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Pentaerythritol Tetranitrate (PETN) Surveillance by HPLC-MS: Instrumental Parameters Development

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Pentaerythritol Tetranitrate (PETN) Surveillance by HPLC-MS: Instrumental Parameters Development

Summary:

Surveillance of PETN Homologs in the stockpile here at LLNL is currently carried out by high performance liquid chromatography (HPLC) with ultra violet (UV) detection. Identification of unknown chromatographic peaks with this detection scheme is severely limited. The design agency is aware of the limitations of this methodology and ordered this study to develop instrumental parameters for the use of a currently owned mass spectrometer (MS) as the detection system. The resulting procedure would be a "drop-in" replacement for the current surveillance method (ERD04-524). The addition of quadrupole mass spectrometry provides qualitative identification of PETN and its homologs (Petrin, DiPEHN, TriPEON, and TetraPEDN) using a LLNL generated database, while providing mass clues to the identity of unknown chromatographic peaks.

Experimental:

Standards Preparation

Stock standards were made in acetonitrile (ACN) from the following bulk materials.

- Pentaerythritol Tetranitrate (PETN): Lot B-331
- Pentaerythritol Trinitrate (PETRIN): Unknown lot, Russ Sanborn owner
- Dipentaerythritol Hexanitrate (DIPEHN): Unknown lot, Mound purified
- Tripentaerythritol Octanitrate (TRIPEON): Unknown lot, Mound purified
- Tetrapentaerythritol Decanitrate (TETRAPEDN): Unknown lot, Mound purified

Calibration standards (50% ACN: 50% Water) were produced from these stocks in a concentration range from 0.5 mg/L to 22 mg/L

Calibration

Peak areas were recorded for both UV and MS detectors. Acceptable linearity was demonstrated with UV detection. The MS detector, while providing powerful qualitative information, did not provide linear response over the selected calibration range.

HPLC Conditions

After systematic evaluation of chromatographic parameters, the HPLC conditions were set as follows and are detailed in Appendix A.

- Column: Agilent LiChrospher RP-8, 125mm x 4mm ID, 100 Å pore size, 5 µm particle size.
- Eluent: 65% Acetonitrile and 35% Organic free Water with 0.05M Ammonium Formate as a modifier.
- Flow Rate: 0.25 ml/min.
- Column Temperature: 40ºC.
- UV Detector Monitor: 204 nm, 4 nm bandwidth, 360 nm reference, 100nm bandwidth.
- Injection volume: 25 µl.

Mass Spectrometer Conditions

Run conditions of the LC/MSD are as follows. Additional detail is found in Appendix A.

- Ion polarity: Negative
- Ionization mode: Atmospheric Pressure Ionization-Electrospray (API-ES).
- Scan mass range: 50 to 1000 amu.
- Spray chamber
  - Gas Temperature: 250ºC.
  - Drying Gas Flow: 10 L/min
  - Nebulizer Pressure: 50 psig
  - Capillary Voltage: 3000 V positive, 4000 V negative.

Method Detection Limits (MDL)

Standards representing sample homolog concentrations of 0.1 to 0.2 % were run seven times to determine the MDL for each analyte. The results were calculated by the following formula and are found in Table 1. Raw data in the form of chromatograms can be found in Appendix B.

$$MDL_{(7)} = s*3.14$$

s = Standard Deviation

Table 1: Method Detection Limits

UV detector	**PETRIN**	**PETN**	**DIPEHN**	**TRIPEON**	**TETRAPEDN**
Run 1	0.206159	0.120998	0.107454	0.107503	0.109236
Run 2	0.20391	0.112308	0.106364	0.104392	0.111241
Run 3	0.208033	0.118146	0.107324	0.10715	0.108766
Run 4	0.203682	0.119003	0.106294	0.105741	0.106282
Run 5	0.206018	0.118078	0.106296	0.107912	0.104756
Run 6	0.206406	0.115106	0.111418	0.11308	0.104134
Run 7	0.213287	0.116912	0.111839	0.107123	0.105963
Average	0.206785	0.117222	0.108141	0.107557	0.107197
Std. Dev.	0.003237	0.002821	0.002433	0.002717	0.002604
MDL (%)	**0.010**	**0.009**	**0.008**	**0.009**	**0.008**
MS detector	**PETRIN**	**PETN**	**DIPEHN**	**TRIPEON**	**TETRAPEDN**
Run 1	0.172987	0.165535	0.128442	0.126056	0.123501
Run 2	0.167646	0.160089	0.120958	0.117041	0.107316
Run 3	0.174055	0.1672	0.125997	0.1202	0.137822
Run 4	0.162921	0.130496	0.116445	0.128098	0.117446
Run 5	0.162582	0.156809	0.114358	0.123708	0.109512
Run 6	0.168198	0.181352	0.114748	0.119172	0.101854
Run 7	0.156901	0.190846	0.119167	0.121275	0.112809
Average	0.16647	0.164618	0.120016	0.122221	0.115751
Std. Dev.	0.006105	0.019241	0.005491	0.003928	0.011986
MDL (%)	**0.019**	**0.060**	**0.017**	**0.012**	**0.038**

Data Analysis

Data reduction and results calculation was done by Agilent Chemstation software. Calibration curves and integration parameters are found in the detailed method listing in Appendix C.

Results and Discussion:

Method Sensitivity

The MS detection platform proved unable to hit the RM Spec detection limit of 0.01%. However, the UV detector meets this requirement for all analytes. Since the UV detector is non-destructive, it is recommended that it be used in series prior to the MS. This will meet current RM Spec criteria while providing qualitative analyte identification.

Key Method Constraints

The use of currently owned technology due to the limited scope and budget of this work led to the following constraints.

- Limiting the analysis to HPLC-MS eliminated the possibility of exploring other techniques potentially better suited to detect PETN breakdown products.
- The silica cartridge based column employed precludes the use of very acidic or basic conditions, limiting our chromatographic flexibility.
- Quadrupole mass spectrometry has limited mass accuracy (± 1 amu), which prevents positive identification of molecular formula.
- HPLC-MS detection with electrospray introduction leads to adduction of the eluted compound to co-sprayed ions due to conditions found in the mass spectrometer source. The effective use of "user generated" libraries is highly subject to run conditions. Stringent control of method parameters and chemical quality is absolutely necessary to maintain functionality.

Recommendations

The focus of this work was on producing a method with the currently owned quadrupole detection platform and chromatography system. It must be emphasized that this instrumentation is not the optimum set-up to generate the best liquid chromatography-mass spectrometry data available today. A broadened scope and funding is required to produce a truly "enhanced" methodology for the characterization of PETN powders. In my opinion, while somewhat underwhelming in overall performance, the procedure produced in this work is an adequate replacement for the current HPLC-UV method used in detonator surveillance (ERD04-524).

