

Simplifying the Setup for Vacuum Gas Chromatography: Using a Restriction inside the Injection Port

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Challenges with existing Fast MS

- **Vacuum outlet..**
 - Capillaries must have high pressure drop
 - Long columns (30 - 60 m, often not needed)
 - Small internal diameter (capacity problem)
 - Flow limitation of 1 ml helium /min
- **Fast analysis requires fast sampling rates due to narrow peaks**
 - Short columns of small ID cannot always be used
- **Coupling of columns**
 - Leaks, activity
- **Bleed spectra at elevated temperature**
 - Contamination of ion source, downtime



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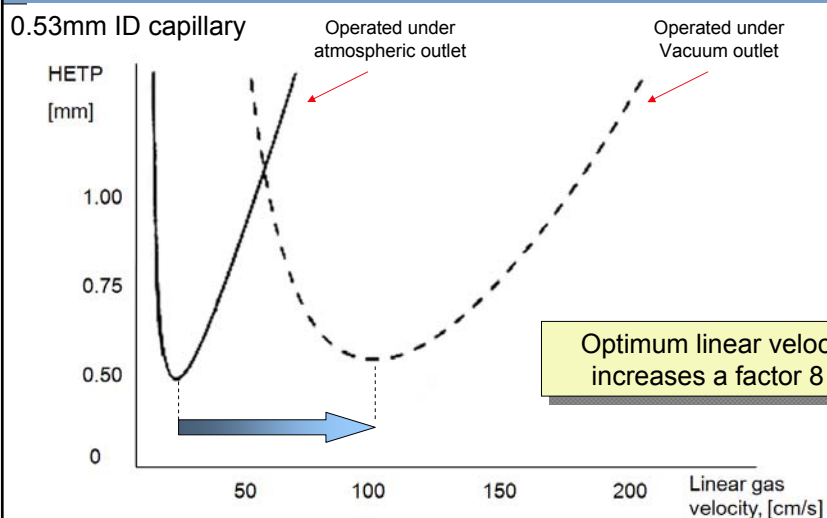
Vacuum - GC

Generate practical conditions that allow to do the separation under reduced pressure inside the column



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Vacuum GC and optimum linear gas velocity



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Why is the analysis faster?

- Optimal linear velocity of carrier gas increases with applying a higher vacuum
Uopt for helium is 80 -100 cm/s (normal: 15 cm/s)
- Short column length can be used
Column length is 5 -10 meters of 0.53 mm
(Normal MS columns are 25 - 30 m x 0.25 mm)

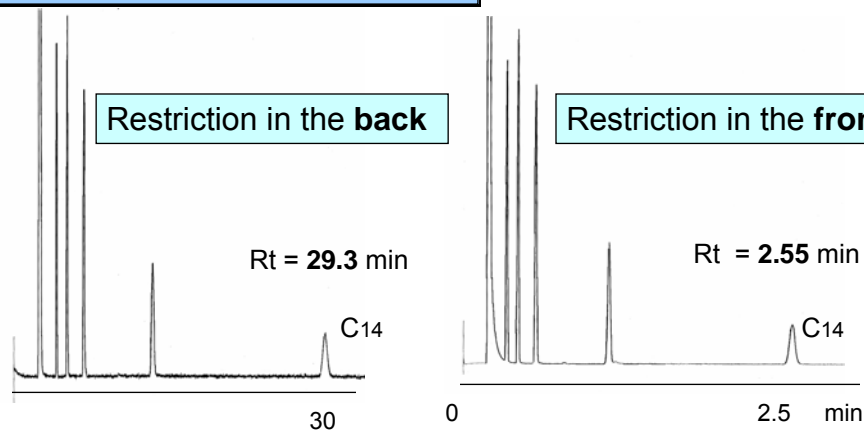
In total a 10-fold decrease in analysis time is possible..



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Impact of vacuum on separation using 0.53mm capillary: first experiment

10 m x 0.53 Metal, 150 °C; 100 kPa He,
Column mounted in a MS



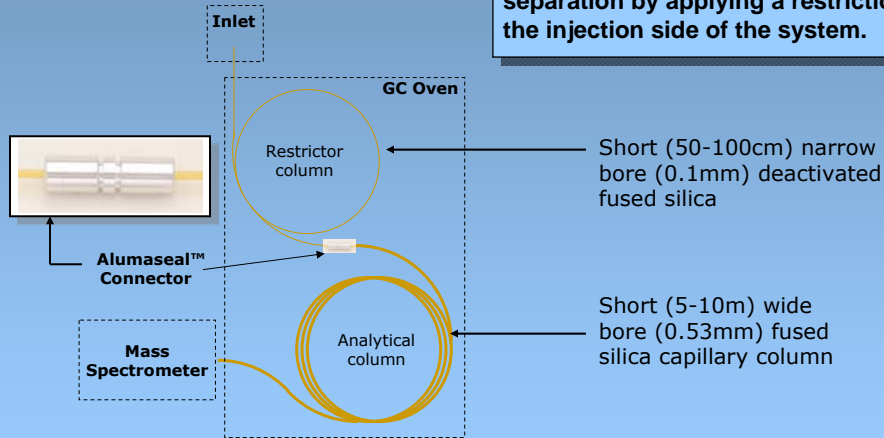
Ref: J of HRC &CC 2000, 23, (12), p 677



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Vacuum-GC Instrument Setup -conventional- Restriction in the GC Oven

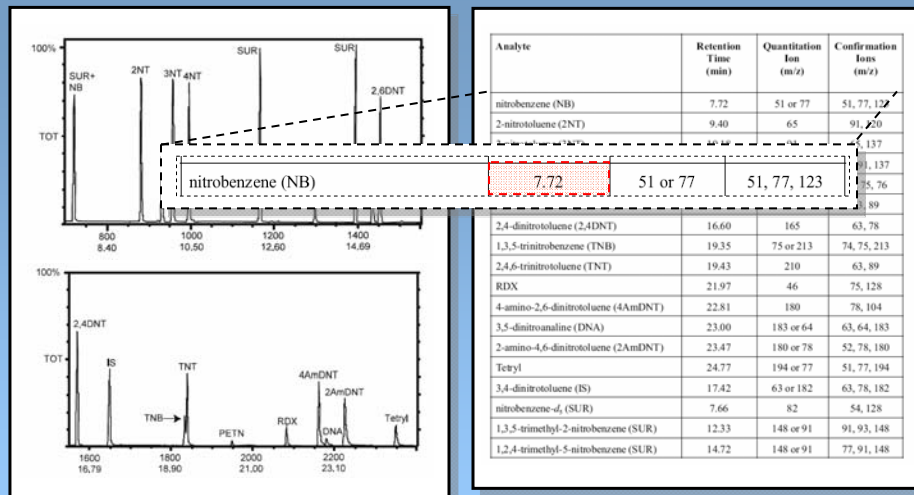
Make use of advantages of vacuum separation by applying a restriction at the injection side of the system.



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Excerpts from EPA Method 529 (Rev. 1.0)* Illustrating GC- MS Analysis of Explosives

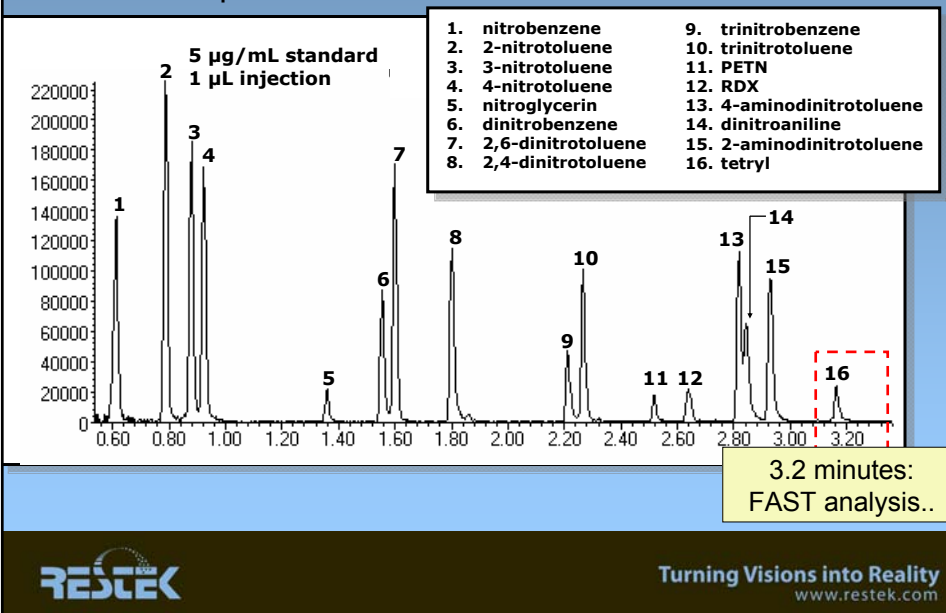


* "Determination of Explosives and Related Compounds in Drinking Water by Solid Phase Extraction and Capillary Gas Chromatography/Mass Spectrometry (GC/MS)"
http://www.epa.gov/nerlcwww/m_529.pdf

