Standoff LIBS: Classification of hazardous residues on painted surfaces

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

Frank De Lucia, Jr., Jennifer L. Gottfried, and Andrzej W. Miziolek
U.S. Army Research Laboratory,
Aberdeen Proving Ground, Md. 21005
frank.c.delucia.civ@mail.mil
July 2011
NASLIBS 2011 Clearwater Beach, Florida

UNCLASSIFIED

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
JUL 2011		**00-00-2011 to 00-00-2011**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Standoff LIBS: Classification of hazardous residues on painted surfaces	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **U.S. Army Research Laboratory,Aberdeen Proving Ground,MD,21005**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
Presented the North American Symposium on LIBS, (Laser Induced Breakdown Spectroscopy), Clearwater Beach, FL, 18-20 July, 2011

14. ABSTRACT

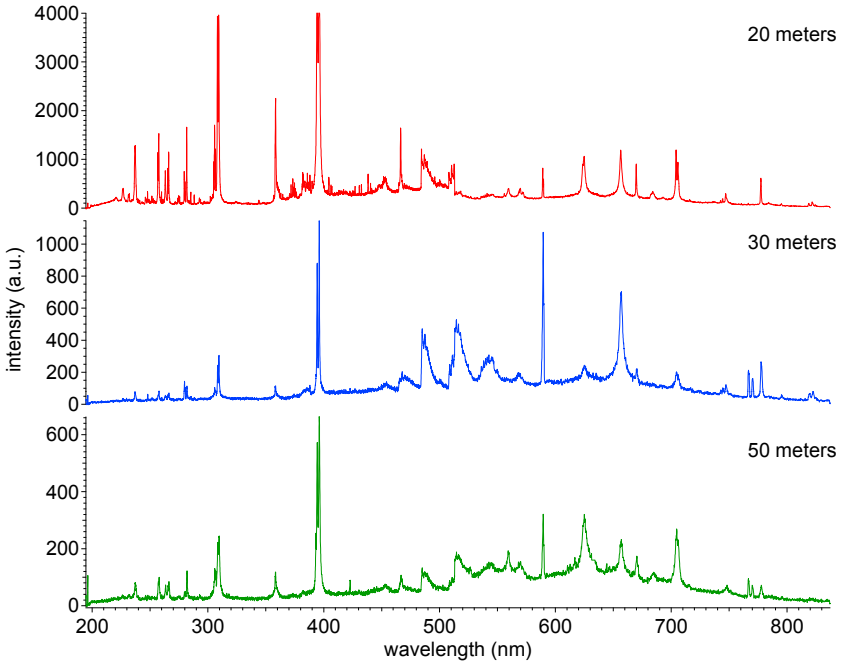
15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**21**	

Introduction

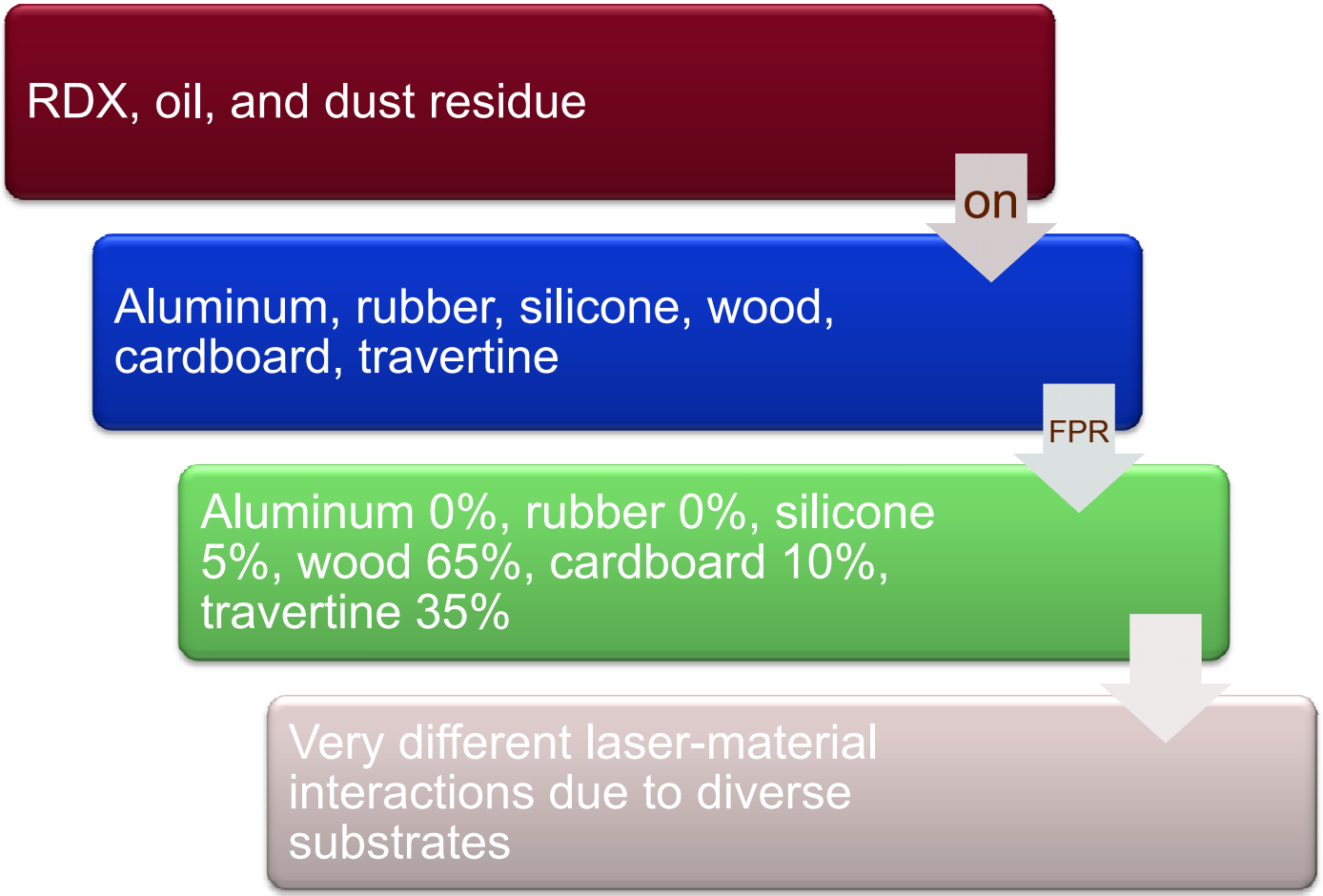
- Standoff LIBS at ARL
- Analysis of painted surfaces
- Multivariate analysis of residues on painted surfaces
- Conclusions

