphor	Dimethyl phthalate	Carbazole	Triacetin
	Diphenyl phthalate	Phenoxazine	

Results: Phenoxazine was removed as a targeted component as little information exists in literature to support it being an additive in NC-based propellants.

2. Literature Review Part 2: Literature was reviewed to determine if methylene chloride is the best solvent choice for the extraction process or if other common organic solvents could be used as a replacement.

   Results: While some alcohols (mostly methanol and ethanol) could be replacement candidates for methylene chloride in the extraction procedure, they will not be utilized as they have the tendency to readily absorb water over time. It is preferential for this procedure to utilize dry solvents, if possible. Also, methylene chloride allows for the removal of propellant additives while leaving nitrocellulose behind.

3. Mass to Solvent Ratio: The goal of this task was to determine the most effective powder mass to solvent ratio for extractions when targeting NG, MC, EC, or DPA for a fixed extraction time (3 hours). This task was also used to determine if there are optimum ratio differences for specific grain morphologies. The heaviest grain mass (IMR4007SSC, Ref #769) was used as the baseline mass at ~1.5 mg, and additional grains were added for all remaining powders until approximately the same mass was reached. This process was repeated for a baseline mass of ~3 mg (2 grains of Ref #769). Volumes considered included 150 µL, 200 µL, and 300 µL.

   Results: The selected mass to solvent ratio is approximately 3 mg (~2-10 grains) extracted in 150 µL methylene chloride. This ratio uses small sample size and allowed for an effective extraction of NC-based propellant additives for all grain morphologies. This ratio was selected based on comparing normalized data from all extraction procedures. For each powder used in the experiment, the major component with the greatest amount (i.e., signal response) was selected then compared across all experiments. A graph with all powders and all components was constructed from these data, and the resultant experiment which extracted the most major components for all powders overall was selected as most efficient (i.e., 2 to 1 grain ratio, 150 µL volume).

4. Extraction Time: The goal of this task was to determine the effect of extraction time on concentration (signal intensity) of NG, MC, EC, and DPA for a given powder. This task was also used to determine if there are optimum extraction time differences for specific grain morphologies. Approximately 3 mg of each powder was extracted in 150 µL for 1, 3, and 5 hours and analyzed. The 6-hour extraction time was omitted because the data for 1, 3, and 5 hours showed that additional extraction time increased the peak intensities for minor components while only small increases were produced for major components.

   Results: A 1 hour extraction time was the minimum extraction time that allowed for an effective extraction of NC-based propellant additives for all grain morphologies. Additional extraction time increased the peak intensities for minor components while only small increases for major components occurred. Increased extraction time of ~5 hours should be considered for powder comparisons with minor components.

5. Extraction Efficiency: The goal of this task was to determine if any additives remain in the powder based on two serial extractions on the same powder sample. Approximately 3 mg of each powder was extracted in 150 µL for 1 hour followed by a second extraction of the same sample in 150 µL for another hour.

   Results: It was determined that the extraction is not 100% efficient. The major components were consistently identified in both extractions of the same sample. Minor components were identified in the first extract but not necessarily in the second (or reduced peak intensities were observed).

6. Effect of Grain Morphology Dissolution on Extractions: The goal of this task was to determine the effect of grain morphology on extraction effectiveness. Each powder was placed in acetone for 16 hours (overnight) in a capped test tube to deform the grain morphology. The acetone-extracted material was then dried and extracted in 150 µL methylene chloride for 1 hour.

   Results: Dissolution of the grain morphology prior to methylene chloride extraction yielded increased peak intensities compared to extraction of the intact grains. However, the major chemical components were identifiable in both.

7. Processed Sample Stability: The goal of this task was to determine the stability of extracts over an extended period in the event casework extracts cannot be immediately analyzed. A 30 mg sample each of HS-7 (double-base) and Ref #70 (single base) was extracted with 1500 µL methylene chloride for 1 hour. Aliquots of 150 µL were transferred to separate autosampler vials prior to analysis and storage. When not being analyzed, the vials were stored at room temperature on the lab bench for the duration of the study (avoiding direct sunlight or any sources of heat). The average responses for analytes of interest were used to evaluate any significant changes over the duration of the study (Day 0, Day 1, Day 4, Day 7, Day 10, Day 15, Day 30).

   Results: The target analytes were stable in both powders for the duration of the study through 30 days.

8. FTIR analysis: The goal of this task was to document the ability to differentiate between powders containing nitrocellulose and those with other additives that are not soluble in methylene chloride (e.g., guanidine nitrate). Extracted grains from each powder were dried and analyzed using FTIR with relevant positive controls. Additionally, crude Blackhorn 209 grains and the insoluble material after extraction was measured on FTIR using the extraction parameters from task 4.