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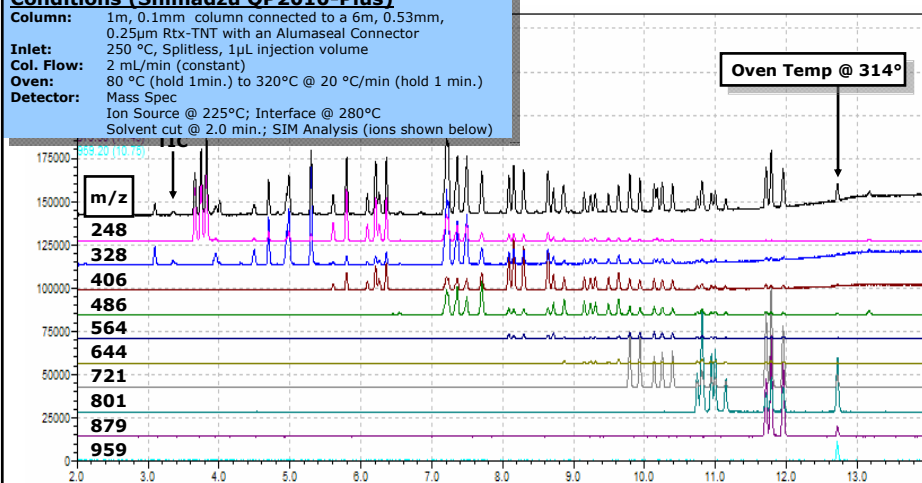
Vacuum GC-MS Analysis of Explosives and Explosive Related Compounds : Restriction in the Oven



Vacuum GC Analysis of Polybromo Diphenyl Ethers: Restriction: 100mm x 0.10mm

Conditions (Shimadzu QP2010-Plus)

Column: 1m, 0.1mm column connected to a 6m, 0.53mm, 0.25µm Rtx-TNT with an Alumaseal Connector
Inlet: 250 °C, Splitless, 1µL injection volume
Col. Flow: 2 mL/min (constant)
Oven: 80 °C (hold 1min.) to 320°C @ 20 °C/min (hold 1 min.)
Detector: Mass Spec
 Ion Source @ 225°C; Interface @ 280°C
 Solvent cut @ 2.0 min.; SIM Analysis (ions shown below)



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Vacuum-GC –TOF MS
Restriction: 2m x 0.18mm, coated capillary

Splitless injection

2m x 0.18mm x 0.2µm Rtx-5

5m x 0.53mm x 0.25µm Rtx-200

Constant flow He at 2 mL/min

Flow velocity column 1: ~200 cm/sec

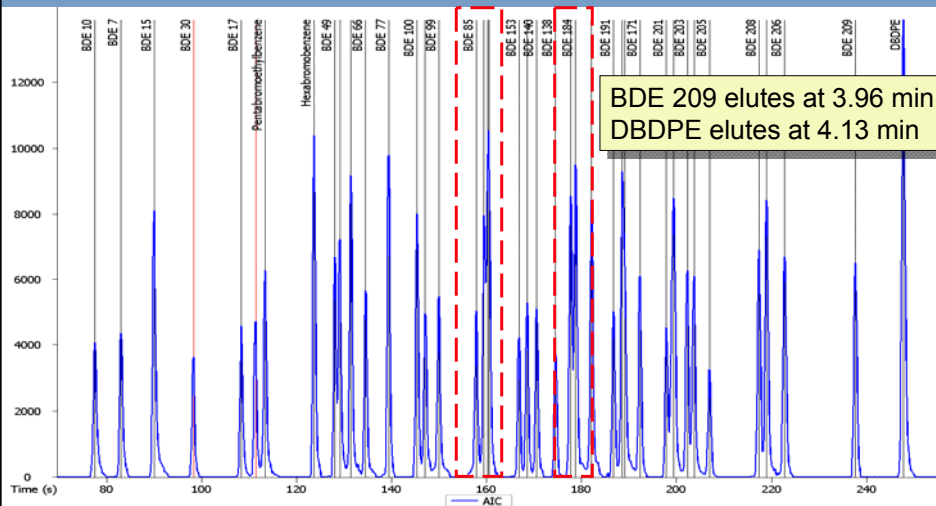
Flow velocity column 2: ~120 cm/sec

Oven : 100°C (0.1 min), 60°/min to 350°



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BFR Fast Chromatogram



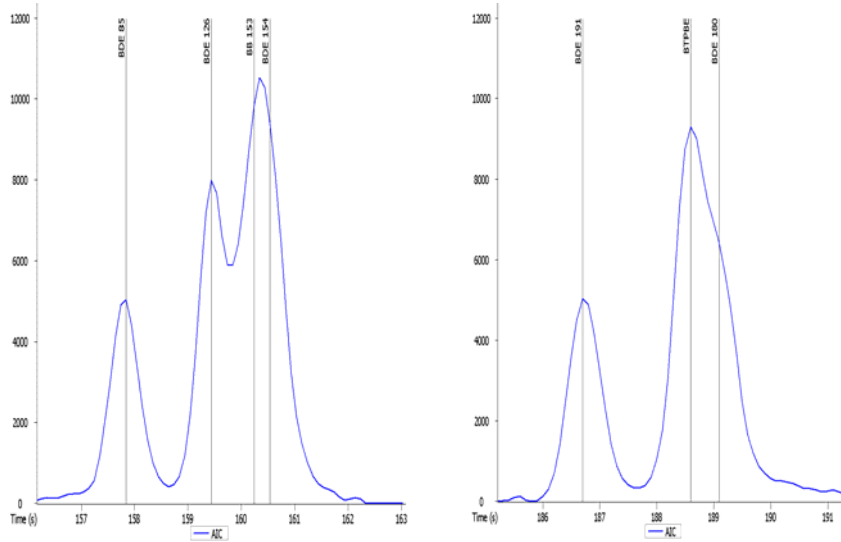
BDE 209 elutes at 3.96 min
DBDPE elutes at 4.13 min

This separation system only offers +/-10,000 theoretical plates..
Impossible to separate all compounds..



