2.8.1 Introduction

No single method is adequate for the separation and identification of all high explosives. To properly analyze and screen for high explosive materials a multi-faceted approach is necessary. Identification of organic high explosives must be made with a confirmatory test. At this time, confirmatory tests available in the MSP Laboratories are Fourier Transform Infrared Spectroscopy (FTIR), Gas-Chromatography-Mass Spectrometry (GC-MS), and Direct Analysis in Real Time Time of Flight Mass Spectroscopy (DART TOF-MS).

High explosives may be submitted in the form of:

- Plastic bonded explosives (PBX'S), such as Composition C4 (containing RDX), SEMTEX H (containing RDX and PETN) and others containing HMX and other compounds. These materials are generally very stable. Separation of the explosive from the polymer/plasticizer system requires chemical extraction and/or chromatography.
- Commercial materials. Cast boosters are formulated with TNT and a sensitizer such as PETN, or RDX. These materials can be thermal and shock sensitive.
- Homemade explosives. This category includes peroxide based explosives, TATP and HMTD. Extreme caution should be used for these materials as they are both thermal and shock sensitive.
- Water gels, slurries, emulsions. These are a concentrated aqueous solution of inorganic oxidizers, suspended fuels and/or gelling agents and/or hydrocarbon oils (emulsions) may be composed of an inorganic oxidizer and fuel. Standard techniques for identification of low explosives may be used with some of these mixtures.

The MSP Lansing laboratory maintains ISO certified standards for the following compounds and methods have been validated for these compounds only:

Compound:	CAS#
2-Amino-4,6-dinitrotoluene	35572-78-2
4-Amino-2,6-dinitrotoluene	19406-51-0
3,5-Dinitroaniline	618-87-1
1,3-Dinitrobenzene	99-65-0
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2
RDX	121-82-4
Nitrobenzene	98-95-3
2-Nitrotoluene	88-72-2

Compound:	CAS#
3-Nitrotoluene	99-08-1
4-Nitrotoluene	99-99-0
1,3,5-Trinitrobenzene	99-35-4
Tetryl	479-45-8
TNT	118-96-7
HMX	2691-41-0
TATP	17088-37-8
PETN	78-11-5
HMTD	283-66-9
Nitroglycerin	55-63-0
EGDN	628-96-6
TEGDN	111-22-8
PGDN	6423-43-4
DEGDN	693-21-0

There are many high explosive compounds aside from those listed above. Reporting of negative case results should include a list of the substances above and that other explosive components may be present but not detectable by these methods. Reports listing identification of any of these materials should also list the limited compounds for which the questioned sample was screened. HMX and HMTD should not be listed if the sole screening technique is Gas Chromatography-Mass Spectrometry.

2.8.2 Safety Considerations

The intake of high explosive cases should be carried out through the MSP Bomb Squad. Larger amounts of plastic-bonded high explosives, such as C4 can be submitted to the laboratory in an intact form once rendered safe. Only a minute amount of non-bonded explosives, such as peroxide based compounds, should be submitted due to the sensitivity and instability of these compounds.

Primary explosives such as mercury fulminate, lead azide and lead styphnate are extremely sensitive and should not be submitted to the MSP Laboratory for analysis.

Care should be taken not to exert high temperature, pressure or shock to any of the samples during the intake, analysis or packaging of the samples.

2.8.3 Instrumentation

- Polarized Light Microscope (PLM)
- Fourier Transform Infrared Spectrometer (FTIR)
- Gas-Chromatograph-Mass Spectrometer (GC-MS)
- DART TOF-Mass Spectrometry

2.8.4 Microscopy

2.8.4.1

Explosive compounds HMX, RDX, PETN and TNT can be examined via polarized light microscopy via fusion methods. Identification by this technique requires the use of positive and negative controls. Confirmation of any identification by this technique via infrared or mass spectrometry is recommended.

2.8.4.2

Inorganic oxidizers present in high explosives can be examined using micro-crystal tests detailed in low explosive procedures.

