



Qualitative Identification of Explosives



Avoid False Positive Results

24 April 2014

Problem Statement

Data users assume compounds are qualitatively identified

- Decisions based on *reliable* data using the following assumptions:
 - DoD ELAP accreditation
 - Comparability between laboratories
 - LOD and LOQ verifications

Definitions

DL – Detection Limit

- Concentration demonstrated to be different from zero with 99% confidence
- At the DL, the false positive rate (Type I error) is 1%
- Detections are reported above this value

LOD – Limits of Detection

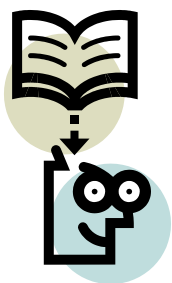
- Concentration demonstrated to be detected at the DL with 99% confidence
- At the LOD, the false negative rate (Type II error) is 1%
- Non-detects are reported as less than this value

LOQ – Limits of Quantitation

- Quantitative result with known precision and bias
- Set at or above the lowest initial calibration standard

Available Methods for Explosives

Method	Method 8095 by Gas Chromatography (GC)	Method 8321 by High Performance Liquid Chromatography / Thermo spray / Mass Spectrometry (HPLC/TS/MS)	Method 8330B by High Performance Liquid Chromatography (HPLC)
DL Range	0.003 - 0.5 µg/L	0.014 - 0.045 µg/L	0.04 - 1.5 µg/L
LOQ Range	0.030 - 5.0 µg/L	0.1 µg/L	0.10 - 2.5 µg/L
# ELAP	1, a mobile laboratory	1	Many



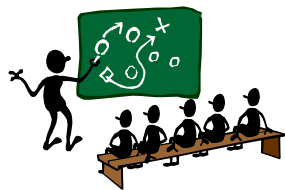
Guidance

DoD QSM v4.2 (October 2010)

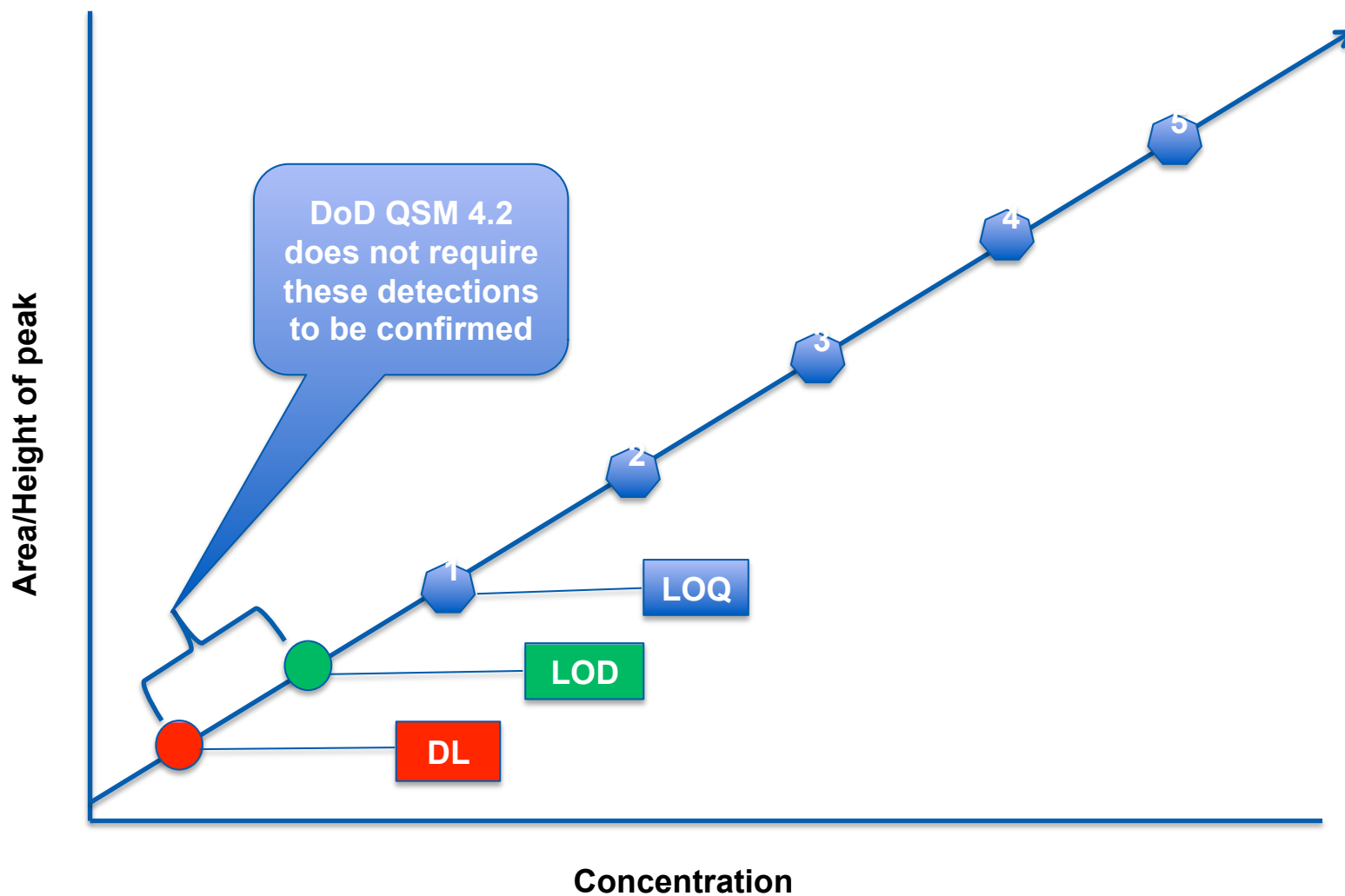
- Preface states version 4.2 and version 5.0 are considered equivalent until laboratories' next ELAP assessment
- Appendix F, Table F-3 Method 8330B
 - LC/MS & LC/MS/MS use column/detector
 - HPLC use column/column
 - **Positive detections less than LOD do not require confirmation**