Standoff LIBS at ARL



	# samples
explosives	603/695
TPR	**87%**
non-explosives	4/320
FPR	**1.2%**

Residues on different substrates



Gottfried, J.L., et al., J. Anal. At. Spectrom. 2009, 24, 288-296

Goal

Classify explosive residues on substrates with similar compositions

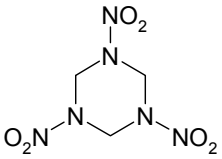
- Minimize differences in laser-material interaction
- Increase number of samples analyzed
- Collect at standoff distance

Use painted surfaces

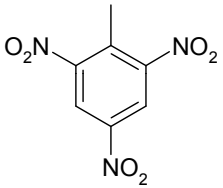
- Contain organic components; C, H, N, and O
- Different colors will have additional additive components
- Surface roughness, porosity, and hardness more consistent

Samples/substrates

Explosives



RDX - $C_3H_6N_6O_6$

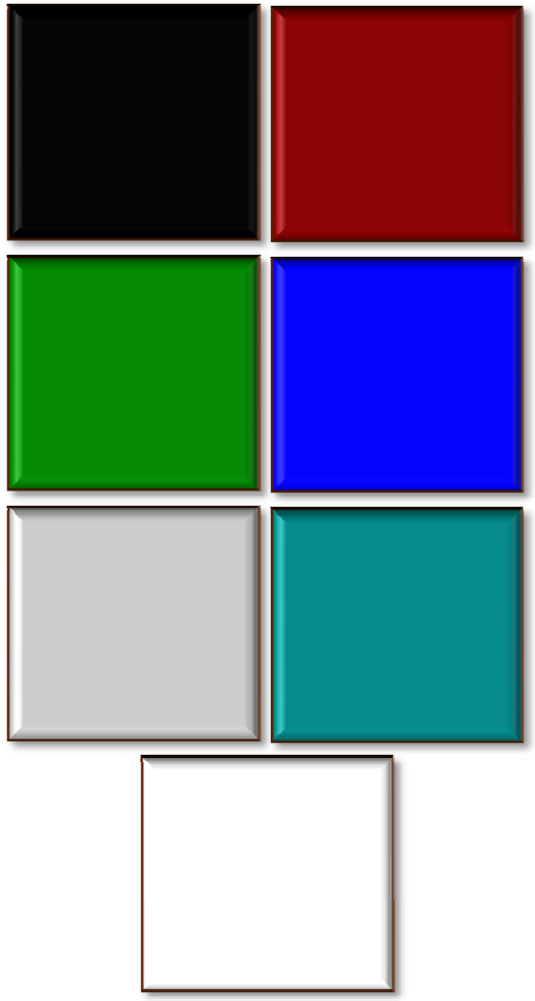


TNT - $C_7H_5N_3O_6$

Non-explosives

Road dust
Sand
Oil
Fingerprints
Blank