Currently published work [(1)], using the exact same instrumentation employed in this work, showed no evidence of newly identified breakdown products. Additionally, work published here at LLNL suggests that potential breakdown products may not be physically amenable to HPLC analysis [(2)]. This suggests that other methodologies must be pursued to potentially unlock degradation pathways not yet documented in stockpile relevant samples. Industrial partnerships with companies willing to run demonstration samples on "state of the art" instrumentation could provide us with vital information to solidify the path an improved understanding of PETN aging in the enduring stockpile.

References

1. Brackett C., "Contaminants and Decomposition Products in Naturally Aged PETN", Dissertation, University of Pacific, 2005.

2. Chambers D. M., "Perspectives on Pentaerythritol Tetranitrate (PETN) Decomposition", UCRL-ID-148956, July 1, 2002.

Appendix A

HPLC Run Method

Method Information

Homolog Content of Pentaerythritol Tetranitrate (PETN) by High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS)--65% Acetonitrile, 35% Water w/0.05M Ammonium Formate

Run Time Checklist

Pre-Run Cmd/Macro:	off
Data Acquisition:	on
Standard Data Analysis:	on
Customized Data Analysis:	off
Save GLP Data:	off
Post-Run Cmd/Macro:	off
Save Method with Data:	off

1100 Binary Pump 1

Control
- Column Flow : 0.250 ml/min
- Stoptime : 50.00 min
- Posttime : Off

Solvents
- Solvent A 1 : 35.0 % (0.05M NH4COOH in Water)
- Solvent B 1 : 65.0 % (Acetonitrile)

PressureLimits
- Minimum Pressure : 10 bar
- Maximum Pressure : 300 bar

Auxiliary
- Maximal Flow Ramp : 100.00 ml/min^2
- Compressibility A : 50*10^-6/bar
- Minimal Stroke A : Auto
- Compressibility B : 115*10^-6/bar
- Minimal Stroke B : Auto

Store Parameters
- Store Ratio A : Yes
- Store Ratio B : Yes
- Store Flow : Yes
- Store Pressure : Yes

Timetable is empty

Agilent 1100 Diode Array Detector 1

Signals

Signal	Store	Signal,Bw		Reference,Bw	[nm]
A:	Yes	204	4	360	100
B:	No	254	16	360	100
C:	No	210	8	360	100
D:	No	230	16	360	100
E:	No	280	16	360	100

Spectrum
- Store Spectra : Apex + Slope + Baselines
- Range from : 190 nm
- Range to : 400 nm
- Range step : 2.00 nm
- Threshold : 1.00 mAU

Time
- Stoptime : As pump
- Posttime : Off

Required Lamps
- UV lamp required : Yes
- Vis lamp required : No

Autobalance
- Prerun balancing : Yes
- Postrun balancing : No

Margin for negative Absorbance: 100 mAU

Peakwidth : > 0.1 min
Slit : 4 nm

Analog Outputs
Zero offset ana. out. 1: 5 %
Zero offset ana. out. 2: 5 %
Attenuation ana. out. 1: 1000 mAU
Attenuation ana. out. 2: 1000 mAU

Timetable is empty

Mass Spectrometer Detector

General Information

Use MSD : Enabled
Ionization Mode : API-ES
Tune File : atunes.tun
StopTime : asPump
Time Filter : Enabled
Data Storage : Condensed
Peakwidth : 0.10 min
Fast Scan : Enabled
Fast Scan Data Reconstruction: Enabled

Signals

[Signal 1]

Polarity : Negative
Fragmentor Ramp : Disabled

Scan Parameters

Time (min)	Mass Range Low	Mass Range High	Fragmentor	Gain EMV	Threshold	Step size
0.00	50.00	1000.00	40	4.0	150	0.10

[Signal 2]

Not Active

[Signal 3]

Not Active

[Signal 4]

Not Active

Spray Chamber

[MSZones]

Gas Temp	: 250 C	maximum 250 C
DryingGas	: 10.0 l/min	maximum 10.0 l/min
Neb Pres	: 50 psig	maximum 50 psig
Quad Temp	: 0 C	maximum 0 C
VCap (Positive)	: 3000 V	
VCap (Negative)	: 4000 V	

[Time Table]

Time Table is empty.

END OF MS ACQUISITION PARAMETERS

FIA Series

FIA Series in this Method : Disabled

Time Setting
- Time between Injections : 2.00 min
- Injection Loop Flush Time : 0.17 min

Agilent 1100 Autosampler 1

Injection
- Injection Mode : Standard
- Injector volume : 25.00 µl
- Optimization : none

Auxiliary
- Drawspeed : 100 µl/min
- Ejectspeed : 100 µl/min
- Draw position : 0.0 mm

Time
- Stoptime : As Pump
- Posttime : Off

Agilent 1100 Column Thermostat 1

Temperature settings
- Left temperature : 40.0°C
- Right temperature : Not controlled
- Enable analysis : When Temp. is within setpoint +/- 0.8°C
- Store left temperature : Yes
- Store right temperature: Yes