2.8.5 FTIR

2.8.5.1

For bulk samples with a suitable reference standard, FTIR is a suitable approach to identification of organic high explosives. Organic explosives must be separated via single or multi-phase extractions from plastic substrates or mixtures, if present. Spectra should be consistent with published spectra and/or known reference materials prepared in the same manner as the questioned sample in order to identify the explosive materials present.

2.8.5.2

For many intact samples, separation of organic high explosives from a complex matrix can be accomplished by extraction with acetone. The acetone extract can then be examined by FTIR or GC-MS. A second extraction of the bulk material with water will then remove any inorganic oxidizers from the sample. The water extract can be examined utilizing the low explosive analysis procedures.

2.8.5.3

RDX can be separated from Composition C4 by dissolving a small amount of C4 in acetone and filtering the solute through cotton and evaporating to dryness.

2.8.5.4

An RDX-HMX mixture can be separated into essentially pure RDX and essentially pure HMX by first treating the mixture with DMSO to dissolve all the HMX present then recovering the remaining undissolved RDX as an essentially pure material. The dissolved mixture which contains a major amount of HMX and a minor amount of RDX is treated with cyclohexanone to dissolve all the RDX present, then the undissolved HMX remaining in the liquor is recovered as an essentially pure material.

2.8.5.5

Mount neat or extracted sample on appropriate microscope accessory and collect spectra on FTIR microscope or prepare a KBr mull of the sample.

2.8.5.6

Record all observations, findings and conclusions on the worksheet.

2.8.6 GC-MS

2.8.6.1

For samples in trace amounts, post-blast residues or post-blast samples, GC-MS maybe used to identify most of the high explosive compounds listed.

2.8.6.2

GC-MS Parameters:
Column: DB-5, 15M x 0.25mm ID
Injector Temp: 250°C
Temp. Program: 40°C for 2 minutes to 220°C @ 15°C/min. to 300°C @ 25 deg/min- 5 minute hold.
Scan Range: 40-450 AMU

2.8.6.3

The peroxide based explosives are very thermally unstable and may require a more concentrated sample, lower injector temperature or may not be detectable by this method. In validation, TATP was detectable but had a lower detection threshold than most of the other detected compounds.

2.8.6.4

HMTD and HMX were undetectable via GC-MS over a variety of instrumental conditions. If HMTD or HMX are suspected, analysis via FTIR or TOF-DART (when available) would be required for identification.

2.8.6.5

PETN has a low detection threshold and the detected compounds will likely include Dimethylolpropane dinitrate, a PETN degradation product that is essentially half of a PETN molecule. Identification of this compound is an indication that PETN is present. Confirmation of PETN can be made via GC-MS with comparison of spectra and retention times to a PETN standard or by FTIR and/or TOF-DART (when available).

2.8.6.6

Samples should be dissolved in a minimal amount of suitable solvent, such as acetone, pentane or acetonitrile and allowed time to dissolve. A 2ul blank of the solvent should be run before each questioned sample under the aforementioned operating conditions.

2.8.6.7

If the solvent blank is suitable, a 2ul sample of the questioned sample can then be injected on the instrument.

2.8.6.8

On the same day as the sample run, an EPA 529 standard mix should be run, as well as standards of PETN, TATP, NG, EGDN, TEGDN, PGDN and DEGDN. If the instrument sensitivity is an order of magnitude less than previous standard runs, the source of the poor sensitivity should be remedied and blanks, samples and standards reexamined.

2.8.6.9

Spectra and retention times should be compared in order to identify any organic high explosive components present.

2.8.7 AccuTOF-DART Mass Spectrometry

Direct Analysis in Real Time (DART) is an atmospheric pressure ionization technique that can analyze solids, liquids and gases by placing the test material into a heated gas flowing through the sampling area. Ionization occurs from the surface of the sampling medium. Coupling of this ion source with an accurate mass time-of-flight mass spectrometer (AccuTOF) gives quick and simple analyses with little to no sample preparation. See 7.6 for general information regarding the technique, calibartion, validation and data reduction requirements.

Analysis of High Explosives by AccuTOF-DART MASS SPECTROMETRY

As some high explosive compounds are best detected in positive ionization mode and others in negative ionization mode, samples should be examined via two different methods.