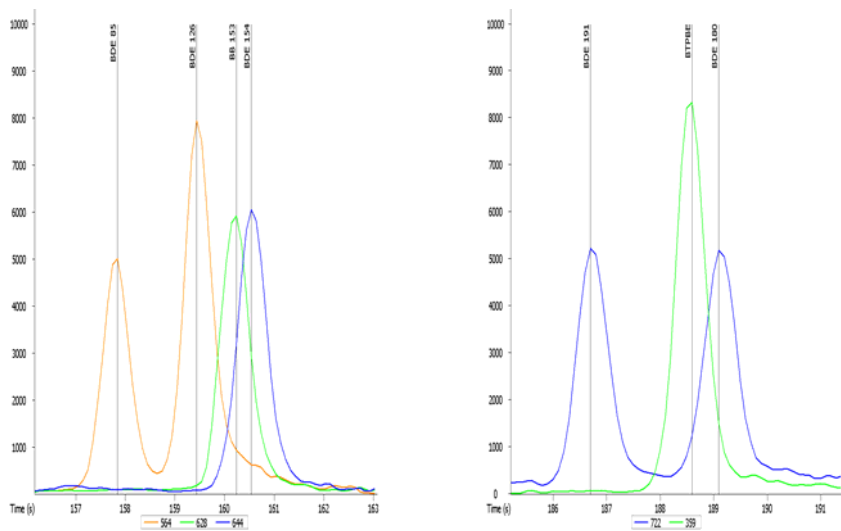
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BFR vacuum GC/TOF Co-elutions



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BFR – vacuum GC/TOF selective scanning



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Vacuum Separation using a 0.10-0.18mm restrictions

- Fast GC-MS analysis with short 0.53 ID capillaries
- Peak width of 2 sec that can be 'seen" by all MS systems
- Low elution temperatures
 - Elution of higher boiling materials
 - elution of thermo labile compounds at 50-80°C lower temperatures
- Low bleed of analytical column because of low elution temp
- Can be used with standard injection techniques
- Can be applied with all stationary phases and used in all MS systems
- High capacity due to 0.53 mm and option of film thickness



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Challenges for a Coupled Restriction

The coupled restriction is positioned in the oven

Coupling of the 60cm x 0.1mm restriction

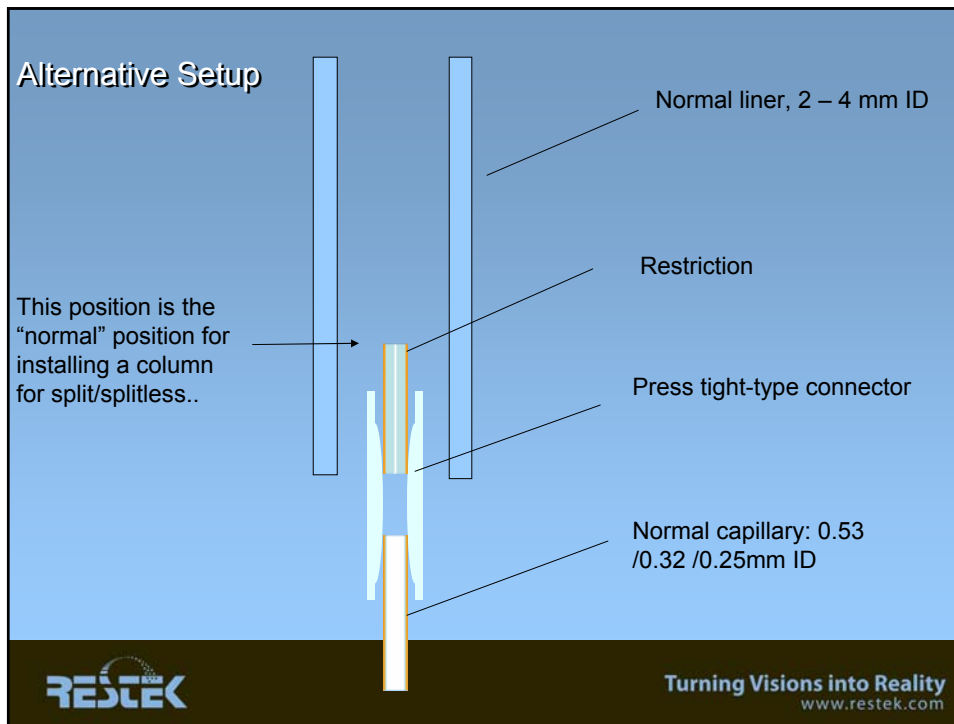
- Leaks
- Dead volume
- Thermal mass

Activation of the surface of the restriction

- Restriction is deactivated, develops activity very fast
- Short maintenance intervals



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What is the difference?

Restriction being in the liner, and is always at high temperature..

- Optimal conditions for vacuum GC as restriction length is minimal
- Leaks in coupling are not relevant; also replacement of restriction is easy;
- Good seal: The temperature in the injector will make sure that the seal will be "glued"
- As restriction is in the HOT zone, contamination/activation of restriction will minimally impact separation providing long maintenance intervals..
- Flows in restriction are VERY high, so little contact time..
- All popular injection techniques applicable: split/splitless/PTV.. (direct?)
- Can be applied with any column dimension: 0.53/0.32 and even 0.25mm, depending what peak width can be dealt with by the MS..

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Flow in capillary systems

By rearrangement of Equation 3-1 above, Poiseuille's Equation is derived. It follows that the flow rate through a capillary can be expressed in terms of pressure drop. More importantly, the flow rate is expressed in terms of the capillary ID, and is given by:

$$F = \frac{\pi \cdot r^4}{8 \cdot \eta \cdot L} \cdot \Delta P \quad (\text{eq. 3-2})$$

The flow rate, F (sometimes expressed as v), varies as the 4th power of the radius, i.e., a 2-fold change in radius creates a 16-fold change in flow rate. Equation 3-3 offers an easy to use version that gives the flow rate, F, in mL/min:

$$F = (r^4 \times \Delta P) / (\eta \times L) \times 1.625 \times 10^{-8} \quad (\text{Eq. 3-3})$$

where, the radius (r) is in μm , the pressure drop (ΔP) is in psi, coefficient of the viscosity (η) is in cp, and the length (L) is in cm.

http://www.explorethecapabilities.com/catalog/3_10.htm



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Small ID diameter fused silica

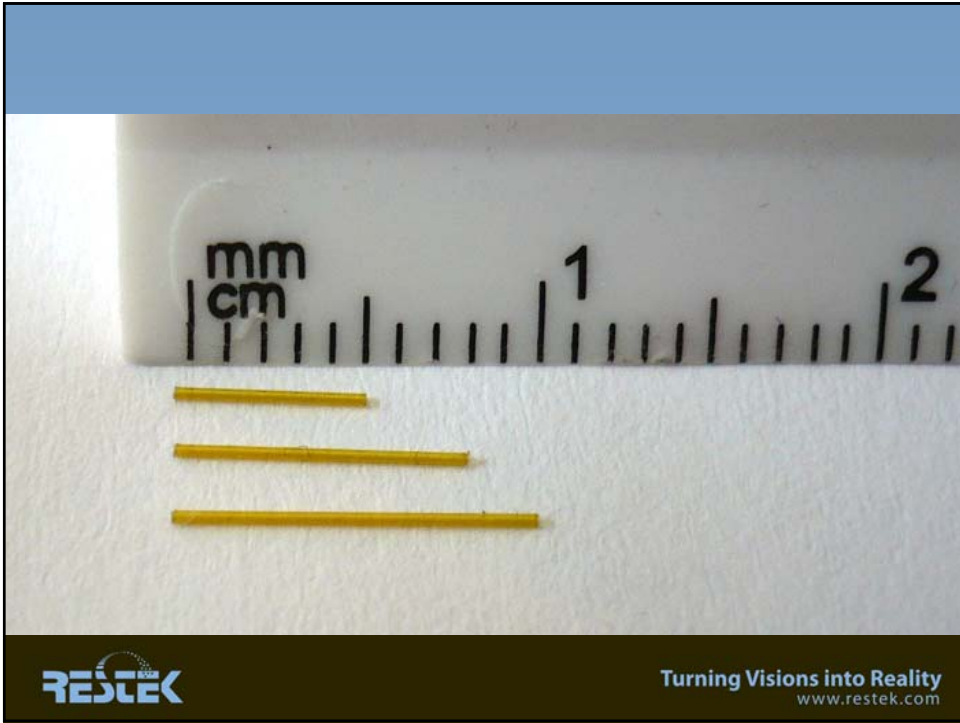
Materials are commercially available..