DoD QSM v5.0 (July 2013)

- Laboratories are working towards compliance
- Appendix A, Table 3 Method 8330B
 - LC/MS or LC/MS/MS use column/detector
 - HPLC use column/column
 - **All positive results must be confirmed**
 - **HPLC photodiode array (PDA) Detector is not a valid confirmation technique**



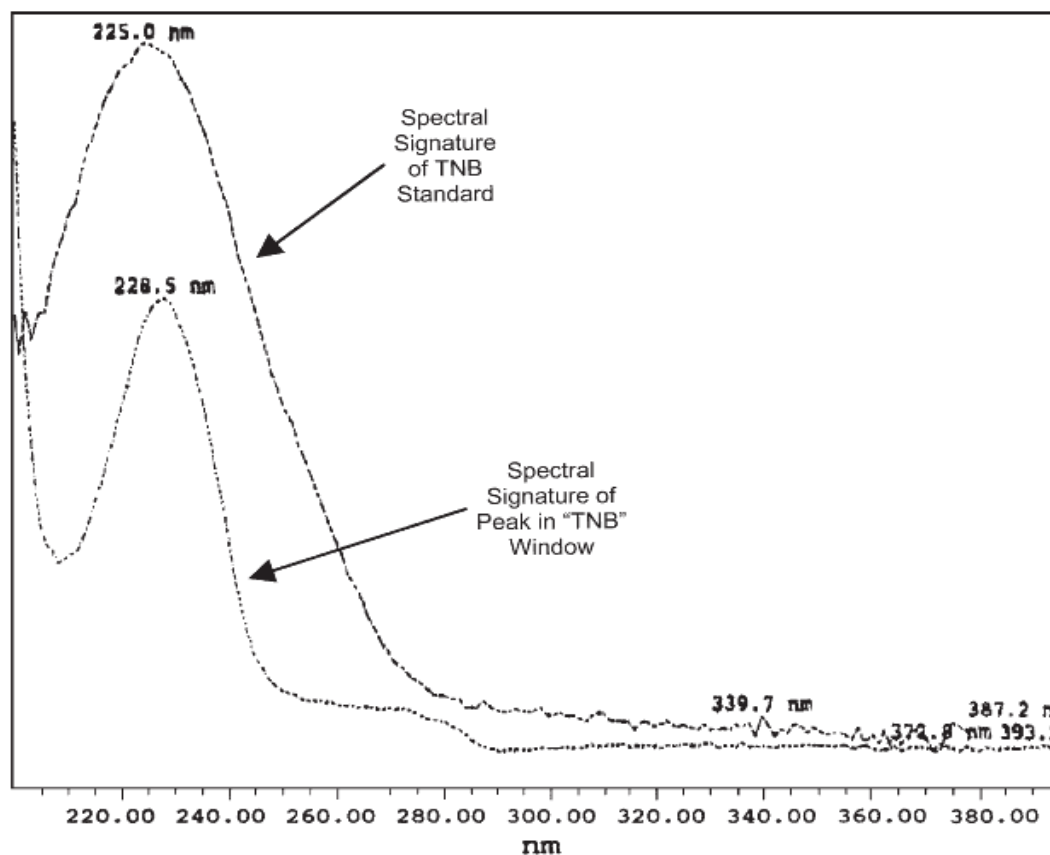
Improved Quality at Lowest Sensitivity Limits