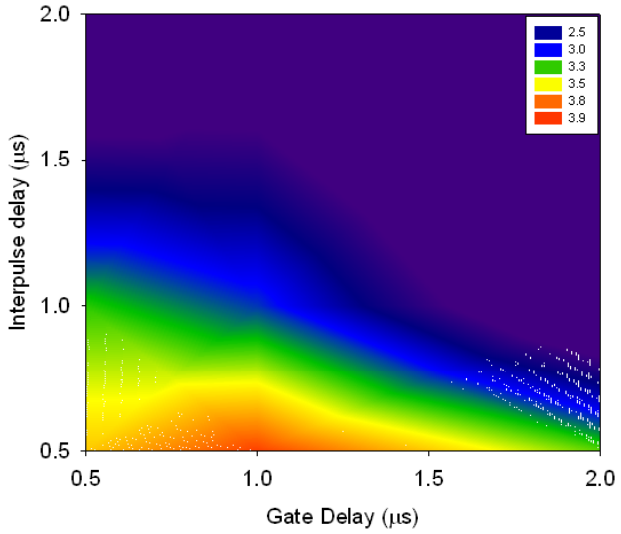
Painted Surfaces



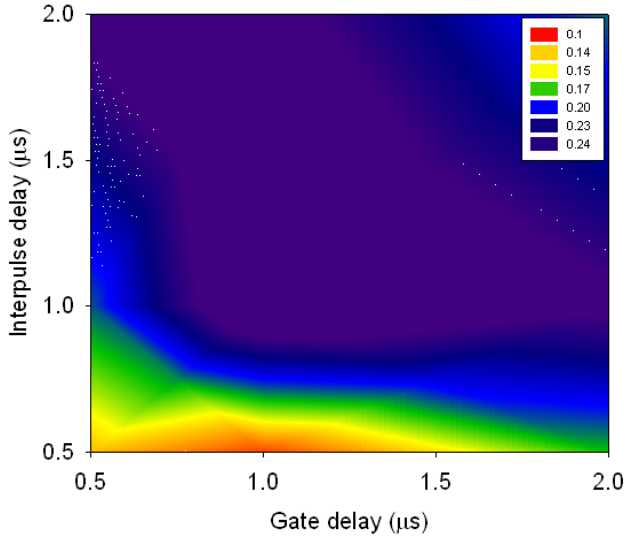
TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

LIBS experiment

- Laser parameters
  - 1064 nm
  - 335 mJ/ pulse
  - double pulse
- Optimal timing
  - 0.5 μs delay
  - 1 μs interpulse
- 25-30 meters



SNR
Signal to noise ratio



RMSEC
Root mean squared error of calibration

Painted surface classification

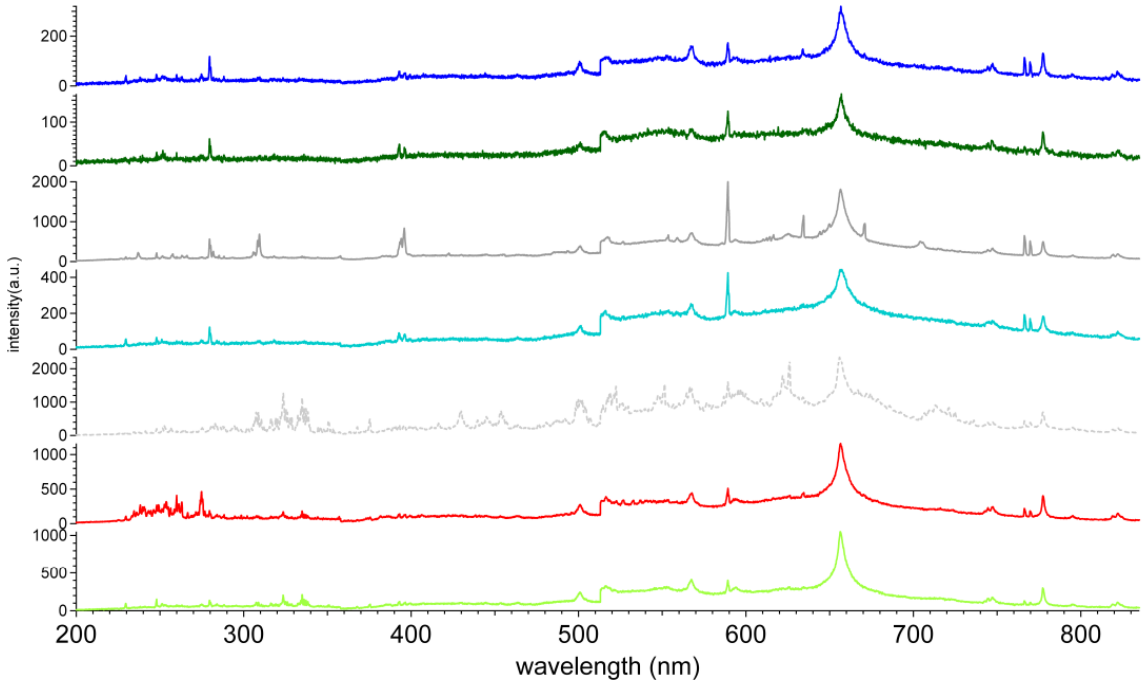
Partial least squares discriminant analysis (PLS-DA)

- Supervised, inverse least squares discrimination method
- Generates predictor variables used to classify
- Finds maximum separation between classes

Collected LIBS spectra

- Model: 495 samples
  - Whole spectra used as variable input
  - 7 classes (based on color)
  - Optimal number of latent variables determined (40)
- Validation: 213 samples