Ionization mode and ionization temperature should be clearly delineated in the title of the data file (example LS11-3211_DartPos250deg).

The methods are detailed in Tables 1 & 2.

Table 1: Method Parameters for DART_POS_SWITCH_Peroxide (Low Temperature Explosive- Positive Mode)

Parameter	Setting	Parameter	Setting
Ion Guide Peak Voltage	600V	Mass Range	66 - 600 Daltons (Da)
Orifice1 Voltage	Variable (20V, 30V, 60V, 90V)	Helium Flow Rate	2.5 L/min.
Spectrum Recording Interval	Every 0.25 seconds	Gas Heater Temperature	200 ºC

Orifice2 Voltage	Approximately 5V	Discharge Electrode Needle	4000V
Ring Lens Voltage	Variable Approximately 3-6V	Electrode1	7.60V
Orifice1 Temperature	80 ºC	Electrode2	250V

Table 2: Method Parameters for DART_NEG_SWITCH_01 (General Screening Method - Negative Mode)

Parameter	Setting	Parameter	Setting
Ion Guide Peak Voltage	600V	Mass Range	66 - 600 Daltons (Da)
Orifice1 Voltage	Variable (20V, 30V, 60V, 90V)	Helium Flow Rate	2.5 L/min.
Spectrum Recording Interval	Every 0.25 seconds	Gas Heater Temperature	250 ºC
Orifice2 Voltage	Approximately 5V	Discharge Electrode Needle	4000V
Ring Lens Voltage	Variable Approximately 3-6V	Electrode1	7.60V
Orifice1 Temperature	80 ºC	Electrode2	250V

AccuTOF-DART MASS SPECTROMETRY Procedure

- Internal mass calibration is accomplished using a dilute solution of polyethylene glycol (PEG) 600 (Emerald Biosystems, Bainbridge Island, WA) in methanol.
- Separate tune files need not be established where the only difference is in the orifice1 voltage.
- Blanks of the glass melting point tube utilized for the sample should be run prior to the sample within the run. If any contaminant is present that interferes with the analyte peaks of interest, the tubes must be cleaned and both the blank and sample re-run.

2.8.7.1

In general, samples are run by dipping the closed end of the glass melting point tubes into the sample solution and then immediately inserting the tube into the DART gas stream for several seconds. Replicate samplings (2-3) are recommended within the data file to more fully represent spectra of the analytes of interest. Let the melting point tube cool briefly between samplings in order to achieve better consistency when sampling volatile solvents. Other sampling methods (e.g., solids, plant materials, gases, dried liquids) may be also be run by insertion directly into the DART gas stream.

- Bring DART and AccuTOF out of standby mode, load an appropriate DART tune file and set the AccuTOF to "Operate".
- PEG 600 calibrant solution shall be run within each data file. Replicate samplings (2-3) are recommended for proper internal mass calibration.
- A methyl stearate standard shall be run within each data file in casework. The methyl stearate protonated molecule (299.295 Da) will be used for drift compensation.
- After data collection has finished, the DART ion source should be switched to standby to conserve helium.
- Averaged, background subtracted, centroided spectra are used for all data reduction.
- Mass calibration is performed utilizing the PEG600 spectra in the 20V function. This calibration can be performed in either the JEOL or TSSpro software when data is generated.
- Data files, which include calibration data, are archived. Overwriting the working calibration file is acceptable since they can be regenerated.
- Internal mass calibration should be applied to all functions where data will be used.
- Internal mass drift compensation is performed using the methyl stearate spectrum in the 20V function.
- Overwriting the working calibration file is acceptable since they can be regenerated.
- Internal drift compensation results should be applied to all functions where data will be used.
- After performing PEG600 internal mass calibration and internal mass drift compensation for methyl stearate, the protonated molecule (20V function) of methyl stearate shall be within ± 5 mmu of the calculated values of 299.295 Da.
- The spectrum demonstrating that the methyl stearate protonated molecules are within the above acceptance criterion shall be included in the case record.