Photodiode Array (PDA)

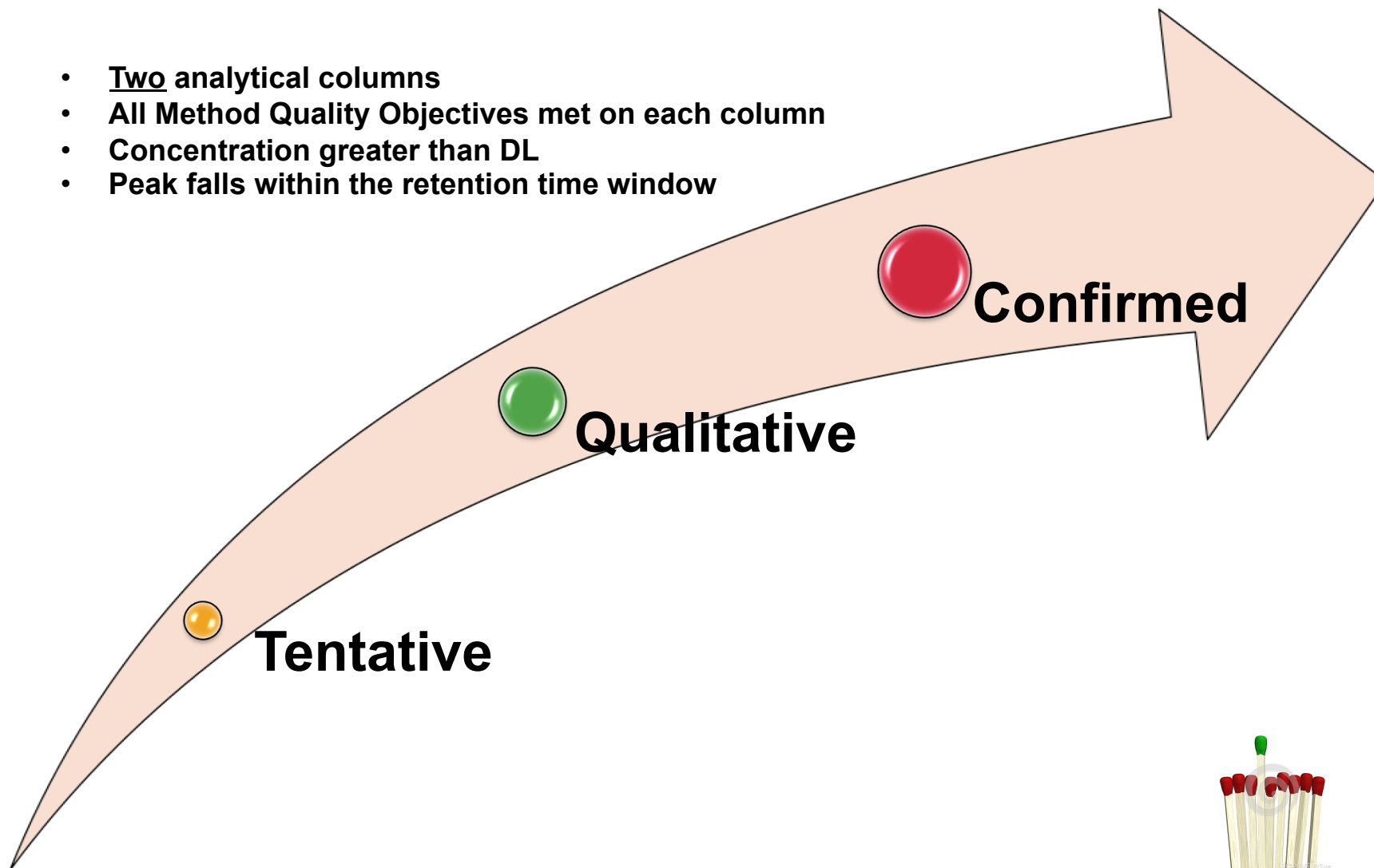
Method 8330B, Section 11.5.1: All positive measurements observed on the primary column should be confirmed by injection onto the secondary column, or by another appropriate technique, e.g., diode array or mass spectral.