Time
- Stoptime : As pump
- Posttime : Off

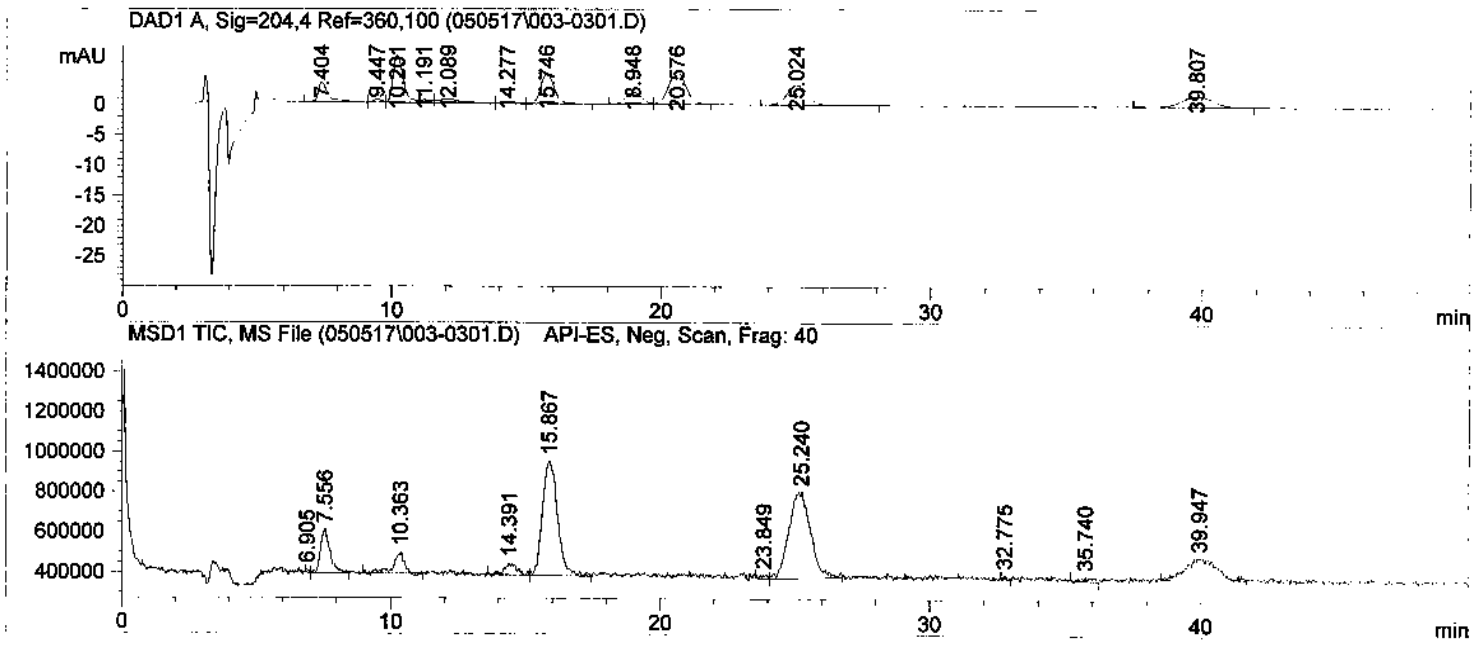
Column Switching Valve : Column 1

Timetable is empty

Appendix B

MDL Raw Data

```
Injection Date  : 5/17/2005 6:44:29 PM          Seq. Line :   3
Sample Name     : 1mg/l PETN+HL                 Location : Vial 3
Acq. Operator   : R. Meissner                      Inj :   1
Acq. Instrument : Instrument 1                 Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed    : 5/18/2005 8:55:03 AM by R. Meissner
                  (modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS
```



External Standard Report

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Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
```

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng/ul]	Grp	Name
7.404	VP	88.54317	2.32834e-2	2.06159		PETRIN
10.201	VB	207.41165	5.83369e-3	1.20998		PETN
15.746	VB	176.72702	6.08022e-3	1.07454		DIPEHN
25.024	VB	173.69185	6.18931e-3	1.07503		TRIPEON
39.807	VB	142.57104	7.66188e-3	1.09236		TETRAPEDN

Totals : 6.51350

Signal 2: MSD1 TIC, MS File

Injection Date : 5/17/2005 6:44:29 PM Seq. Line : 3
Sample Name : 1mg/l PETN+HL Location : Vial 3
Acq. Operator : R. Meissner Inj : 1
Acq. Instrument : Instrument 1 Inj Volume : 25 µl
Acq. Method : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.556	VB	5.38170e6	3.52073e-7	1.89475		PETRIN
10.363	BP	2.94514e6	6.44215e-7	1.89730		PETN
15.867	VP	2.23655e7	5.67580e-8	1.26942		DIPEHN
25.240	VB	2.41875e7	5.29007e-8	1.27953		TRIPEON
39.947	BB	8.88557e6	1.39766e-7	1.24190		TETRAPEDN
Totals :				7.58291		

*** End of Report ***

```
Injection Date  : 5/17/2005 7:36:39 PM          Seq. Line :   3
Sample Name     : 1mg/l PETN+HL                 Location : Vial 3
Acq. Operator   : R. Meissner                      Inj :   2
Acq. Instrument : Instrument 1                 Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
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Homolog Content of PETN by High Performance Liquid HPLC/MS
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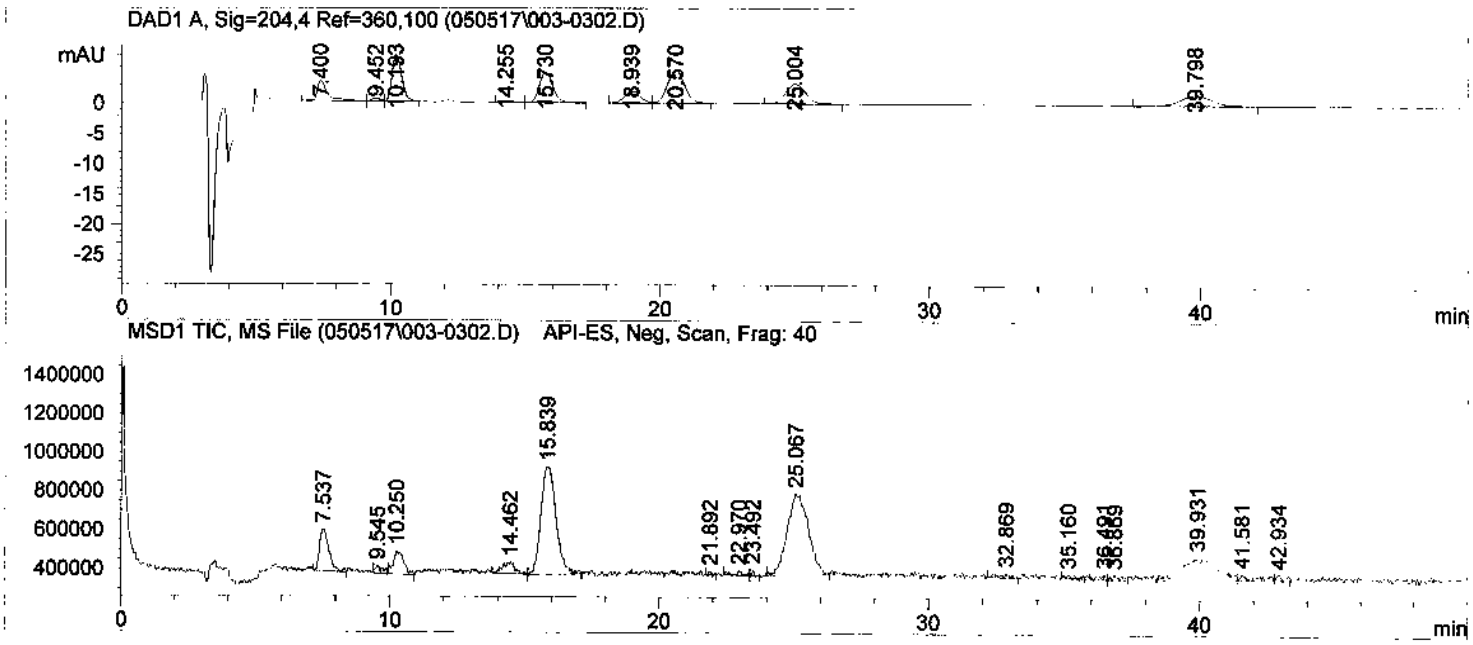

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Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
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RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng/ul]	Grp	Name
7.400	VP	87.57712	2.32834e-2	2.03910		PETRIN
10.193	VB	192.51671	5.83369e-3	1.12308		PETN
15.730	VB	174.93390	6.08022e-3	1.06364		DIPEHN
25.004	BP	168.66493	6.18931e-3	1.04392		TRIPEON
39.798	PB	145.18730	7.66188e-3	1.11241		TETRAPEDN
Totals :				6.38214		

```
Signal 2: MSD1 TIC, MS File
```