2.8.7.2 Data processing:

Spectra should be saved in JEOL-DX format for use by other data reduction software (e.g., TSSpro, SearchFromList, Elemental Composition Workshop). Repeat as necessary for spectra from other orifice1 functions.

2.8.7.3 Monitoring for TATP:

TATP is detectable in DART positive mode but the instrument response is muted as TATP is thermally labile and relatively unstable in the DART ionization. Prior to sample screening for TATP, a standard should be run in this mode with a peak at the calculated 91.0399 +/- 5mmu detectable for the $C_3H_7O_3$+

fragment. When screening samples for TATP, the analyst should monitor the instrument at mass 91 for instrument response. To confirm a TATP identification via AccuTOF-DART MASS SPECTROMETRY, the sample must be ammonianated and compared to an ammonianated standard of TATP. The mass of the ammonianated molecule should be within 5 mmu of the calculated 240.1441.

2.8.7.4 Return AccuTOF and DART to standby mode

Do not turn the DART gas off before the temperature is down.

2.8.7.5 AccuTOF-DART MASS SPECTROMETRY Data Interpretation

- Data from the 20V is used to obtain information regarding molecular weight and should be searched against the mass library for the same voltage.
- Data from functions with Orifice1values above 20V result in greater fragmentation, and should be searched against libraries for those voltages. Care must be taken to evaluate search results using both types of information.
- Comparison of spectra to in-house library search results should be included in the case record.
- Identification for any compound by this method must include comparison with a reference standard, examined after the sample, run on the same day as the sample under the same conditions. The sample must be within be within ± 5 mmu of the standard for identification. The data in Table 3 may be used as a general guide for screening samples for high explosives; however, mass measurements will vary from those listed and not all masses are diagnostic.

Table 3: Mass measurements of high explosive compounds at various ionization conditions and oraface 1 voltages (* diagnostic mass for compound)

Compound	DART ⊖ 20V	DART ⊖ 30V	DART ⊖ 60V	DART ⊖ 90V	DART ⊕ 20V	DART ⊕ 30V	DART ⊕ 60V	DART ⊕ 90V
2-Amino-4,6-dinitrotoluene	212.03 196.03	196.03 180.04	196.03 180.04	136.03 150.03				
4-Amino-2,6-dinitrotoluene	212.03 196.03	196.03 181.02	196.03 181.02	None				
1,3-Dinitrobenzene	168.01 138.01	138.01 108.02	None	None				
2,4-	181.02	181.02	181.02	135.01				

Dinitrotoluene	152.03	152.03	135.01	105.02				
2,6-Dinitrotoluene	182.03 152.03	182.03 152.03	152.03 122.03	121.03 137.02				
RDX	324.07 268.02	324.07 268.02	102.03 82.04	None				
Nitrobenzene	138.01 123.03	None	None	None				
2-Nitrotoluene					113.07 124.09	113.07 124.09	None	None
3-Nitrotoluene					115.09 74.06	74.06 83.06	None	None
4-Nitrotoluene	136.04 152.03	136.04 120.05	136.04 121.03	None	115.09 74.06	115.09 124.09	None	None
1,3,5-Trinitrobenzene	246.00 213.00 183.00	183.00 213.00 183.00	183.00 213.00 125.00	183.00 125.00 95.02				
Tetryl	266.01 241.01	241.01 181.01	195.99 115.02	195.99 88.01				
TNT	260.01 226.01	226.01 197.01	226.01 197.01	109.02 197.01				
HMTD					209.03*	209.03*	None	None
Nitroglycerin	288.99	288.99 76.99	None	None				
EGDN	None	None	None	None	118.13	118.13	129.06 147.07	None

PETN					182.01* 227.02	182.01* 227.02		None
DEGDN	313.08 239.06	313.08 239.06	223.03 297.05	223.03 149.01				
Nitroguanidine	207.06 103.02	207.06 103.02	103.02 97.03	97.03 103.02				
HMX					203.05* 102.04			
TATP					91.04*	None	None	None
TATP + NH4					240.14*	None	None	None

2.8.8 References

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