LIBS spectra of painted surfaces



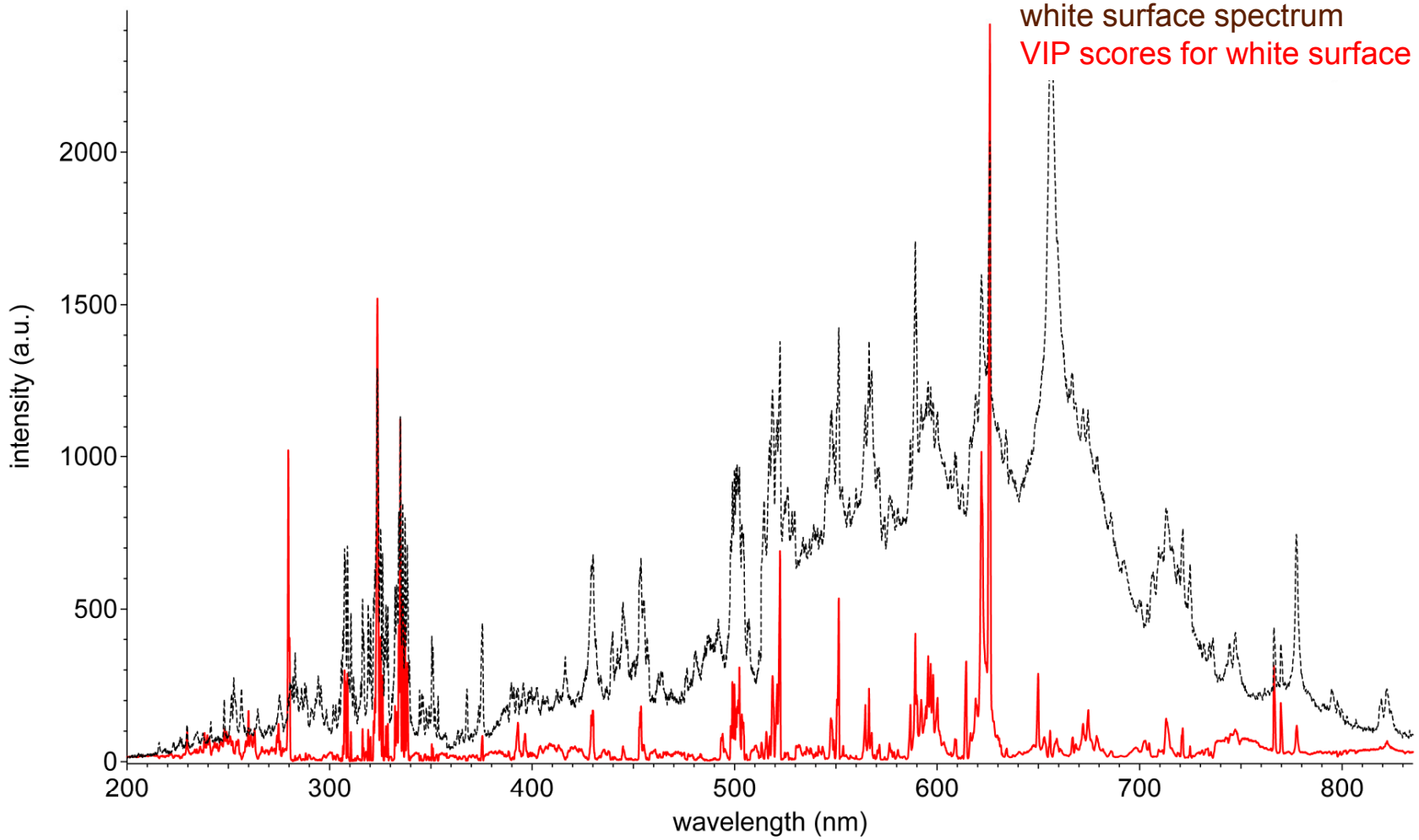
Determine probability of each test sample

- Classified: >75% belongs to correct class
- Misclassified: >75% belongs to incorrect class
- Unclassified: >75% belongs to multiple classes

PLS-DA results

	Classified	Misclassified	Unclassified
Black	97%	0%	3%
Blue	93%	0%	7%
Dark green	97%	0%	3%
Silver	100%	0%	0%
Teal	100%	0%	0%
Red	100%	0%	0%
White	100%	0%	0%
All	**98%**	**0%**	**2%**

Variable importance in projection (VIP) scores



Residues on painted surface

PLS-DA model: 414 spectra	Three PLS-DA models	Model classes based on residue not color
• 69 RDX • 25 TNT • 70 blank surfaces • 70 oil • 60 dust • 60 fingerprints • 60 sand	• Whole spectra • Intensity and ratios • “Fused”	• Explosive • Blank • Oil • Dust • Fingerprints • Sand