Injection Date : 5/17/2005 7:36:39 PM Seq. Line : 3
Sample Name : 1mg/l PETN+HL Location : Vial 3
Acq. Operator : R. Meissner Inj : 2
Acq. Instrument : Instrument 1 Inj Volume : 25 µl
Acq. Method : C:\HPCHEM\1\METHODS\PETNLCMS.M
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Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.537	PB	5.20483e6	3.52073e-7	1.83248		PETRIN
10.250	BP	3.28198e6	6.44215e-7	2.11430		PETN
15.839	VB	2.17218e7	5.67580e-8	1.23289		DIPEHN
25.067	BV	2.28299e7	5.29007e-8	1.20772		TRIPEON
39.931	BB	1.01905e7	1.39766e-7	1.42428		TETRAPEDN
Totals :				7.81167		

*** End of Report ***

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Injection Date  : 5/17/2005 8:28:47 PM          Seq. Line :   3
Sample Name     : 1mg/l PETN+HL                 Location : Vial 3
Acq. Operator   : R. Meissner                       Inj :   3
Acq. Instrument : Instrument 1                Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
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Homolog Content of PETN by High Performance Liquid HPLC/MS
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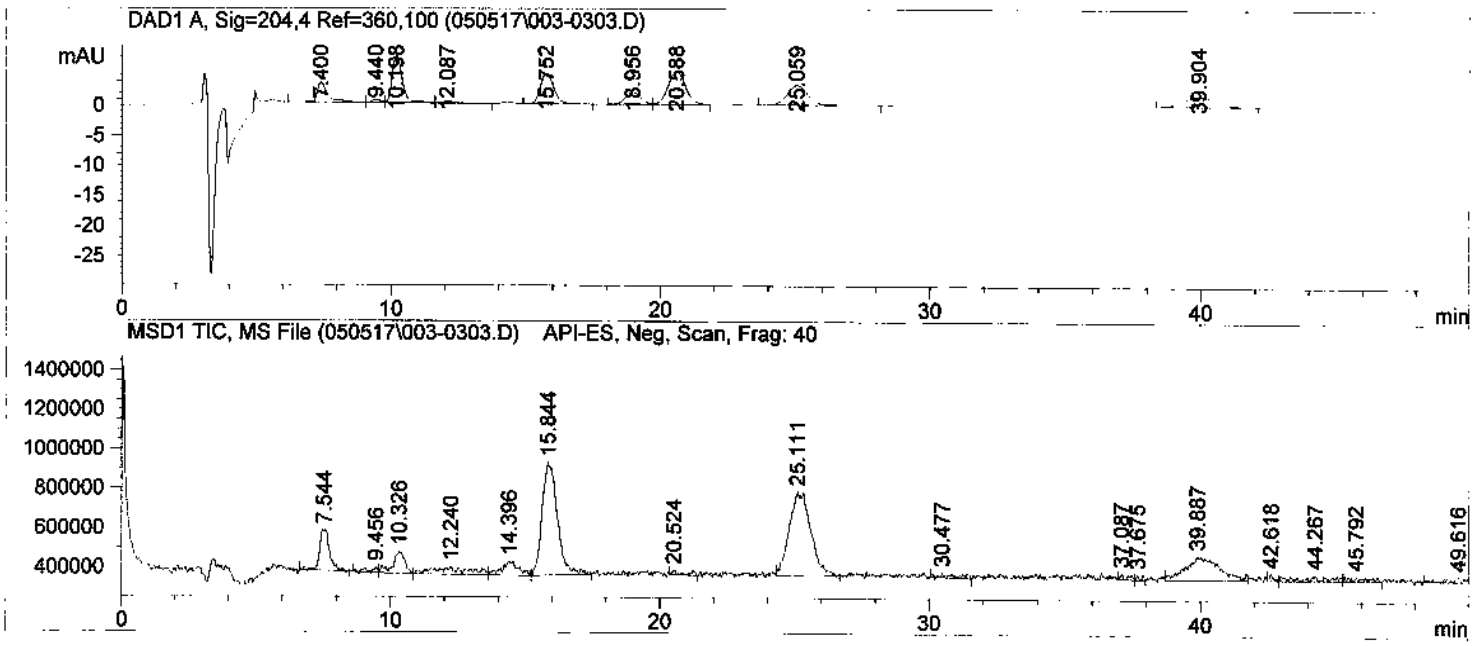

External Standard Report

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
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RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng/ul]	Grp	Name
7.400	BV	89.34819	2.32834e-2	2.08033		PETRIN
10.198	VB	202.52371	5.83369e-3	1.18146		PETN
15.752	VB	176.51363	6.08022e-3	1.07324		DIPEHN
25.059	VB	173.12132	6.18931e-3	1.07150		TRIPEON
39.904	BP	141.95709	7.66188e-3	1.08766		TETRAPEDN

```
Totals :                                  6.49419

Signal 2: MSD1 TIC, MS File
```

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Sample Name : 1mg/l PETN+HL Location : Vial 3
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Acq. Instrument : Instrument 1 Inj Volume : 25 µl
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Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)

Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.544	BB	5.27285e6	3.52073e-7	1.85643		PETRIN
10.326	VP	3.38568e6	6.44215e-7	2.18111		PETN
15.844	VB	2.25486e7	5.67580e-8	1.27982		DIPEHN
25.111	BB	2.30834e7	5.29007e-8	1.22113		TRIPEON
39.887	BB	1.06411e7	1.39766e-7	1.48726		TETRAPEDN
Totals :				8.02573		