- DoD QSM v5.0 prohibits use of PDA as confirmation technique
- Most laboratories do not employ LC/MS or LC/MS/MS
- **Confirmation is predominantly by dual column analyses**

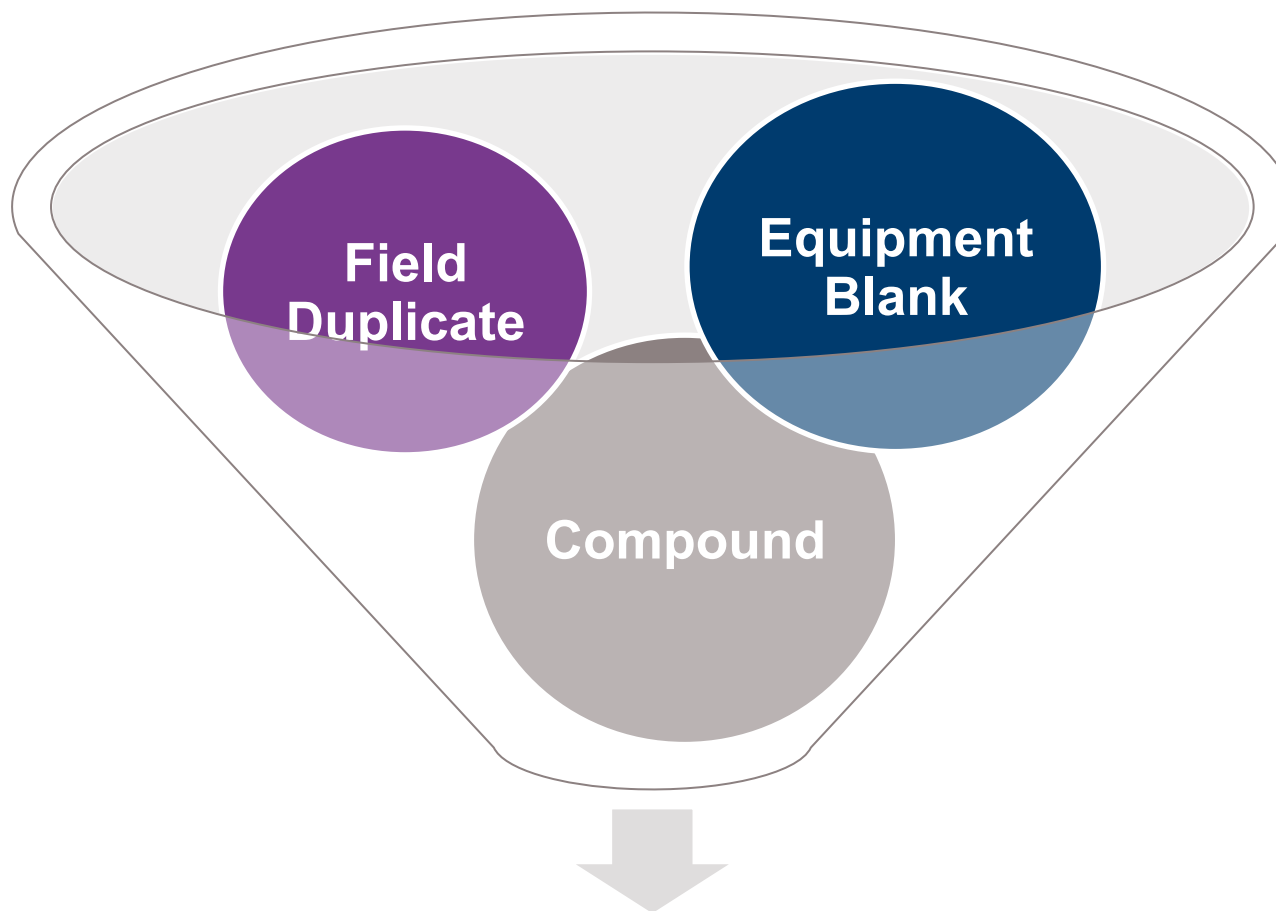


Dual Column Identification

- Two analytical columns
- All Method Quality Objectives met on each column
- Concentration greater than DL
- Peak falls within the retention time window