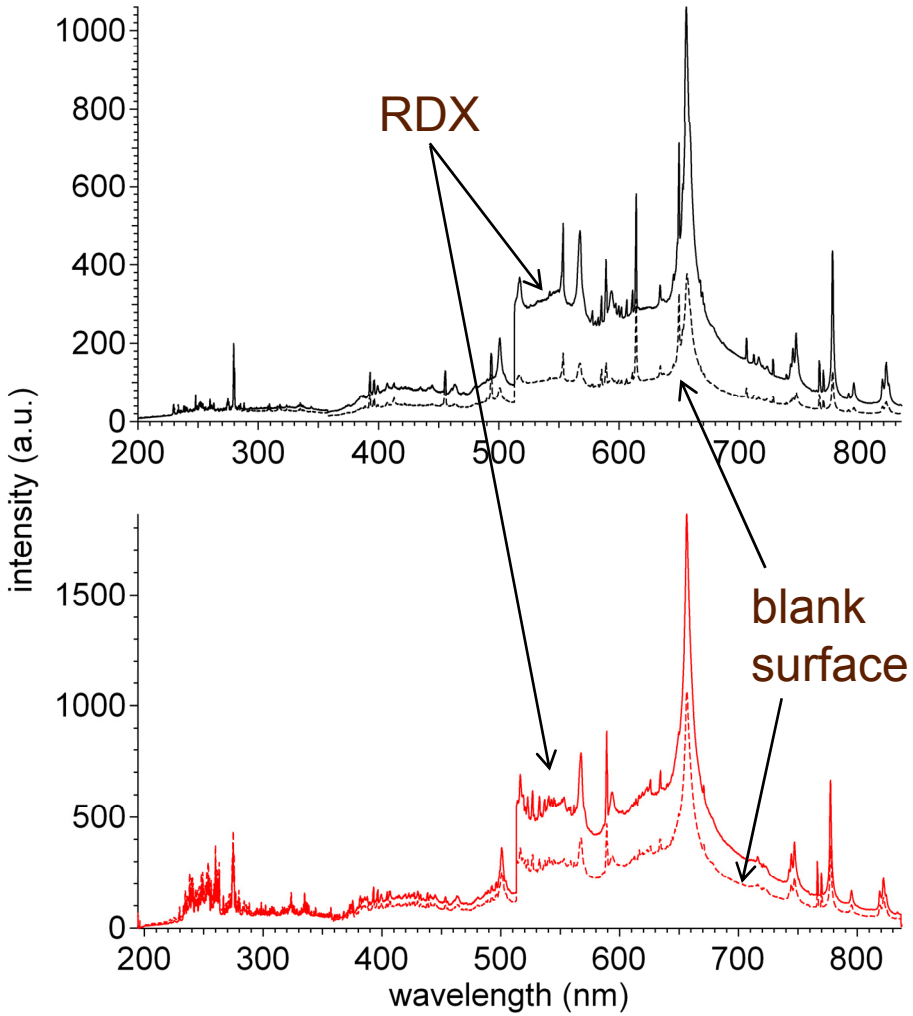
Whole spectra model

850 test samples

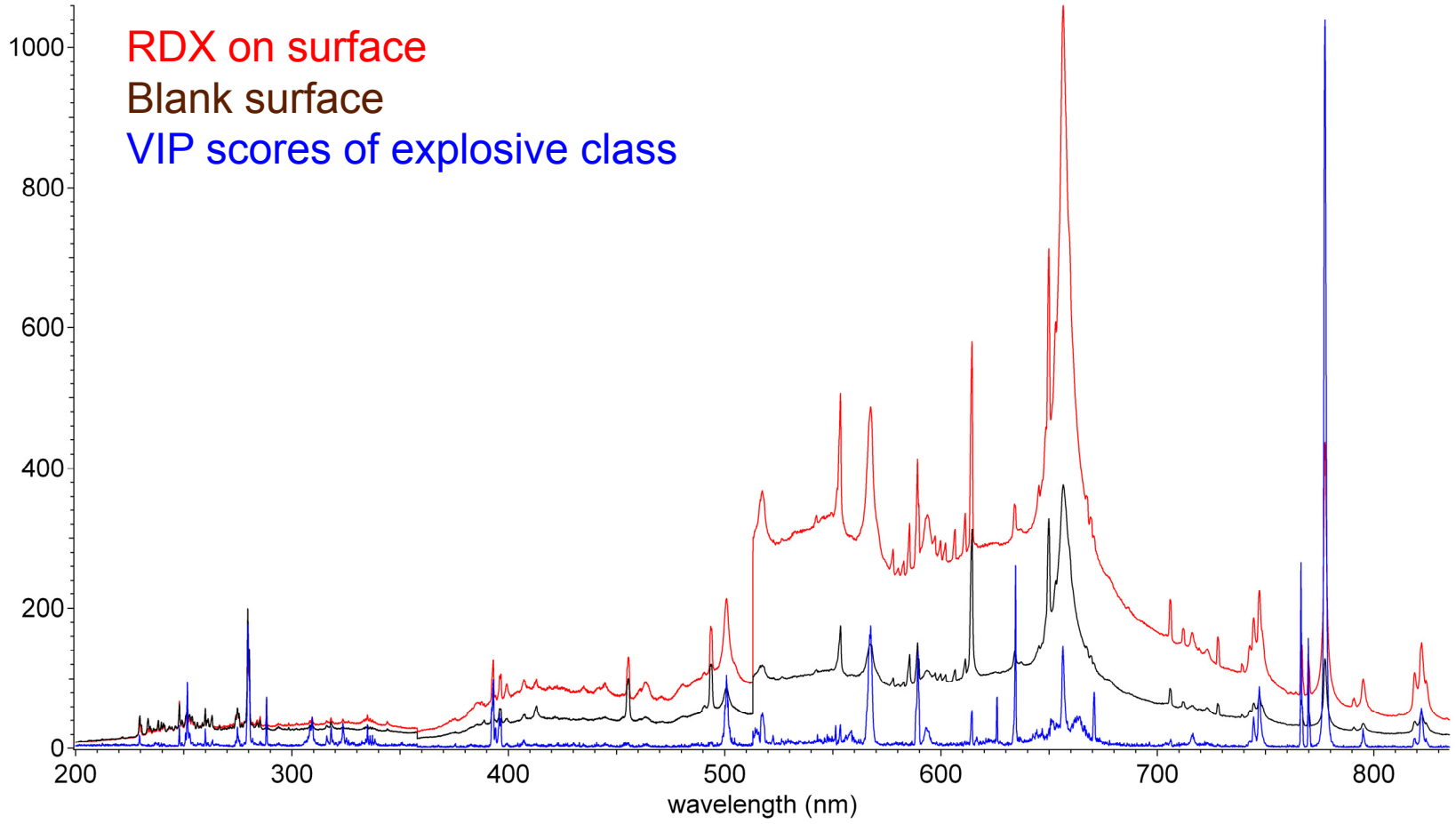
- 210 explosives
- 640 non-explosives

Probability >75% sample belongs to explosive class

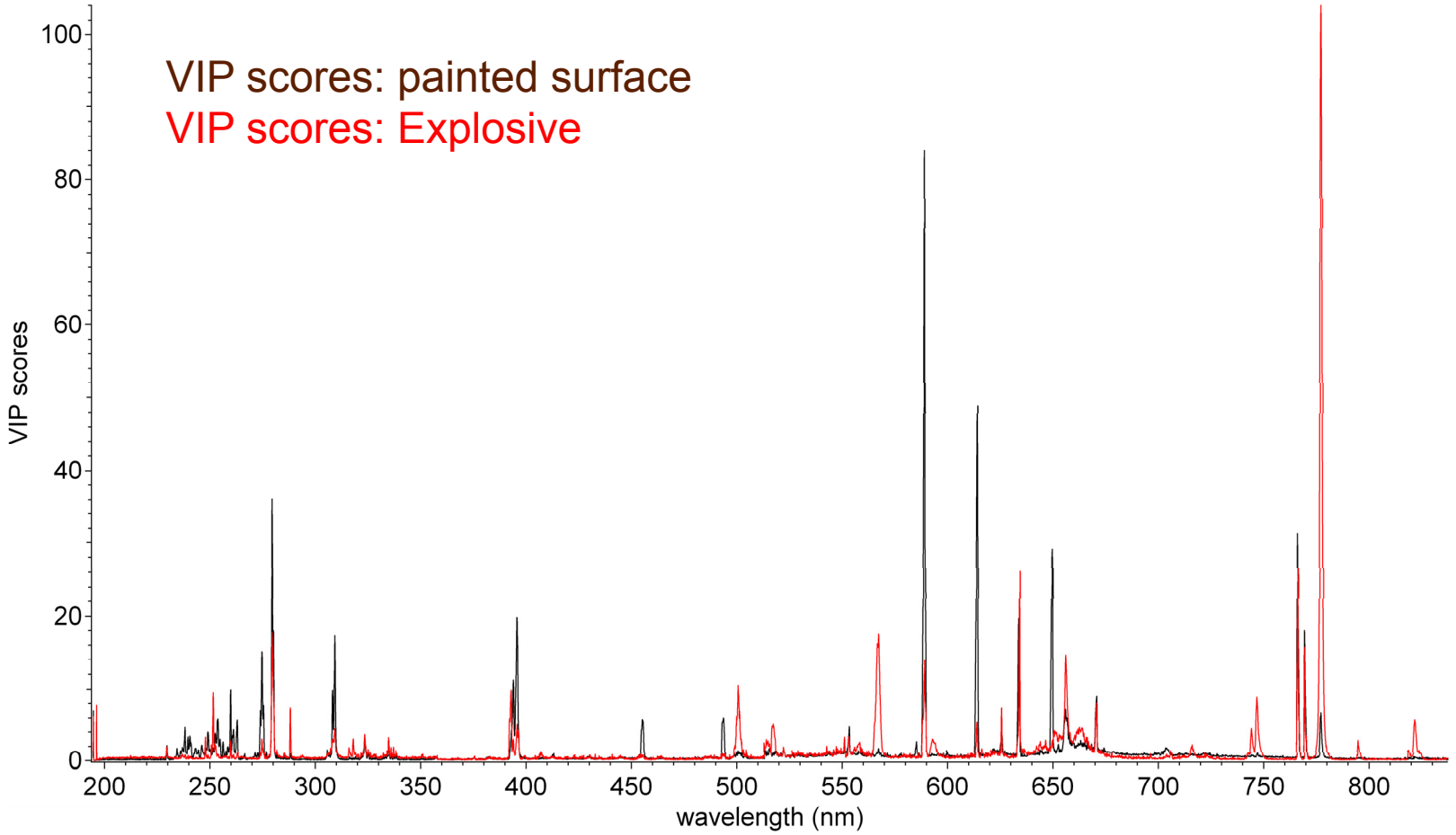