Product Descriptor	ID μm	OD μm	CT* μm
TSP002150	002 \pm 01	150 \pm 06	12
TSP005150	005 \pm 02	150 \pm 06	12
TSP005375	005 \pm 02	363 \pm 10	20
TSP010150	010 \pm 02	150 \pm 06	12
TSP010375	010 \pm 02	363 \pm 10	20
TSP015150	015 \pm 02	150 \pm 06	12
TSP015375	015 \pm 02	363 \pm 10	20
TSP020090	020 \pm 02	090 \pm 06	12
TSP020150	020 \pm 02	150 \pm 06	12
TSP020375	020 \pm 02	363 \pm 10	20
TSP025150	025 \pm 02	150 \pm 06	12
TSP025375	025 \pm 02	363 \pm 10	20
TSP030150	030 \pm 02	150 \pm 06	12
TSP030375	030 \pm 02	363 \pm 10	20
TSP040105	040 \pm 03	105 \pm 06	12
TSP040150	040 \pm 03	150 \pm 06	12
TSP040375	040 \pm 03	363 \pm 10	20
TSP050150	050 \pm 03	150 \pm 06	12
TSP050192	050 \pm 03	186 \pm 06	16
TSP050375	050 \pm 03	363 \pm 10	20

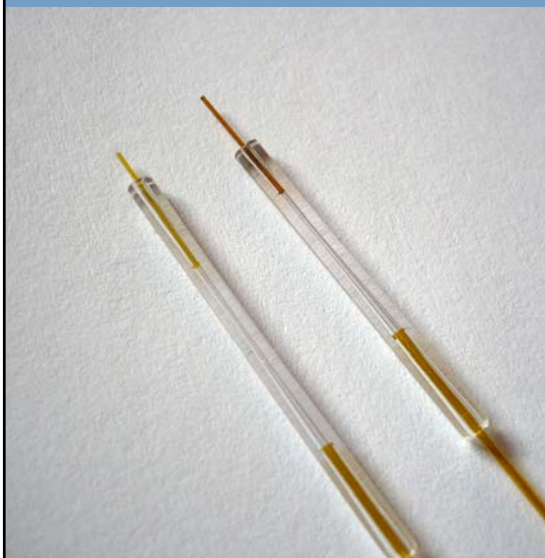
Ref: Polymicro Technologies



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In-liner restriction

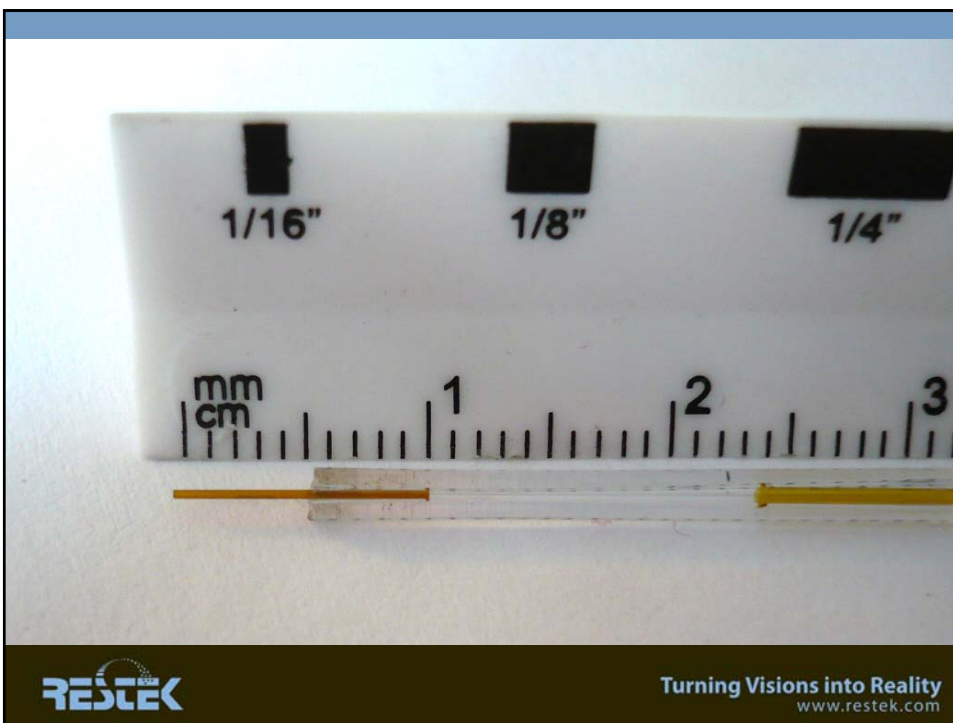


0.025mm capillary

0.53m capillary



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Position of Restriction in liner



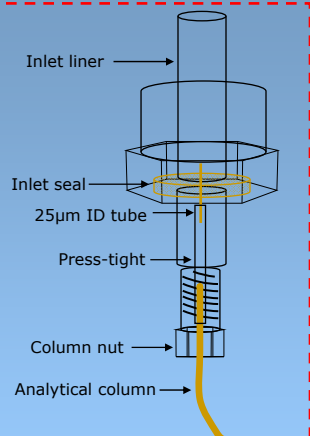
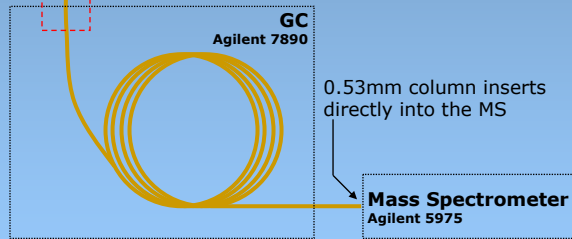
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The Experimental Setup Restriction-in-the-Inlet Concept

Analytical Column
10m, 0.53mm, 0.25 μ m
Rxi[®]-5ms (5% diphenyl, 95% dimethylpolysiloxane)

**S/SL
Inlet**



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Test samples used

Mixture of explosives & explosive-related compounds

1. **nitrobenzene**
2. **2-nitrotoluene**
3. **3-nitrotoluene**
4. **4-nitrotoluene**
5. **nitroglycerin**
6. **dinitrobenzene**
7. **2,6-dinitrotoluene**
8. **2,4-dinitrotoluene**
9. **trinitrobenzene**
10. **trinitrotoluene**
11. **PETN**
12. **RDX**
13. **4-aminodinitrotoluene**
14. **dinitroaniline**
15. **2-aminodinitrotoluene**
16. **tetryl**

Concentrations : 5 µg/mL

Solvent : Acetonitrile



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The injection/evaporation process

Split Injection:

Fast evaporation, and transfer to analytical column;
Similar to pressurized GC

Splitless Injection:

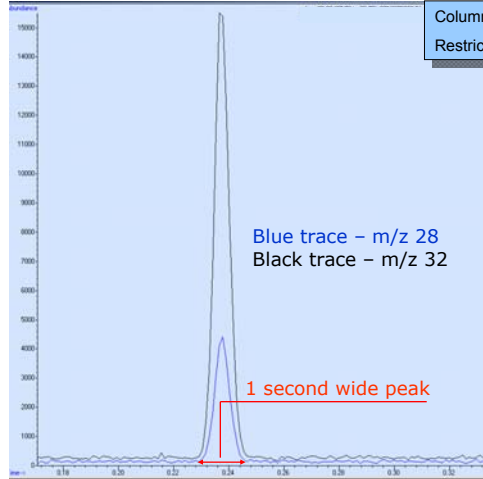
Evaporation and transfer will take more time;
Need a focusing effect



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Shape and Width of Air Peak

Used for Dead-time Measurements and Linear Velocity Calculations



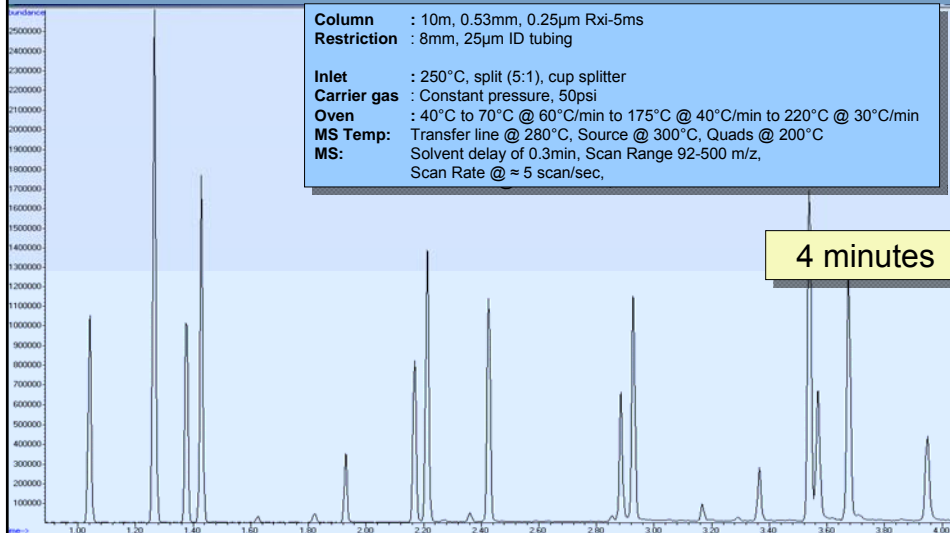
Column : 10m x 0.53mm Rxi-5ms, df = 0.25 μ m
Restriction : 8mm x 25 μ m in injector