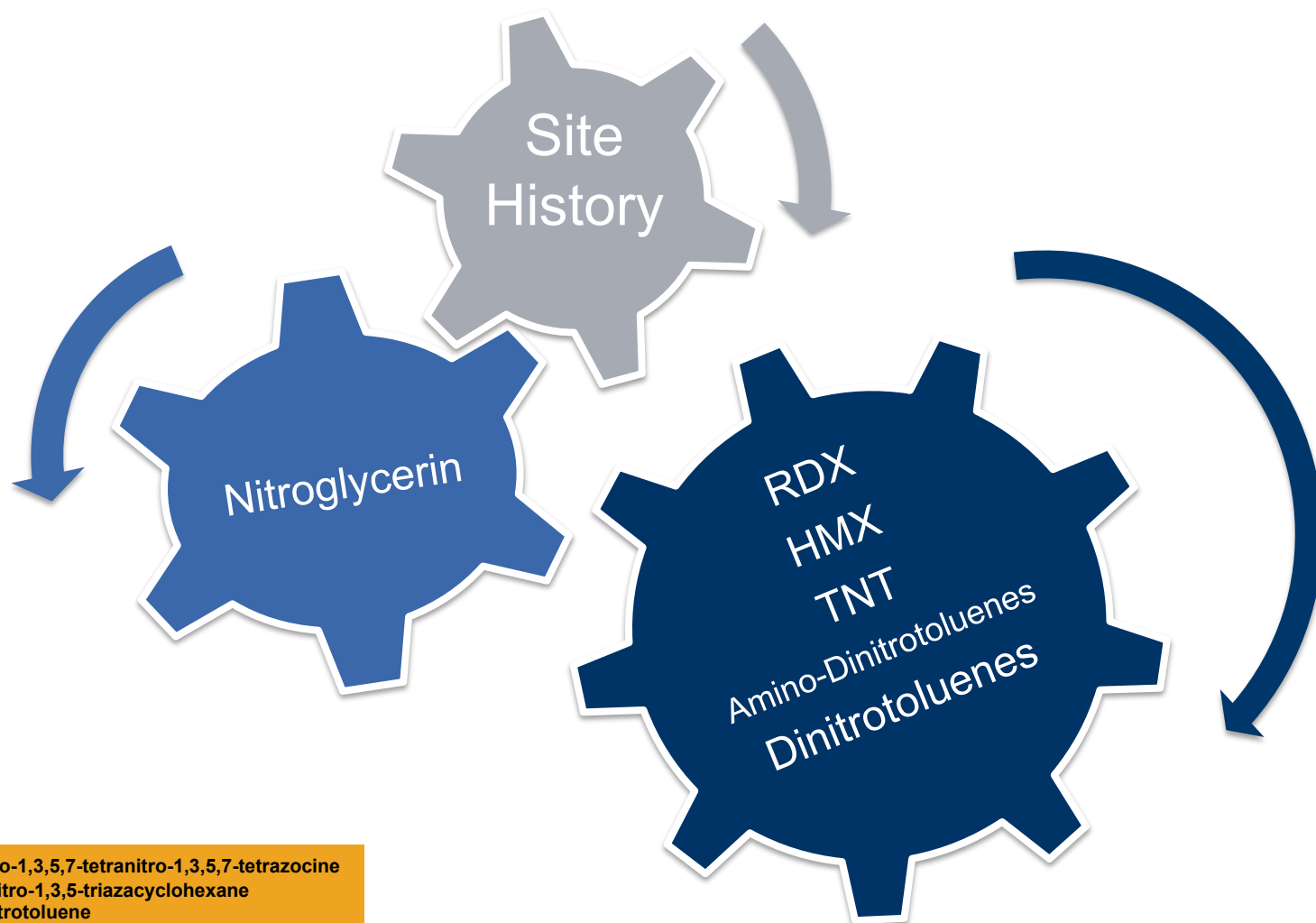


Clues to What May be Present



Logical expectations

Expected Explosives Linked to Site History



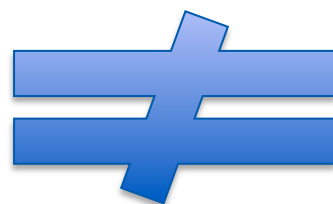
HMX: Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
RDX: 1,3,5-Trinitro-1,3,5-triazacyclohexane
TNT: 2,4,6-Trinitrotoluene