TPR 99.5% and FPR 3.1%



VIP scores



VIP scores: explosive class vs. color class



Selected intensities and ratios model

3800 test samples

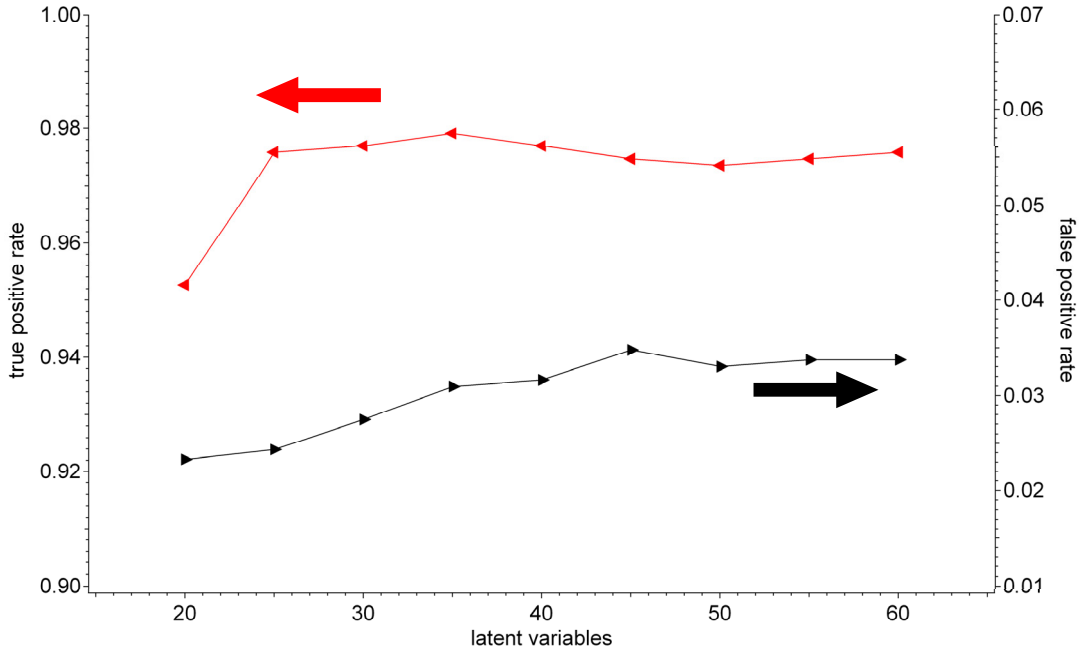
- 908 explosives
- 2876 non-explosives

Used intensities and ratios