   Results: The procedure effectively differentiated between powders containing nitrocellulose and those with other additives that are not soluble in methylene chloride (e.g., guanidine nitrate). It was determined that approximately 50% of the Blackhorn 209 grains contain guanidine nitrate

(detectable in both the crude and post-extracted grains). Therefore, FTIR analysis of more than one grain may be necessary to detect guanidine nitrate.

Specifically, assuming the grains are uniformly mixed, the two grain types are visually indistinguishable, each is present at 50%, and grains are randomly selected:

The probability of detecting it = (1- the probability of not detecting it) = $\mathbf{1 - (0.5^{x})}$ where x is the number of grains.

These probabilities are:

# of grains examined (x)	Probability of detecting guanidine nitrate
1	50%
2	75%
3	87.5%
4	93.75%
5	96.88%
6	98.44%
7	99.22%
8	99.61%
9	99.80%
10	99.90%

Sample size permitting, up to 10 grains should be examined if guanidine nitrate is not detected. There is only ~1:1000 chance of observing that outcome if this component is actually present in the powder.

9. Accuracy: The NC-Based Propellant Analysis technical procedure uses a qualitative method without measured values to be used for accuracy determination as a percent difference. Therefore, accuracy will be measured via task #8 (accurately differentiate between powders), task #10 (accurately differentiate neat standards using retention time and mass spectra), and task #12 (black box study).

   Results: The extraction procedure of ~3 mg sample in 150 µL methylene chloride for 1 hour for GC/MS followed by FTIR analysis of the methylene chloride insoluble material will generate accurate results. Specifically, the extraction process effectively removes NG and other additives such that methylene chloride-insoluble components (e.g., guanidine nitrate) can be detected by FTIR. Of note, this procedure allows for the differentiation between smokeless powder and other NC-based propellants such as Blackhorn 209. In addition, the existing GC/MS method can

accurately differentiate target components. Lastly, a sampling of five test participants accurately followed the procedure and generated the expected results.

10. Matrix Effects/Interferences (Selectivity): Matrix effects do not apply to this procedure as it does not involve co-extraction of different matrices. Therefore, neat standards of potentially interfering compounds were analyzed to test for interferences. Specifically, the individual components in the Smokeless Powder Standard Mix #1 and Smokeless Powder Standard Mix #2 were be analyzed.

    The Smokeless Powder Standard Mix #1 is a 50 ppm solution of camphor, 4-NT, triacetin, 2,6-DNT, 2,4-DNT, diethyl phthalate, diphenylamine, methyl centralite, ethyl centralite, dibutyl phthalate, 2-nitrodiphenylamine, akardite II (3-methyl-1,1-diphenyl urea), 4-nitrosodiphenylamine, dipentyl phthalate, 4-nitrodiphenylamine, and diphenylphthalate in methylene chloride.

    The Smokeless Powder Standard Mix #2 is a 50 ppm solution of 2-nitroresorcinol, dimethyl phthalate, diisobutyl phthalate, carbazole, and diisopentyl phthalate in methylene chloride. Carbanilide (1,3-diphenyl urea) may be added as an optional component in Smokeless Powder Standard Mix #2 or used as an individual standard.

    Results: Although the manufacturer considers the DB-5MS and HP-5MS columns technically equivalent, carbazole and diisobutyl phthalate coelute when the HP-5MS column is used. These components can generally still be differentiated via mass spectral data with background subtractions. However, it is recommended that the DB-5MS column be used for NC-based propellant analysis.

11. Limit of Detection (LOD): Serial dilutions of each individual component in the Smokeless Powder Standard Mix #1 and Smokeless Powder Standard Mix #2 were analyzed. The LOD was defined as the lowest concentration (or amount) of an analyte that reproducibly yields a signal greater than or equal to 3x the noise level of the background signal.

    Results: The LOD ranged from 1-50 ng depending on the target compound and specific column/instrument used. The most common NC-based propellant additives (MC, EC, DPA) were reliably identified at a minimum of 10 ng.

12. Repeatability/Ruggedness: A final black box study was used to assess the repeatability/ruggedness of the method. Repeatability by a single analyst (minimum three times) was accomplished by tasks #3 through #5. Five explosive chemistry personnel (chemists and examiners) were instructed to analyze three powder samples of known compositions. The analysis results were compared to the expected answers and between participants.

    Results: All the data produced by the participants met the expected results. Data interpretation issues were noted; however, these did not affect the actual results. The test results support the validation findings regarding the suggested extraction procedure: 2 to 10 grains of powder (approximately 3 mg) extracted with 150 µL of methylene chloride for 1 hour.