• Using Nitrogen instead of Helium as carrier gas, while maintaining exact the same separation efficiency, retention times, peak elution order, without changing the oven temperature conditions.

Jaap de Zeeuw

Restek Corporation,
Middelburg, The Netherlands
Considerations for using a certain carrier gas

- Availability / delivery
- Price
- Purity
- Speed of analysis
- Type of detection system (PDD, MS..)
- Sensitivity (TCD)

Helium supply is under pressure
What are the alternatives?

Nitrogen or Hydrogen

“Slow” carrier gas
Cheap
Can be generated

“Fast” carrier gas
Cheap
Can be generated
Safety

If there is “enough” resolution

If there is “Just enough” resolution
Both carrier gases are relatively Cheap

Both gases can be generated using generators

- Unlimited supply
- Low cost
- Relative small investment

For use as carrier gas need to make sure the purity is very high;
Consider Gas filtration
Van Deemter curve for different gases

optimum gas velocities

Van Deemter Plot

HETP (mm)

Average Linear Velocity [cm/sec]

Flow [mL/min]

N₂ Slow

He

H₂ FAST

10 20 30 40 50 60 70

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Impact of optimum velocity on analysis time

- **Hydrogen, 45 cm/sec, 80°C, 0.9 mL/min constant**
  - Oven rate, 13.5°C/min
  - 13 min

- **Helium, 30 cm/sec, 80°C, 0.7 mL/min constant**
  - Oven rate, 9°C/min
  - 19 min

- **Nitrogen, 12 cm/sec, 80°C, 0.2 mL/min constant**
  - Oven rate, 3.5°C/min
  - 48.5 min

*Organochlorine pesticides, GC-ECD*
Using Nitrogen at the same linear velocity as Helium will result in an increase of HETP by approx. a factor 2.
Impact on Resolution

\[ R_s = \frac{1}{4} \times \left[ \alpha - 1 \right] \times \left[ \frac{k}{k + 1} \right] \times \sqrt{N_{th}} \]

- \( R \) = resolution
- \( N_{th} \) = theoretical Plate number
- \( \alpha \) = selectivity
- \( K \) = retention factor

\( N_{th} \) is linear with Column length
Resolution is not..

Loss of efficiency by a factor 2 only results in a loss of 1.4 on resolution.
Impact on Resolution

$$R_s = \frac{1}{4} \times \left[ \alpha - 1 \right] \times \left[ \frac{k}{k + 1} \right] \times \sqrt{N_{th}}$$

Loss of efficiency by a factor 2 only results in a loss of 1.4 on resolution.

Nth = 200.000
Nth = 100.000
Nth = 50.000
Maintain the separation efficiency using N2

Using same column and nitrogen under OPTIMAL conditions (12 cm/s)

Impact

- 2 x slower than Helium, analysis time will be 2x longer
- Peaks will be lower (sensitivity)

Need to change temperature program for same peak elution order
He carrier, constant flow, 30 cm/sec at 50 °C
50°C (2 min), 15 °C/min to 300°C (1.4 min)

19 min

N₂ carrier, 0.63 mL/min constant flow, 18 cm/sec at 50°C
50°C (3 min), 9°C/min to 300°C (3.2 min)

31.1 min
How to maintain the separation efficiency using N2...

Using a smaller diameter column

Using the SAME carrier gas we know that:
Replacing a 30m x 0.25mm for a 20m x 0.15mm,

Analysis times are approximate 2x shorter..
Using a 0.15mm ID instead of 0.25mm, under HELIUM

30m x 0.25mm Rxi-5Sil MS, 
df = 0.25 μm

28 min

20m x 0.15mm Rxi-5Sil MS, 
df = 0.15 μm

15 min
How to maintain the separation efficiency using N2...

Using a smaller diameter column

Replacing a 30m x 0.25mm for a 20m x 0.15mm

Operate the 0.15mm at a higher velocity to get the SAME analysis time..

We know we will loose some “efficiency”..
Loss of efficiency using N2 a higher velocity

This is not as bad as expected

Under optimum, N2 already generated higher efficiency;

Using smaller diameter columns:
- The optimum is at higher velocity
- The slope of the curve reduces
Calculating the impact
Using method translator

Helium $\rightarrow$ Nitrogen

30/0.25 $\rightarrow$ 20/0.15

32 $\rightarrow$ 21.5 cm/s

Can use the SAME oven program

Same analysis time
Work done with Pro EZ-GC Modeler; Helium, 30m x 0.25mm
Work done with Pro EZ-GC Modeler; Nitrogen, 20m x 0.15mm
Overlay of 2 chromatograms...
The Practical test
Challenge