- C,H,N and O
- C_2 and CN
- ratios based on non-linear combinations of intensities

TPR 97-98%

FPR 2.5-3.5%



More testing

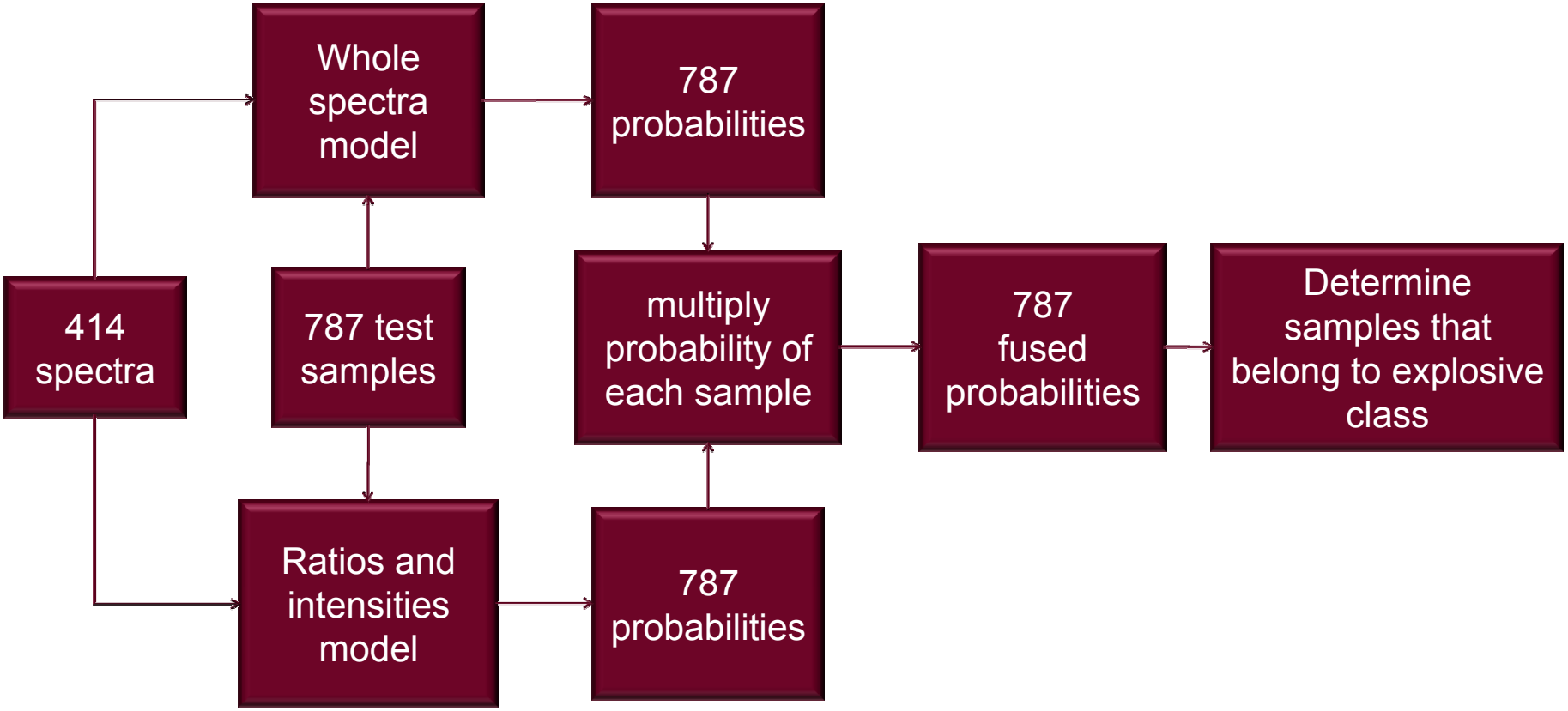
Further tested intensities and ratios model using samples not included in model