Sharp Injection band



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Explosives and Explosive-Related Compounds



Column : 10m, 0.53mm, 0.25 μ m Rxi-5ms
Restriction : 8mm, 25 μ m ID tubing
Inlet : 250°C, split (5:1), cup splitter
Carrier gas : Constant pressure, 50psi
Oven : 40°C to 70°C @ 60°C/min to 175°C @ 40°C/min to 220°C @ 30°C/min
MS Temp: Transfer line @ 280°C, Source @ 300°C, Quads @ 200°C
MS: Solvent delay of 0.3min, Scan Range 92-500 m/z,
Scan Rate @ \approx 5 scan/sec,

4 minutes

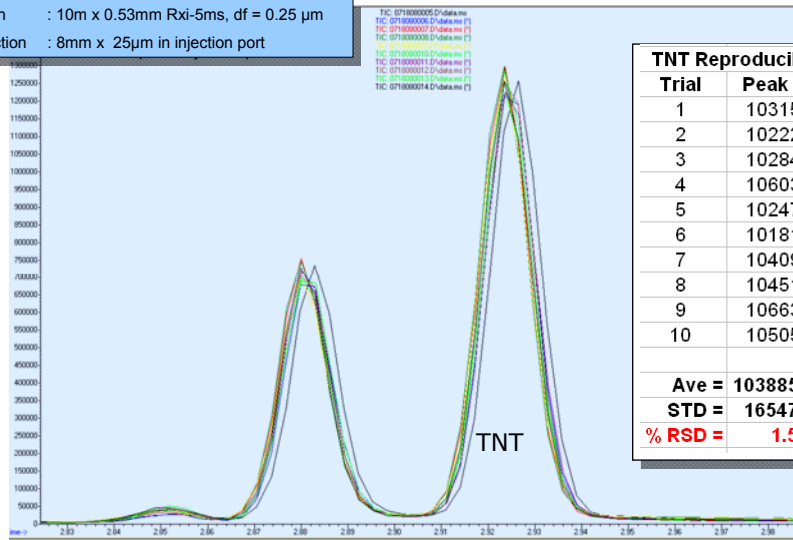


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Split Injection Reproducibility

Absolute Area Counts – Not Relative Internal Standard Measurements

Column : 10m x 0.53mm Rxi-5ms, df = 0.25 μ m
Restriction : 8mm x 25 μ m in injection port



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Splitless injection

Splitless Injection: need a focusing effect

In vacuum GC solvent condensation will not be there:

May be an issue with volatile components

- low initial temperature
- columns with lower phase ratio

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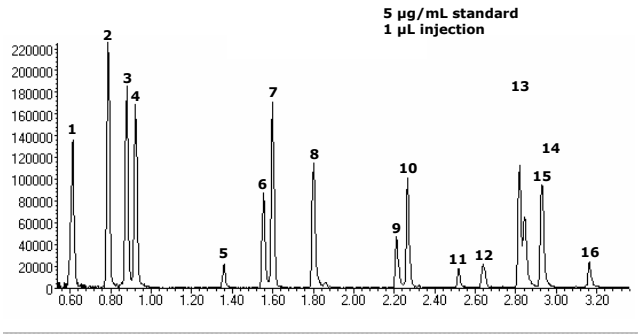
Vacuum GC-MS Analysis of Explosives, splitless injection Restriction in the Oven

Conditions (Agilent 7890/5975)

Splitless injection

Column: 0.5m, 0.1mm Restriction, IP deactivated a 6m, 0.53mm, 0.5µm Rtx®-TNT column via an alumaseal connector
Inlet: 250°C, split (5:1), 4mm Drilled Uniliner® (Siltek deactivated, hole on bottom), column flow nominally at 2mL/min (constant flow)
Oven: 50°C (hold 0.1min) to 70°C @ 60°C/min to 175°C @ 40°C/min to 300°C @ 30°C/min [oven program meant to max out capability of the 7890 configuration we have]
MS Temp: Transfer line @ 280°C, Source @ 250°C, Quads @ 150°C
MS: Solvent delay of 0.3min, Scan Range 42-300 m/z, Scan Rate @ ≈ 5 scan/sec,

1. nitrobenzene
2. 2-nitrotoluene
3. 3-nitrotoluene
4. 4-nitrotoluene
5. nitroglycerin
6. dinitrobenzene
7. 2,6-dinitrotoluene
8. 2,4-dinitrotoluene
9. trinitrobenzene
10. trinitrotoluene
11. PETN
12. RDX
13. 4-aminodinitrotoluene
14. dinitroaniline
15. 2-aminodinitrotoluene
16. tetryl



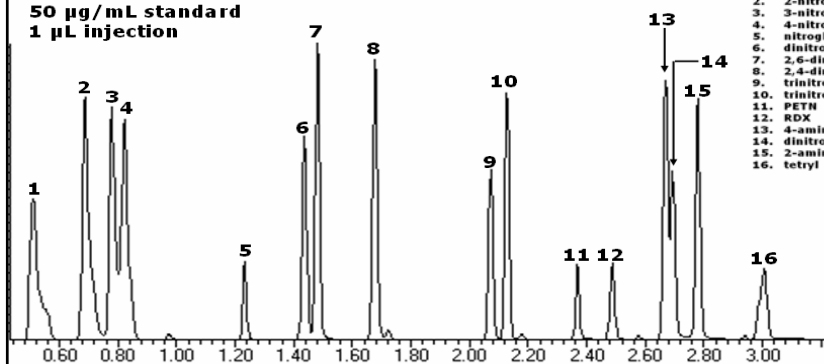
Notes: HMX is not included in the standard because of suspected role in reducing reproducibility through breakdown and subsequent interference with remaining

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Vacuum GC-MS Analysis of Explosives Restriction in the Injection Port

Column: 6m, 0.53mm, 0.5µm Rtx®-TNT column, restriction in injection port
Inlet: 250°C, splitless, 0.1min. hold-time,
Oven: 50°C (hold 0.1min) to 70°C @ 60°C/min to 175°C @ 40°C/min to 300°C @ 30°C/min
MS: Agilent 5975, Solvent delay of 0.3min, Scan Range 45-300 m/z, Scan Rate @ ≈ 5 scan/sec,

50 µg/mL standard
1 µL injection

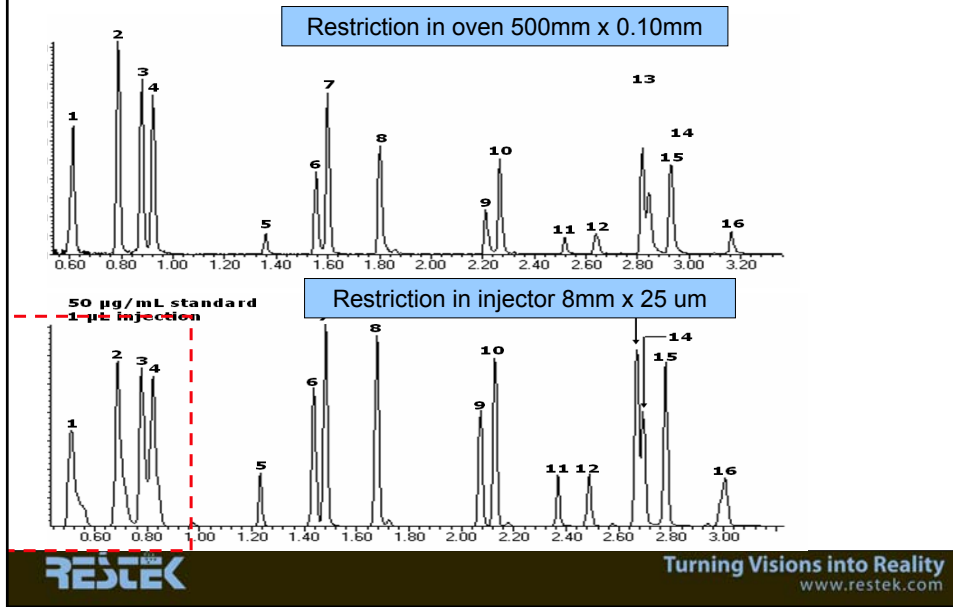


1. nitrobenzene
2. 2-nitrotoluene
3. 3-nitrotoluene
4. 4-nitrotoluene
5. nitroglycerin
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8. 2,4-dinitrotoluene
9. trinitrobenzene
10. trinitrotoluene
11. PETN
12. RDX
13. 4-aminodinitrotoluene
14. dinitroaniline
15. 2-aminodinitrotoluene
16. tetryl