- Take POLAR column: Stabilwax
- Use COMPLEX mixture: Fragrances
- Compare 30m x 0.25mm with 20m x 0.15mm

Operate with same temperature programming using pre-selected flow / linear velocities

Two situations:
Efficiency and Speed optimized flow setting for He
### Optimized Flows for He and N2

<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Efficiency</th>
<th>Speed</th>
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</thead>
<tbody>
<tr>
<td>0.25mm He</td>
<td>1.4 mL/min</td>
<td>2.0 mL/min</td>
</tr>
<tr>
<td>0.15mm N2</td>
<td>0.27 mL/min</td>
<td>0.38 mL/min</td>
</tr>
</tbody>
</table>

**Actual Flows used to use the same program and obtain same analysis time**

<table>
<thead>
<tr>
<th>Flow Rate</th>
<th>Efficiency</th>
<th>Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15mm N2</td>
<td>0.36 ml/min</td>
<td>0.52 mL/min</td>
</tr>
</tbody>
</table>

---

**Optimized**

**Speed**

---

**Optimized**
30m x 0.25mm x 0.25µm Stabilwax

He constant 1.4 mL/min
40°C (0.1 min), 6.4°C/min to 250°C

Efficiency optimized flow
20.2m x 0.15mm x 0.15μm Stabilwax

$N_2$ constant 0.36 mL/min

40°C (0.1 min), 6.4°C/min to 250°C

6.75 min

31.24 min
30m x 0.25mm x 0.25µm Stabilwax

He constant 1.4 mL/min
40°C (0.1 min), 6.4°C/min to 250°C

Efficiency-optimized flow
Optimal heating rate

Men’s After Shave
6.81 min
31.23 min

20.2m x 0.15mm x 0.15µm Stabilwax

N₂ constant 0.36 mL/min
40°C (0.1 min), 6.4°C/min to 250°C

Men’s After Shave
6.75 min
31.24 min
Detail of separation
30m x 0.25mm x 0.25μm Stabilwax

He constant 1.4 mL/min
40°C (0.1 min), 6.4°C/min to 250°C

Efficiency optimized flow
20.2m x 0.15mm x 0.15μm Stabilwax

$N_2$ constant 0.36 mL/min

40°C (0.1 min), 6.4°C/min to 250°C

15.78 min

17.39 min
Note the Pressures and flows used

For Helium
- Pressure: 15.27 psi
- Flow: 1.40 mL/min

For Nitrogen
- Pressure: 17.42 psi
- Flow: 0.36 mL/min

Very small difference

4 times lower flow
Cost of helium and Nitrogen

Helium $300 per cylinder
Nitrogen $60 per cylinder

Save 400% on carrier gas costs..
Another example:

Pesticides using an optimized selective phase
20m x 0.15mm x 0.15µm Rtx-CLPesticides: Nitrogen
30m x 0.25mm x 0.25µm Rtx-CLPesticides: Helium

Agilent 6890 GC-ECD with split/splitless inlet
Restek Sky® Liner
  Split, Precision® with Wool, 4mm
Organochlorine pesticides, 1 µL fast autosampler injection
250°C, split ratio 50

20m x 0.15mm x 0.15µm Rtx-CLPesticides
  **Nitrogen, constant flow 0.41 mL/min**
  Holdup time 1.37 min
  150°C (0.1 min), 14°C/min to 320°C (0.76 min)

30m x 0.25mm x 0.25µm Rtx-CLPesticides
  **Helium, constant flow 1.42 mL/min**
  Holdup time 1.38 min
  150°C (0.1 min), 14°C/min to 320°C (0.76 min)
<table>
<thead>
<tr>
<th>Carrier Gas</th>
<th>Original</th>
<th>Translation</th>
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</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>Helium</td>
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### Column

<table>
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<tr>
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<tr>
<td>Length</td>
<td>21.40</td>
<td>30.50       m</td>
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<tr>
<td>Inner Diameter</td>
<td>0.15</td>
<td>0.25        mm</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>0.15</td>
<td>0.25        μm</td>
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<td>Phase Ratio</td>
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### Control Parameters

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<tr>
<td>Outlet Flow</td>
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<td>1.42        mL/min</td>
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<tr>
<td>Average Velocity</td>
<td>26.02</td>
<td>36.96       cm/sec</td>
</tr>
<tr>
<td>Holdup Time</td>
<td>1.37</td>
<td>1.38        min</td>
</tr>
<tr>
<td>Inlet Pressure (gauge)</td>
<td>28.74</td>
<td>22.53        psi</td>
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<tr>
<td>Outlet Pressure (abs)</td>
<td>14.70</td>
<td>14.70       psi</td>
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### Oven Program