- Composition-B (36% TNT, 63% RDX, 1% wax)
- Diesel fuel

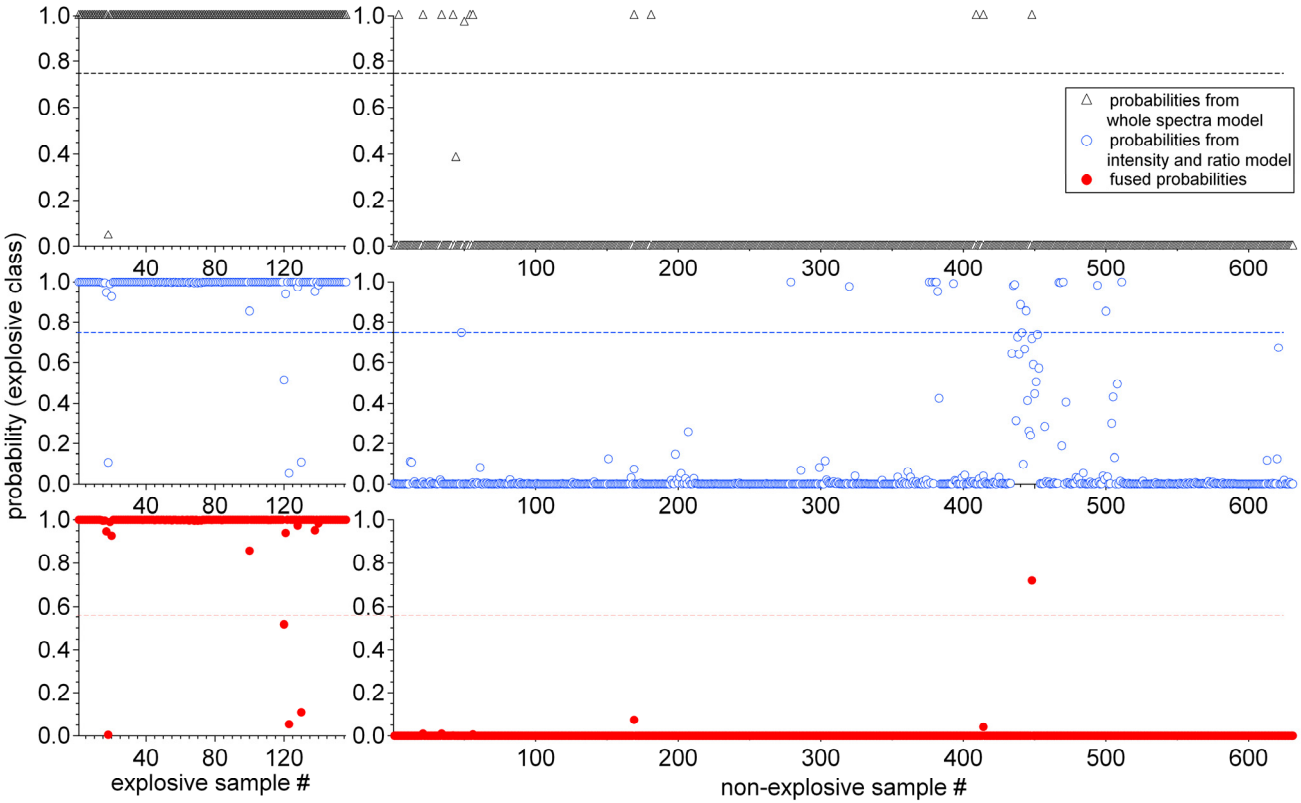
Results

- 85% TPR (Comp-B) 331 samples
- 4% FPR (diesel) 593 samples

Fused model


Whole spectra model
787 probabilities
414 spectra
787 test samples
multiply probability of each sample
787 fused probabilities
Determine samples that belong to explosive class
Ratios and intensities model
787 probabilities

Probabilities



whole

ratios

fused

Fused results

	Whole	Ratio	Fused
TPR	99%	97%	97%
FPR	1.9%	2.9%	0.16%

Conclusions

Classified painted surfaces by color

Classified residues as explosive or non-explosive on painted surfaces

Whole spectra PLS-DA model

- Classification due to constituent elements
- Classification also due to substrate

Ratio PLS-DA model

- Classification can only be due to constituent elements

Fused model decreases false positive rate