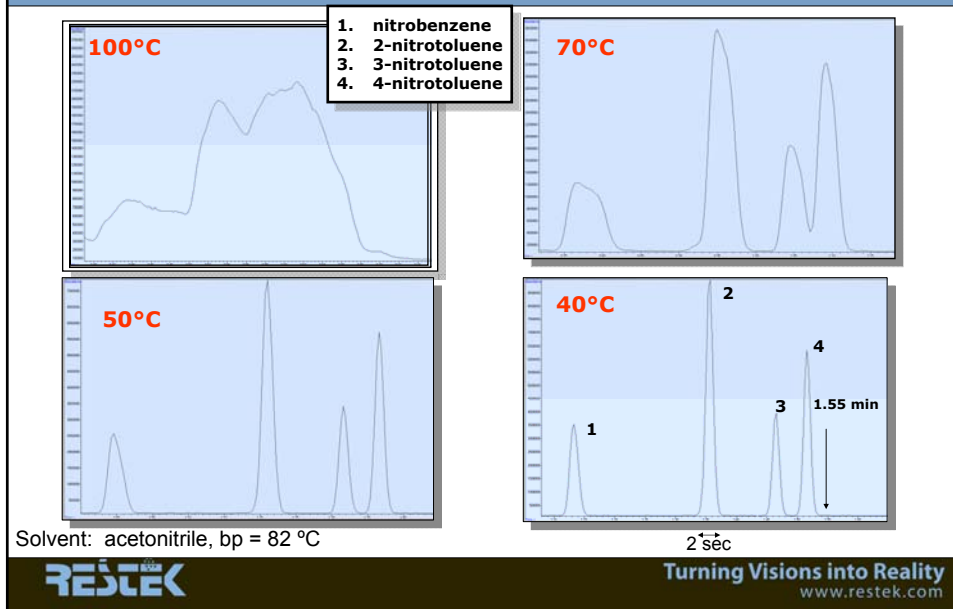


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Vacuum GC-MS Analysis of Explosives, splitless injection



Effect of Initial Oven Temperature on Early Eluting Compound Peak Shapes using Splitless Injection



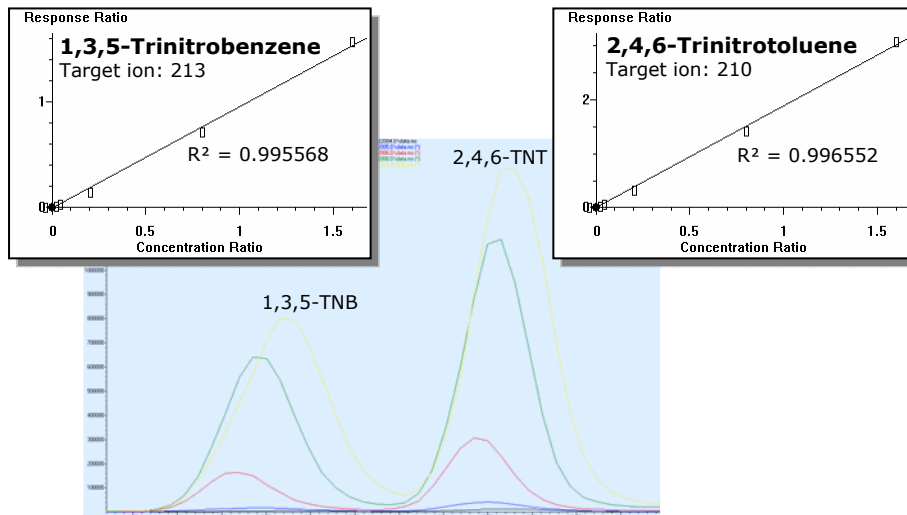
Peak width of 2-nitro toluene

Starting temperature [°C]	Base peak width [s]
100	XX
70	3.3
50	2.4
40	2.0



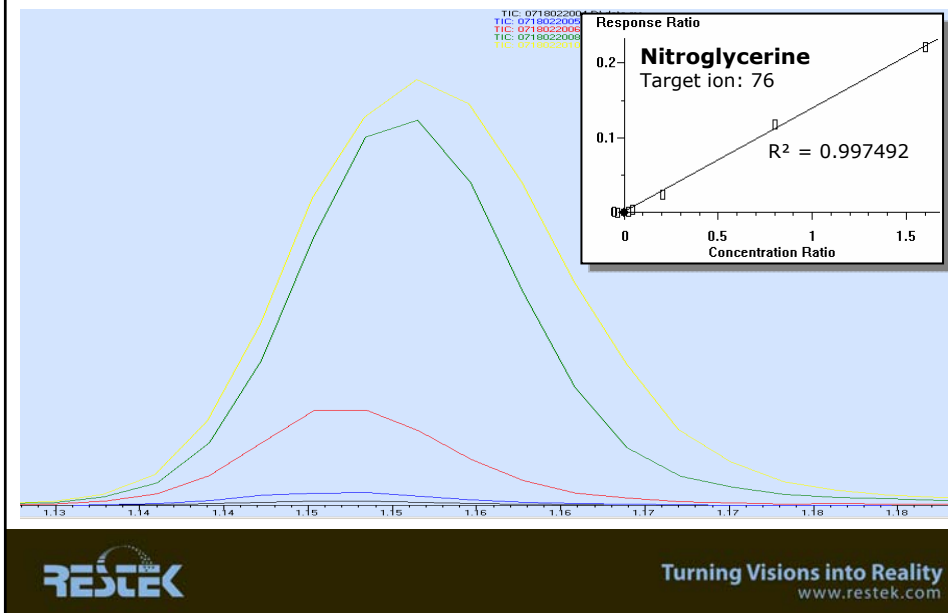
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Calibration Linearity with Vacuum-GC Conditions



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Calibration Linearity of nitroglycerine with Vacuum-GC Conditions

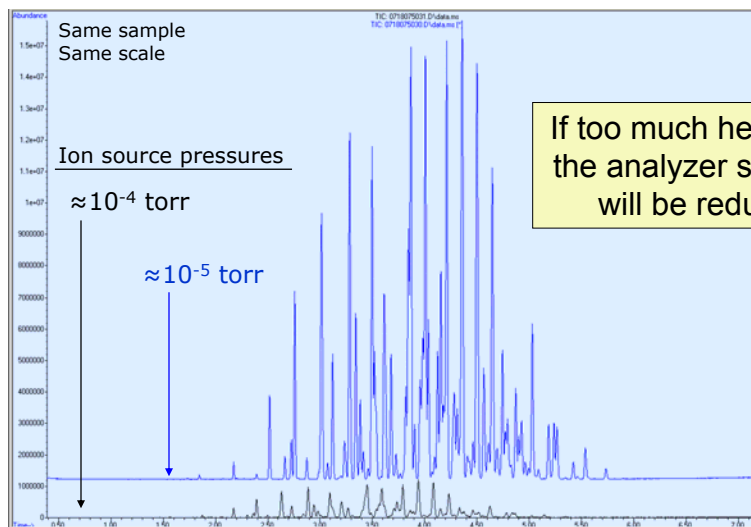


Impact of Flow variations

Flow variations: considerations..