1 Warnings or Errors :

Warning : Elution order of calibrated compounds may have changed

*** End of Report ***

```
Injection Date  : 5/17/2005 9:21:01 PM          Seq. Line :   3
Sample Name     : 1mg/l PETN+HL                 Location : Vial 3
Acq. Operator   : R. Meissner                       Inj :   4
Acq. Instrument : Instrument 1                Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
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Homolog Content of PETN by High Performance Liquid HPLC/MS
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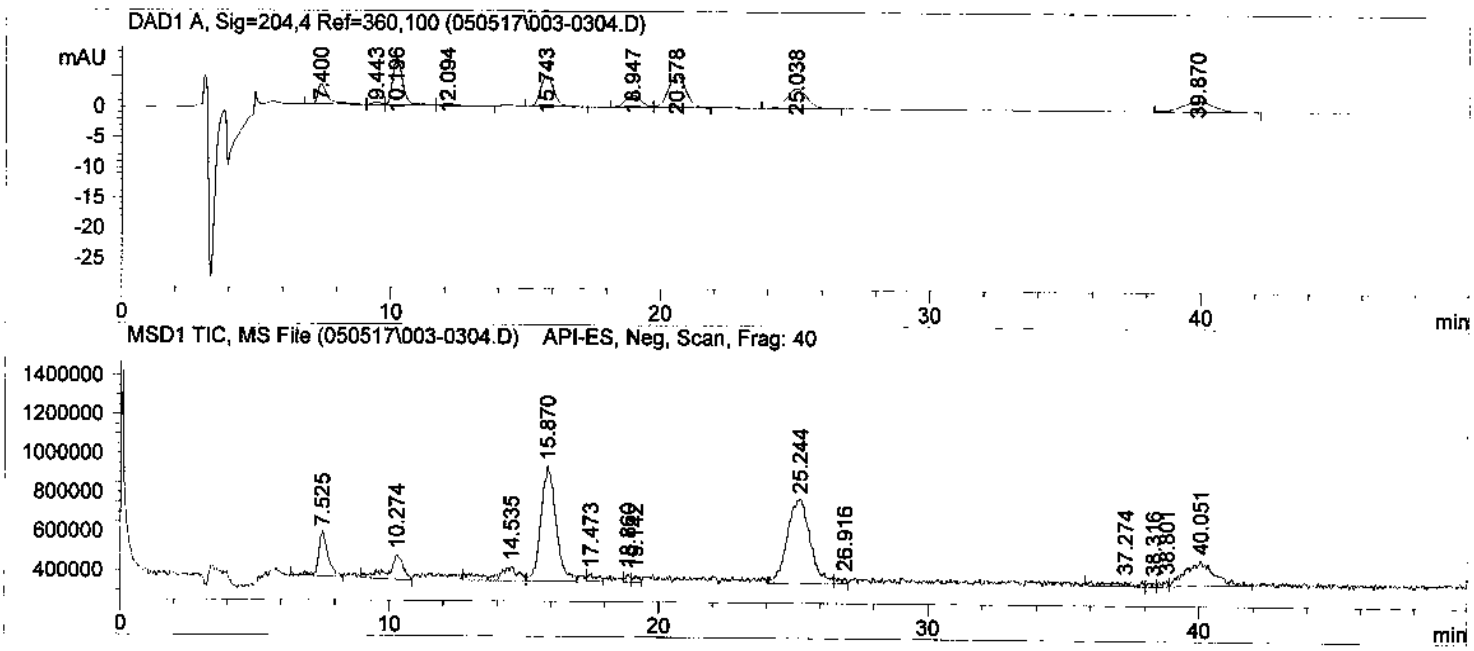


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                    External Standard Report

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Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100

RetTime  Type     Area      Amt/Area    Amount    Grp   Name
 [min]          [mAU*s]                [ng/ul]
-------|------|----------|----------|----------|--|-----------------
  7.400 BP       87.47935 2.32834e-2    2.03682    PETRIN
 10.196 VV      203.99232 5.83369e-3    1.19003    PETN
 15.743 VB      174.81976 6.08022e-3    1.06294    DIPEHN
 25.038 VB      170.84465 6.18931e-3    1.05741    TRIPEON
 39.870 BP      138.71533 7.66188e-3    1.06282    TETRAPEDN

Totals :                                6.41002


Signal 2: MSD1 TIC, MS File
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Sample Name : 1mg/l PETN+HL Location : Vial 3
Acq. Operator : R. Meissner Inj : 4
Acq. Instrument : Instrument 1 Inj Volume : 25 µl
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Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.525	BB	5.64236e6	3.52073e-7	1.98652		PETRIN
10.274	BP	4.83963e6	6.44215e-7	3.11777		PETN
15.870	VB	2.28228e7	5.67580e-8	1.29538		DIPEHN
25.244	PV	2.51970e7	5.29007e-8	1.33294		TRIPEON
40.051	VB	9.37737e6	1.39766e-7	1.31064		TETRAPEDN
Totals :				9.04324		

*** End of Report ***

```
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Sample Name     : 1mg/l PETN+HL                  Location : Vial 3
Acq. Operator   : R. Meissner                       Inj :   5
Acq. Instrument : Instrument 1                  Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed    : 5/18/2005 8:55:03 AM by R. Meissner
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Homolog Content of PETN by High Performance Liquid HPLC/MS
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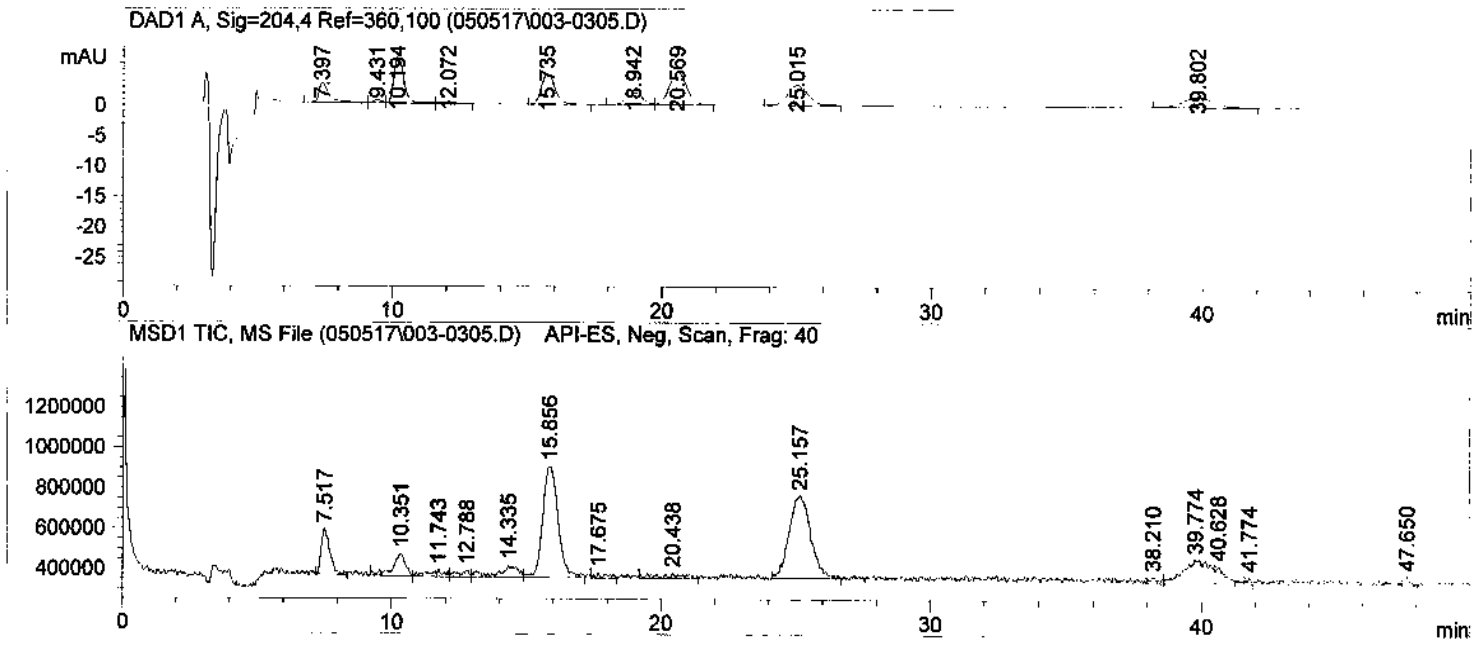