Lab Created Guidance for Dual Column Confirmation

- DL studies; 40 CFR 136, Appendix B
- Retention Time Windows; SW846 Method 8000B



Laboratory A



Laboratory B

Method 8330B Sensitivity

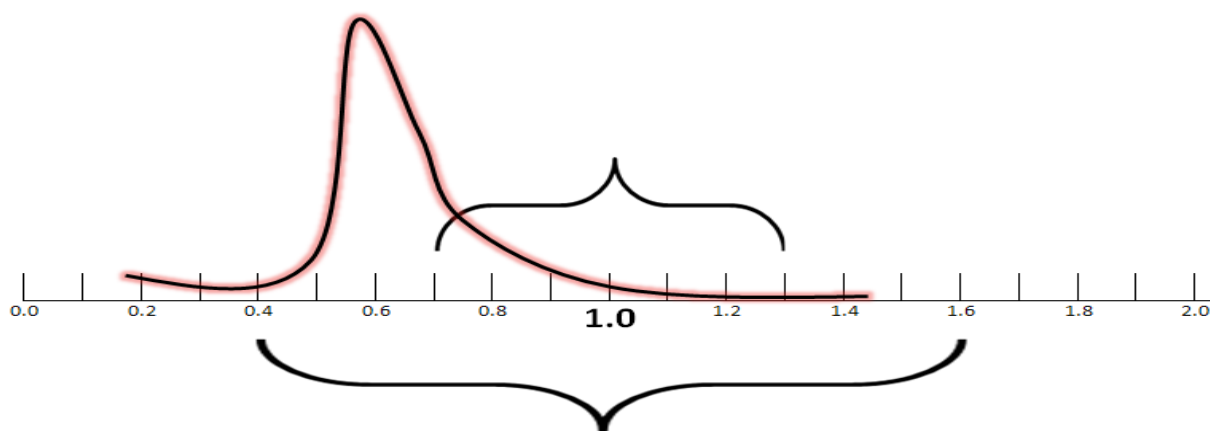
Pooled detection limits from five commercial laboratories