- Flow variation vs Sensitivity of MS
- Impact on efficiency (Optimum linear velocity)
- Restriction Temperature

Flow & MS sensitivity



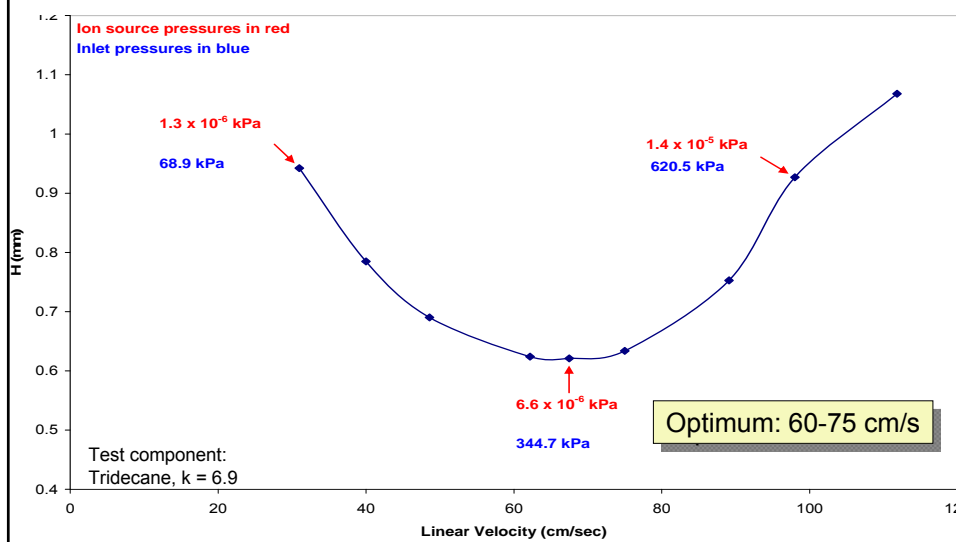
If too much helium is in the analyzer sensitivity will be reduced..

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Van Deemter plot under vacuum GC conditions

Column : 10m x 0.53mm, Rxi-5ms, $df = 0.25 \mu\text{m}$, Restriction 8 mm x 25 μm



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Impact of restriction temperature

As the restriction is located inside the injection port, the restriction will be subjected to different temperatures

At higher temperatures:

- Carrier gas becomes more viscous : flow decreases
- Restriction ID will expand : flow increases

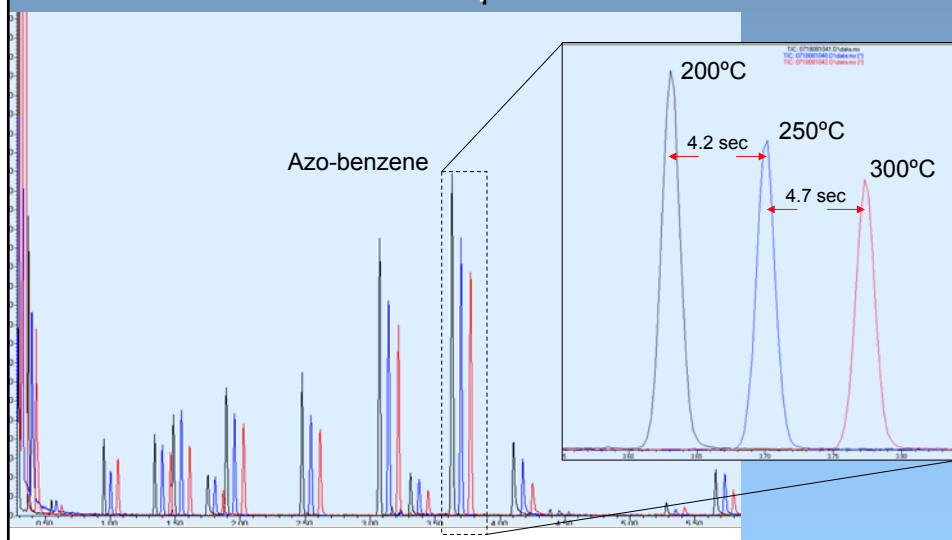
Retention times of explosives were measured by changing the injection port temperature respectively: 200, 250 and 300°C ;

System in constant pressure mode



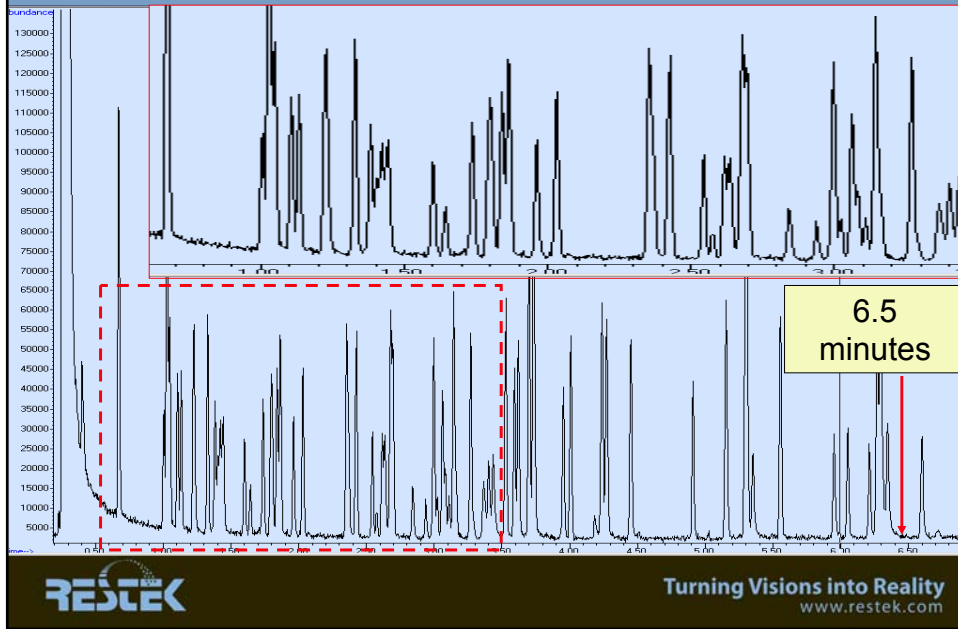
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Effect of restriction temperature

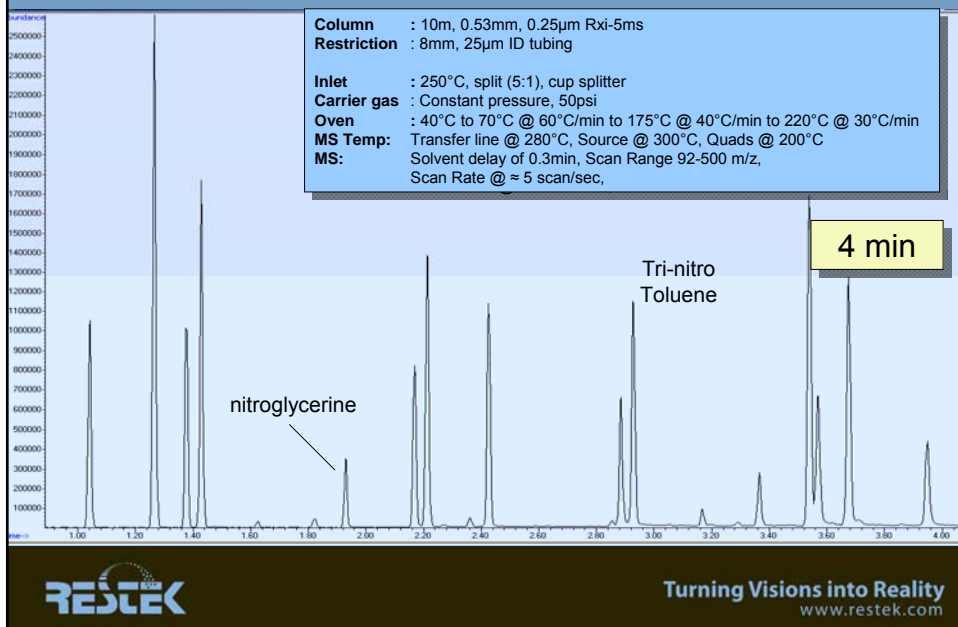


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Environmental Semi-volatile Compounds