External Standard Report

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Sorted By             :      Signal
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Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
```

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng/ul]	Grp	Name
7.397	VP	88.48266	2.32834e-2	2.06018		PETRIN
10.194	VV	202.40721	5.83369e-3	1.18078		PETN
15.735	VP	174.82202	6.08022e-3	1.06296		DIPEHN
25.015	BB	174.35257	6.18931e-3	1.07912		TRIPEON
39.802	BB	136.72397	7.66188e-3	1.04756		TETRAPEDN

Totals : 6.43060

Signal 2: MSD1 TIC, MS File

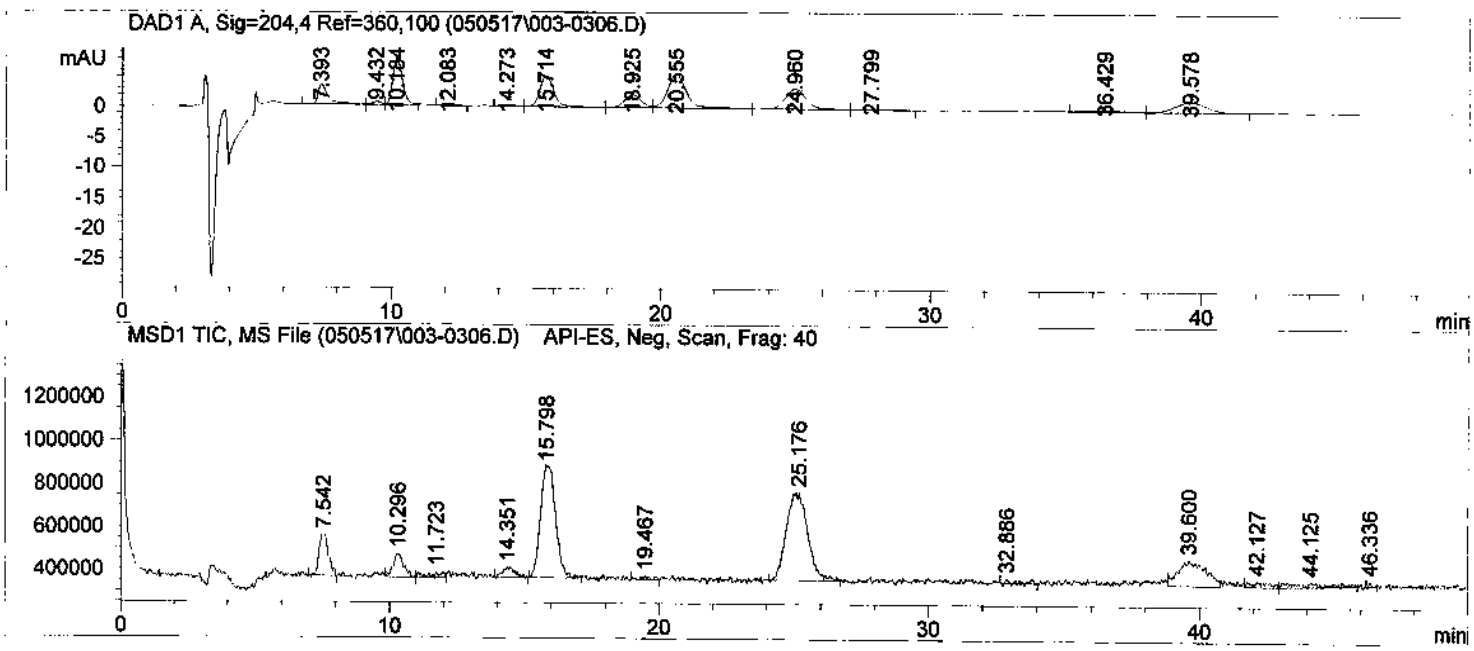
Injection Date : 5/17/2005 10:13:08 PM Seq. Line : 3
Sample Name : 1mg/l PETN+HL Location : Vial 5
Acq. Operator : R. Meissner Inj : 5
Acq. Instrument : Instrument 1 Inj Volume : 25 µl
Acq. Method : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)

Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.517	PB	5.07498e6	3.52073e-7	1.78676		PETRIN
10.351	BP	3.63243e6	6.44215e-7	2.34007		PETN
15.856	VB	2.21522e7	5.67580e-8	1.25732		DIPEHN
25.157	BB	2.29474e7	5.29007e-8	1.21394		TRIPEON
40.628	VB	2.02553e6	1.39766e-7	2.83099e-1		TETRAPEDN
Totals :				6.88118		

*** End of Report ***

```
Injection Date  : 5/17/2005 11:05:20 PM          Seq. Line :   3
Sample Name     : 1mg/l PETN+HL                  Location : Vial 5
Acq. Operator   : R. Meissner                        Inj :   6
Acq. Instrument : Instrument 1                Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed    : 5/18/2005 8:55:03 AM by R. Meissner
                  (modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS
```



External Standard Report