- Isothermal
- Ramps

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<tr>
<th>Ramps</th>
<th>Ramp (°C/min)</th>
<th>Temp (°C)</th>
<th>Hold (min)</th>
<th>Ramp (°C/min)</th>
<th>Temp (°C)</th>
<th>Hold (min)</th>
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<tbody>
<tr>
<td>1 (1-4)</td>
<td>150</td>
<td>0.1</td>
<td></td>
<td>150</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>320</td>
<td>0.76</td>
<td>14</td>
<td>320</td>
<td>0.75</td>
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</table>

### Control Method

- Constant Flow

### Results

<table>
<thead>
<tr>
<th></th>
<th>Solve for</th>
<th>Efficiency</th>
<th>Speed</th>
<th>Translate</th>
<th>Custom</th>
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<tbody>
<tr>
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<td></td>
<td>13.00</td>
<td>12.99</td>
<td>min</td>
</tr>
<tr>
<td>Speed</td>
<td></td>
<td></td>
<td></td>
<td>1.00</td>
<td>x</td>
</tr>
</tbody>
</table>

Use FC Values for Original  Use FC Values for Translation
20m x 0.15mm x 0.15µm Rtx-CLPesticides

N<sub>2</sub> constant 0.41 mL/min

150°C (0.1 min), 14°C/min to 320°C

3.65 min

10.58 min

Organochlorine Pesticides Mix

30m x 0.25mm x 0.25µm Rtx-CLPesticides

H<sub>e</sub> constant 1.52 mL/min

150°C (0.1 min), 14°C/min to 320°C

Organochlorine Pesticides Mix

3.63 min

10.59 min
20m x 0.15mm x 0.15µm Rtx-CLPesticides

N₂ constant 0.41 mL/min
150°C (0.1 min), 14°C/min to 320°C
3.65 min
Organochlorine Pesticides Mix
10.58 min

30m x 0.25mm x 0.25µm Rtx-CLPesticides

He constant 1.52 mL/min
150°C (0.1 min), 14°C/min to 320°C
3.63 min
Organochlorine Pesticides Mix
10.59 min
20m x 0.15mm x 0.15µm Rtx-CLPesticides  
N\textsubscript{2} constant 0.41 mL/min

Heptachlor epoxide  
6.55 min

trans-Chlordane

cis-Chlordane

4,4’-DDE

Endosulfan I  
7.05 min

30m x 0.25mm x 0.25µm Rtx-CLPesticides  
He constant 1.52 mL/min

6.56 min

7.06 min
Example 3: PAH on Rxi-17Sil MS

EU 15+1 PAH Standard (16 components)

- Formulated to contain the 16 major European Food Safety Authority (EFSA) PAH compounds.
- High concentration (100 μg/mL) solution provides value and flexibility. Dilute as needed for fortification and calibration mixes.
- Low-volatility toluene solvent provides longer shelf life, which helps ensure more accurate results.
- Broad solvent miscibility—compatible with acetonitrile, the QuEChERS solvent.
- Certified reference material (CRM) meets strict ISO quality requirements.
- Pair with Rxi®-PAH GC column for easy separation of critical PAH compounds from common interferences in food and environmental samples: www.restek.com/rxi-pah
- HPLC compatible when diluted in appropriate solvent and analyzed with Pinnacle® II PAH columns or UHPLC compatible on the Pinnacle® DB PAH column.
Medium polar phase: Rxi-17Sil MS GC-FID

- EU 15+1 PAH Standard, 1 µL
- Precision split liner with wool, 4 mm ID
- 275°C, split ratios 50/250 for 0.25/0.15mm
- GC oven program
  - 200°C (1.7 min)
  - 3.75°C/min to 260°C
  - 35°C/min to 350°C (10 min)
- Flame Ionization Detector, 360°C
Oven: 200°C (1.7 min), 3.75°C/min to 260°C, 35°C/min to 350°C (10 min)  
EU 15+1 PAH Standard

- 5-Methylchrysene: 19.80 min
- Benz[a]pyrene: 21.38 min
- Benz[a]anthracene: 18.57 min
- Benzo[c]fluorene: 14.15 min
- Benzo[ghi]perylene: 23.87 min
- Dibenz[a,h]pyrene: 28.66 min
20.0m x 0.15mm x 0.15µm Rxi-17Sil MS N₂ at 0.32 mL/min constant flow

Oven: 200°C (1.7 min), 3.75°C/min to 260°C, 35°C/min to 350°C (10 min)