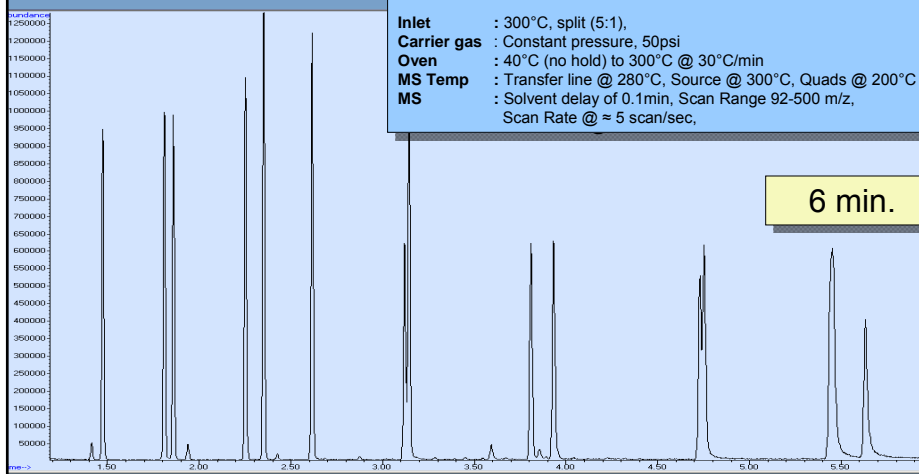


Explosives and Explosive-Related Compounds



Polyaromatic Hydrocarbons

Column : 10m, 0.53mm, 0.25µm Rxi-5ms
Restriction : 8mm, 25µm ID tubing inside the injection port
Inlet : 300°C, split (5:1),
Carrier gas : Constant pressure, 50psi
Oven : 40°C (no hold) to 300°C @ 30°C/min
MS Temp : Transfer line @ 280°C, Source @ 300°C, Quads @ 200°C
MS : Solvent delay of 0.1min, Scan Range 92-500 m/z,
Scan Rate @ ≈ 5 scan/sec,



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Other applications of
restriction..



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Coupling of 0.25, 0.32 and 0.53mm analytical columns



To use with MS, using short columns of 0.32 /0.25mm..

Non-ms detector applications..



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Application of restriction with non-vacuum detectors

Injection of gas sample at HIGHER pressure..



Injection volume (gas) will be compressed:

- Smaller injection band
- Injection of larger volumes

F.I. measurement of impurities in: methane, ethylene, ethane, acetylene, propane, propylene, propadiene, C4 isomers



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Application of restriction with non-vacuum detectors

Injection of sample at a HIGHER inlet pressure..



When using short 0.53mm columns, the digital pressure regulation of many systems is difficult..

.. adding this restriction allows higher pressure setting..



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Restriction alternative setup: double seal application

Double seal on same side

Offers possibility for a Direct semi-on-column injection.. Due to the high velocity and the vacuum, there will be virtually No solvent condensation..

Avoids stress to less stable stationary phases

Cyanopropyl phases in dioxin, furan or FAME

Challenges:

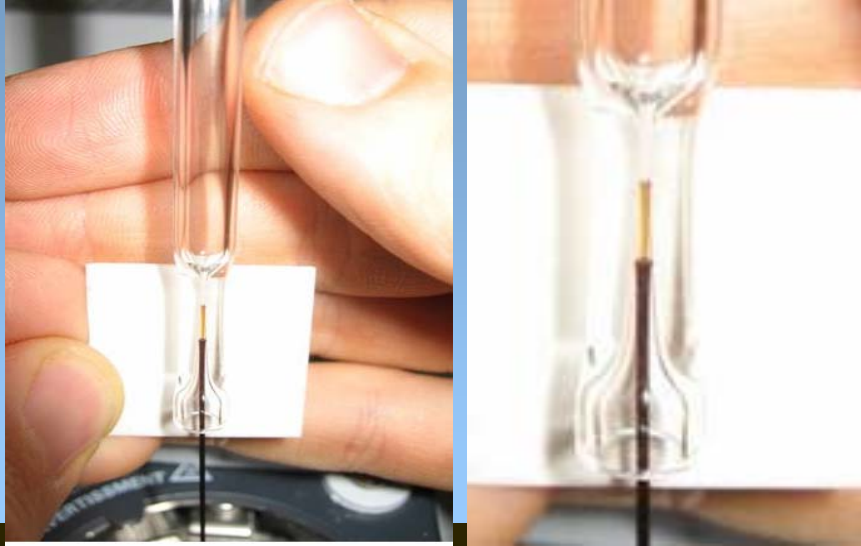
- dead volume
- release of restriction
- blockage

NOTE: this may work also in “non-vacuum” systems



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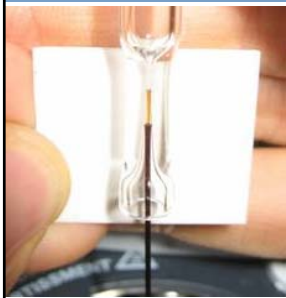
Practical setup using a "Uni-Liner" ..



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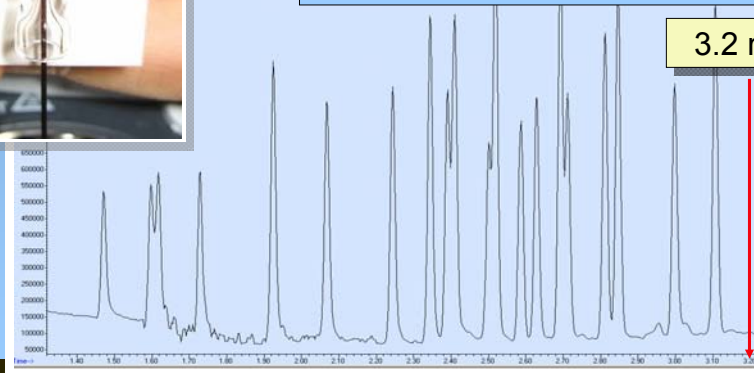
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Vacuum GC of Organochlorine Pesticides: Column & restriction positioned in a "Uniliner"



Column : 10m, 0.53mm, 0.25 μ m Rxi-5ms
Restriction : 8mm, 25 μ m ID tubing inside a drilled uniliner

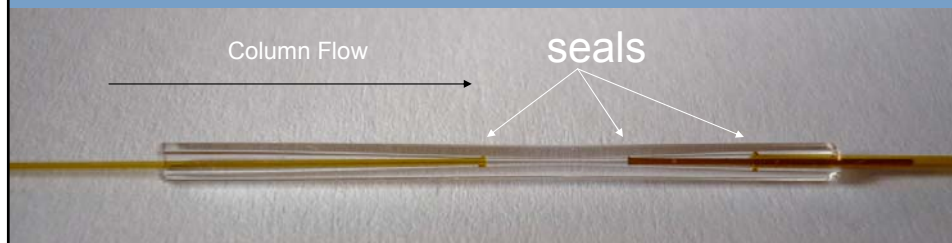
Inlet : 300°C, 4mm Drilled Uniliner, hole on top
Carrier gas : Constant pressure, 50psi
Oven : 100°C (no hold) to 300°C @ 45°C/min
MS Temp: Transfer line @ 280°C, Source @ 300°C, Quads @ 200°C
MS: Solvent delay of 0.1min, Scan Range 92-500 m/z,
Scan Rate @ \approx 5 scan/sec,



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Double seal Restriction



Coupling at the end of the analytical column

Position at the end of fused silica capillary..

Potential application in 2D-GC?

Using Vacuum GC and 3-5m x 0.53mm columns with linear velocity of 200 cm/s..



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Summary

- A new simple method is presented for applying vacuum GC using a restriction positioned in the injection port;
- Column coupling and setup is simple, no issues with leaks
- Restriction allows fast separations with split, splitless and direct injection techniques offering all advantages reported with separations under vacuum
- Data obtained on explosive analysis shows that the technique can be applied quantitatively
- The small restriction allows the use of different column dimensions with vacuum or pressurized GC



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- With splitless injection, due to vacuum, solvent condensation will be minimal, which requires lower oven starting temperatures..
- Release of septum particles can block restriction
- In order to set the desired flows, the GC control software must be manipulated
- The 25 μm restrictions can also be very helpful in several pressurized GC applications



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