Analyte	CAS#	LOD Range	LOQ Range
HMX	2691-41-0	0.040 - 0.300	0.100 - 1.000
RDX	121-82-4	0.040 - 0.300	0.100 - 1.000
TNT	118-96-7	0.040 - 0.300	0.100 - 1.000
1,3,5-Trinitrobenzene	99-35-4	0.100 - 0.300	0.200 - 1.000
1,3-Dinitrobenzene	99-65-0	0.040 - 0.300	0.100 - 1.000
Tetryl	479-45-8	0.040 - 0.300	0.100 - 1.000
Nitrobenzene	98-95-3	0.040 - 0.300	0.100 - 1.000
2A-4,6-Dinitrotoluene	35572-78-2	0.040 - 0.300	0.100 - 1.000
4A-2,6-Dinitrotoluene	1946-51-0	0.040 - 0.300	0.100 - 1.000
2,6-Dinitrotoluene	606-20-2	0.100 - 0.300	0.200 - 1.000
2,4-Dinitrotoluene	121-14-2	0.040 - 0.300	0.100 - 1.000
2-Nitrotoluene	88-72-2	0.100 - 0.300	0.100 - 1.000
3-Nitrotoluene	99-08-1	0.040 - 0.300	0.100 - 1.000
4-Nitrotoluene	99-99-0	0.040 - 0.300	0.100 - 1.000
Nitroglycerin	55-63-0	0.200 - 0.400	0.400 - 1.000
PETN	78-11-5	0.250 - 1.500	0.500 - 2.500

Retention Time Windows

Method 8000B, Section 7.6.4: The retention time window for each analyte is defined as ± 3 times the standard deviation of the mean absolute retention time established during the 72-hour period.

Tight retention time windows may result in false negatives; minimum allowed is ± 0.3 minutes.



Overly wide retention time windows may result in false positive results; no maximum is prescribed.

Example Retention Time Windows

Analyte	Column 1			Column 2		
	σ	$3*\sigma$	Default	σ	$3*\sigma$	Default
HMX	0.01	0.03	0.1	0.00	0.00	0.1
RDX	0.03	0.09	0.1	0.00	0.01	0.1
1,3,5-Trinitrobenzene	0.04	0.12		0.01	0.04	0.1
1,3-Dinitrobenzene	0.06	0.17		0.01	0.02	0.1
Tetryl	0.09	0.26		0.01	0.04	0.1
Nitrobenzene	0.06	0.18		0.00	0.01	0.1
2,4,6-Trinitrotoluene	0.09	0.26		0.02	0.06	0.1
4-Amino-2,6-dinitrotoluene	0.12	0.35		0.01	0.02	0.1
2-Amino-4,6-dinitrotoluene	0.12	0.35		0.01	0.04	0.1
2,6-Dinitrotoluene	0.13	0.39		0.01	0.02	0.1
2,4-Dinitrotoluene	0.13	0.40		0.00	0.01	0.1
2-Nitrotoluene	0.12	0.37		0.00	0.01	0.1
4-Nitrotoluene	0.11	0.34		0.01	0.03	0.1
3-Nitrotoluene	0.12	0.35		0.01	0.02	0.1
Nitroglycerine	0.08	0.24		0.00	0.00	0.1
PETN	0.14	0.41		0.01	0.02	0.1

σ : standard deviation between three consecutive standards analyzed over 72 hours.

Revisions Requested

Should Column 1 be referred to as Primary and Column 2 as Confirmation?

Analyte Reported	Column 1		Column 2		Qualitatively Identified
	RT out	<DL	RT out	<DL	
3-Nitrotoluene	x		x		no
Nitroglycerin			x		no
Nitroglycerin	x			x	no
Nitroglycerin			x	x	no
PETN			no peak		no
2,4-Dinitrotoluene	x		no peak		no
3-Nitrotoluene	x		x		no
Nitroglycerin	x		x	x	no

RT: Retention Time
DL: Detection Limit

True False

Lessons Learned

Data users should ensure compounds were qualitatively identified

- Project screening criteria more sensitive than current instrument technology
- Concentrations near the DL are the most questionable
- Laboratory Standard Operating Procedures

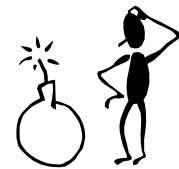
Quote

“Integrity simply means a willingness not to violate one's identity.”

-Erich Fromm

“We really don't know of any explosives that we can't detect.”

-Justin Wiseman





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