```
Sorted By             :      Signal
Calib. Data Modified  :      5/6/2005 12:06:48 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
```

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng/ul]	Grp	Name
7.393	VP	88.64935	2.32834e-2	2.06406		PETRIN
10.184	VV	197.31152	5.83369e-3	1.15106		PETN
15.714	VP	183.24591	6.08022e-3	1.11418		DIPEHN
24.960	VV	182.70198	6.18931e-3	1.13080		TRIPEON
39.578	VV	135.91180	7.66188e-3	1.04134		TETRAPEDN
Totals :				6.50143		

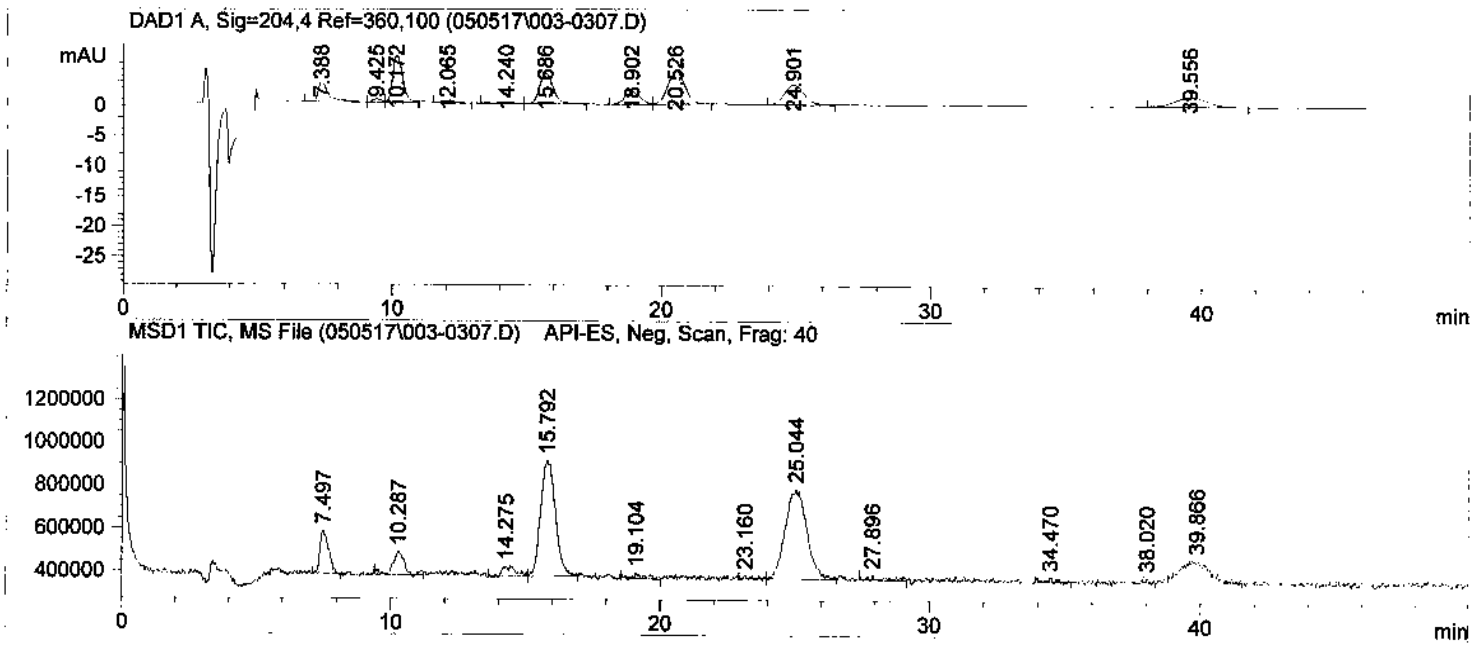
```
Signal 2: MSD1 TIC, MS File
```

Injection Date : 5/17/2005 11:05:20 PM Seq. Line : 3
Sample Name : 1mg/l PETN+HL Location : Vial 3
Acq. Operator : R. Meissner Inj : 6
Acq. Instrument : Instrument 1 Inj Volume : 25 µl
Acq. Method : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.542	PP	4.75882e6	3.52073e-7	1.67545		PETRIN
10.296	BP	3.06897e6	6.44215e-7	1.97708		PETN
15.798	BB	2.04323e7	5.67580e-8	1.15970		DIPEHN
25.176	BB	2.26709e7	5.29007e-8	1.19931		TRIPEON
39.600	BB	8.52627e6	1.39766e-7	1.19168		TETRAPEDN
Totals :				7.20321		

*** End of Report ***

```
Injection Date  : 5/17/2005 11:57:33 PM        Seq. Line :   3
Sample Name     : 1mg/l PETN+HL                Location  : Vial 7
Acq. Operator   : R. Meissner                      Inj :   7
Acq. Instrument : Instrument 1               Inj Volume : 25 µl
Acq. Method     : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed    : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed    : 5/18/2005 8:55:03 AM by R. Meissner
                  (modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS
```



External Standard Report

```
Sorted By             :      Signal
Calib. Data Modified  :      5/6/2005 12:06:48 PM
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
```

RetTime [min]	Type	Area [mAU*s]	Amt/Area	Amount [ng/ul]	Grp	Name
7.388	VP	91.60476	2.32834e-2	2.13287		PETRIN
10.172	VV	200.40895	5.83369e-3	1.16912		PETN
15.686	VB	183.93938	6.08022e-3	1.11839		DIPEHN
24.901	BB	173.07683	6.18931e-3	1.07123		TRIPEON
39.556	BB	138.29953	7.66188e-3	1.05963		TETRAPEDN

Totals : 6.55125

Signal 2: MSD1 TIC, MS File

Injection Date : 5/17/2005 11:57:33 PM Seq. Line : 3
Sample Name : 1mg/l PETN+HL Location : Vial 7
Acq. Operator : R. Meissner Inj : 7
Acq. Instrument : Instrument 1 Inj Volume : 25 µl
Acq. Method : C:\HPCHEM\1\METHODS\PETNLCMS.M
Last changed : 5/11/2005 1:35:14 PM by R. Meissner
Analysis Method : C:\HPCHEM\1\METHODS\PETNRO1.M
Last changed : 5/18/2005 8:55:03 AM by R. Meissner
(modified after loading)
Homolog Content of PETN by High Performance Liquid HPLC/MS

RetTime [min]	Type	Area	Amt/Area	Amount [ng/ul]	Grp	Name
7.497	PB	4.40261e6	3.52073e-7	1.55004		PETRIN
10.287	BB	3.30767e6	6.44215e-7	2.13085		PETN
15.792	VB	2.08461e7	5.67580e-8	1.18318		DIPEHN
25.044	BB	2.34369e7	5.29007e-8	1.23983		TRIPEON
39.866	BB	7.84607e6	1.39766e-7	1.09661		TETRAPEDN
Totals :				7.20052		

*** End of Report ***

Appendix C

Data Reprocessing Method

Method Information

Homolog Content of PETN by High Performance Liquid HPLC/MS--Offline recalculation method.

Estimated Sample Purity Calculation

General
Estimated Sample Purity Calculation is disabled.

Integration Events

Default Integration Event Table "Event"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_ADC"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_FLD"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Signal Specific Integration Event Table "Event_MSD1SPC"

Event	Value	Time
Initial Slope Sensitivity(Full Scan)	1.000	Initial
Initial Peak Width(Full Scan)	0.250	Initial
Initial Slope Sensitivity(Cond. Scan/SIM)	0.100	Initial
Initial Peak Width(Cond. Scan/SIM)	0.050	Initial
Initial Area Reject	0.000	Initial
Initial Height Reject	5.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_VWD"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_ECD"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_MWD"

Event	Value	Time
Initial Slope Sensitivity	1.000	Initial
Initial Peak Width	0.040	Initial
Initial Area Reject	1.000	Initial
Initial Height Reject	1.700	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_MSD"

Event	Value	Time
Initial Slope Sensitivity	10000.000	Initial
Initial Peak Width	0.070	Initial
Initial Area Reject	1000.000	Initial
Initial Height Reject	100.000	Initial
Initial Shoulders	OFF	Initial

Detector Default Integration Event Table "Event_DAD"

Event	Value	Time
Initial Slope Sensitivity	0.515	Initial
Initial Peak Width	0.089	Initial
Initial Area Reject	10.000	Initial
Initial Height Reject	0.028	Initial
Initial Shoulders	OFF	Initial
Integration	OFF	0.000
Integration	ON	2.000

Signal Specific Integration Event Table "Event_DAD1A"

Event	Value	Time
Initial Slope Sensitivity	0.100	Initial
Initial Peak Width	0.200	Initial
Initial Area Reject	10.000	Initial
Initial Height Reject	0.028	Initial
Initial Shoulders	OFF	Initial
Integration	OFF	0.000
Integration	ON	6.000

Signal Specific Integration Event Table "Event_MSD1TIC"

Event	Value	Time
Initial Slope Sensitivity	90000.000	Initial
Initial Peak Width	0.500	Initial
Initial Area Reject	20000.000	Initial
Initial Height Reject	10000.000	Initial
Initial Shoulders	OFF	Initial
Integration	OFF	0.000
Integration	ON	6.000

Apply Manual Integration Events: No

Advanced Baseline : No

Specify Report

Destination: Screen
Quantitative Results sorted by: Signal
Report Style: Short
Sample info on each page: Yes
Add Chromatogram Output: Yes
Chromatogram Output: Portrait
Size in Time direction: 100 % of Page
Size in Response direction: 40 % of Page

Signal Options

Include: Axes, Retention Times, Baselines, Tick Marks
Font: Arial, Size: 8

Ranges: Use Ranges

	Min Value	Max Value
Time	0.000	50.000
Response		

Multi Chromatograms: Separated, Each in full Scale

Calibration Table

Calib. Data Modified : 5/6/2005 12:06:48 PM

```
Calculate              :      External Standard
Based on               :      Peak Area

Rel. Reference Window :       5.000 %
Abs. Reference Window :       0.000 min
Rel. Non-ref. Window  :       5.000 %
Abs. Non-ref. Window  :       0.000 min
Use Multiplier & Dilution Factor with ISTDs
Uncalibrated Peaks     :      not reported
Partial Calibration    :      Yes, identified peaks are recalibrated
Correct All Ret. Times:       No, only for identified peaks

Curve Type             :      Average Response/Amount
Origin                 :      Ignored
Weight                 :      Equal

Recalibration Settings:
Average Response       :      Average all calibrations
Average Retention Time:       Floating Average New 75%

Calibration Report Options :
    Printout of recalibrations within a sequence:
        Calibration Table after Recalibration
        Normal Report after Recalibration
    If the sequence is done with bracketing:
        Results of first cycle (ending previous bracket)

Signal 1: DAD1 A, Sig=204,4 Ref=360,100
Signal 2: MSD1 TIC, MS File
```

RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref	Grp	Name
7.411	1	4	3.20200e-1	21.10326	1.51730e-2			PETRIN
		3	8.00500e-1	32.30188	2.47818e-2			
		1	1.60100	57.62590	2.77826e-2			
		2	3.20200	117.37147	2.72809e-2			
		5	8.00500	295.15897	2.71210e-2			
		10	16.01000	717.93854	2.23000e-2			
		20	32.02000	1281.44275	2.49875e-2			
7.569	2	4	3.20200e-1	1.71619e6	1.86576e-7			PETRIN
		3	8.00500e-1	2.67383e6	2.99383e-7			
		1	1.60100	3.95461e6	4.04844e-7			
		2	3.20200	8.55226e6	3.74404e-7			
		5	8.00500	1.75550e7	4.55996e-7			
		10	16.01000	3.41416e7	4.68929e-7			
		20	32.02000	5.49389e7	5.82829e-7			
10.244	1	4	2.12800e-1	39.26180	5.42003e-3			PETN
		3	5.32000e-1	92.09941	5.77637e-3			
		1	1.06400	164.72203	6.45937e-3			
		2	2.12800	336.47046	6.32448e-3			
		5	5.32000	852.20819	6.24261e-3			
		10	10.64000	2082.84595	5.10840e-3			
		20	21.28000	3690.59302	5.76601e-3			
10.292	2	4	2.12800e-1	2.56349e4	8.30118e-6			PETN
		3	5.32000e-1	6.47165e5	8.22047e-7			
		1	1.06400	2.00867e6	5.29704e-7			
		2	2.12800	4.47120e6	4.75935e-7			
		5	5.32000	1.13131e7	4.70250e-7			
		10	10.64000	2.01378e7	5.28359e-7			
		20	21.28000	3.23634e7	6.57533e-7			
15.867	1	4	2.01800e-1	38.17426	5.28629e-3			DIPEHN
		3	5.04500e-1	85.46818	5.90278e-3			
		1	1.00900	152.95752	6.59660e-3			
		2	2.01800	303.11578	6.65752e-3			
		5	5.04500	754.09277	6.69016e-3			
		10	10.09000	1835.50110	5.49714e-3			

RetTime [min]	Sig	Lvl	Amount [ng/ul]	Area	Amt/Area	Ref Grp	Name
		20	20.18000	3218.86792	6.26928e-3		
15.969	2	4	2.01800e-1	5.40204e6	3.73562e-8		DIPEHN
		3	5.04500e-1	1.19974e7	4.20506e-8		
		1	1.00900	1.88990e7	5.33891e-8		
		2	2.01800	3.35915e7	6.00748e-8		
		5	5.04500	6.84058e7	7.37511e-8		
		10	10.09000	1.34841e8	7.48290e-8		
		20	20.18000	2.11510e8	9.54092e-8		
25.237	1	4	2.02000e-1	38.45569	5.25280e-3		TRIPEON
		3	5.05000e-1	83.18657	6.07069e-3		
		1	1.01000	145.42653	6.94509e-3		
		2	2.02000	298.88165	6.75853e-3		
		5	5.05000	736.34021	6.85824e-3		
		10	10.10000	1813.55432	5.56917e-3		
		20	20.20000	3203.00122	6.30659e-3		
25.492	2	4	2.02000e-1	5.94654e6	3.39694e-8		TRIPEON
		3	5.05000e-1	1.28702e7	3.92379e-8		
		1	1.01000	1.83797e7	5.49519e-8		
		2	2.02000	3.69940e7	5.46034e-8		
		5	5.05000	7.58113e7	6.66128e-8		
		10	10.10000	1.47407e8	6.85177e-8		
		20	20.20000	2.27876e8	8.86447e-8		
39.974	1	4	2.24200e-1	34.64077	6.47214e-3		TETRAPEDN
		3	5.60500e-1	80.59784	6.95428e-3		
		1	1.12100	131.03842	8.55474e-3		
		2	2.24200	246.60544	9.09145e-3		
		5	5.60500	599.11951	9.35540e-3		
		10	11.21000	1639.77954	6.83628e-3		
		20	22.42000	3032.37524	7.39354e-3		
40.275	2	4	2.24200e-1	4.27958e5	5.23883e-7		TETRAPEDN
		3	5.60500e-1	6.52629e6	8.58835e-8		
		1	1.12100	8.79406e6	1.27472e-7		
		2	2.24200	1.82329e7	1.22964e-7		
		5	5.60500	3.67238e7	1.52626e-7		
		10	11.21000	8.36064e7	1.34081e-7		
		20	22.42000	1.46712e8	1.52816e-7		

Peak Sum Table

No Entries in table