EU 15+1 PAH Standard

- Benzo[c]fluorene
  - Retention time: 14.22 min

- Benz[a]anthracene
  - Retention time: 18.61 min

- 5-Methylchrysene
  - Retention time: 19.81 min

- Benzo[a]pyrene
  - Retention time: 21.39 min

- Benzo[ghi]perylene
  - Retention time: 23.95 min

- Dibenzo[a,h]pyrene
  - Retention time: 28.93 min
30.2m x 0.25mm x 0.25µm Rxi-17Sil MS

He at 1.4 mL/min constant flow

Oven: 200°C (1.7 min), 3.75°C/min to 260°C, 35°C/min to 350°C (10 min)

Benzo fluoranthenes

[b] 20.75 min \( R_s = 1.2 \)

[k] \( R_s = 1.4 \)

[j] 20.83 min
20.0m x 0.15mm x 0.15µm Rxi-17Sil MS  \( \text{N}_2 \) at 0.32 mL/min constant flow

Oven: 200°C (1.7 min), 3.75°C/min to 260°C, 35°C/min to 350°C (10 min)

Benzo fluoranthenes

- Peak [b] at 20.75 min with \( R_s = 1.2 \)
- Peak [k] with \( R_s = 1.4 \)
- Peak [j] at 20.83 min
Example 4: Dioxin analysis using Waters APGC T-QS comparing 30m/0.25 under He with 20m/0.15 under N2

- Splitless injections of 1.0µL with inlet temperature of 290°C and purge time of 2.8 minutes
- GC column flow of 0.66mL/min for 2.8 minutes, reducing to 0.33 mL/min thereafter
- Initial oven temperature of 130°C, hold for 2.8 minutes, ramps as follows:
  - Ramp 1: 25°C/min to 220°C, hold 0 minutes
  - Ramp 1: 4°C/min to 280°C, hold 0 minutes
  - Ramp 1: 14°C/min to 310°C, hold 4 minutes
  - Total time 27.5 minutes
<table>
<thead>
<tr>
<th>Species</th>
<th>Helium Carrier Gas</th>
<th>Nitrogen Carrier Gas</th>
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<tbody>
<tr>
<td></td>
<td>Retention Time</td>
<td>Peak Response 1st isotope</td>
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<td>2,3,7,8 TCDD</td>
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</tbody>
</table>

Data generated by Rhys Jones, Waters UK
Robustness study

Repeated injections of used motor oil, follow EPA 8081B
Endrin DDT Breakdown Mix

**EPA Method 8081B:**
"If degradation of either DDT or Endrin exceeds 15%... corrective action..."

- **Nitrogen carrier gas**
  - 0.41 mL/min constant flow
- **Split injection**
  - Split ratio 50
  - Inlet split flow 20.5 mL/min
- Higher flow through inlet minimizes sample contact with surfaces that can cause analyte breakdown

**Endrin breakdown = 1.7%**
**DDT breakdown = 0.7%**

20m x 0.15mm x 0.15µm Rtx-CL pesticides, constant flow N₂ 0.41 mL/min; SGE Focus split liner, 250°C, 50:1 GC oven: 150°C (0.1 min), 14°C/min to 320°C (0.76 min); μ Electron Capture Detector 335°C
Ruggedness Experiment

- Standard × 2
- Used Motor Oil × 1
- Standard × 2
- Used Motor Oil × 2
- Standard × 2
- Used Motor Oil × 4
- Standard × 2
- Used Motor Oil × 4
- Standard × 2
- Used Motor Oil × 4
- And repeat…

Endrin / DDT Standard = 100 / 200 pg/µL
Used Motor Oil = 5000 ng/µL

Innovative Chromatography Products  www.restek.com
Start of experiment...

EPA Method 8081B criteria of < 15% breakdown for Endrin and DDT easily met at start of experiment...

After 111 injections of used motor oil...

Endrin breakdown (%): 1.7
DDT breakdown (%): 0.7

Endrin breakdown (%): 6.6
DDT breakdown (%): 9.8

Endrin and DDT breakdown still meeting criteria!
After 111 injections of used motor oil...

Peak responses are still strong!
Summary of features using N2 and 0.15mm columns

• Separations are exact identical
• Analysis time is the same
• No change in oven temperature program
• Pressure required for N2 is just a little higher
• Nitrogen is always available
• Price advantage for nitrogen and volume used
• 0.15mm columns have same OD as 0.25mm: can use the same ferrules
• 0.15mm columns have proven to work for many years and can be manufactured with different phase technologies
• Robustness for high matrix samples is acceptable
Limitations

• Loadability is factor 5 lower; Not ideal for injecting strong matrix samples: the used motor oil experiments showed promising results.

• N2 is not a very good "MS" gas, but flow is VERY low...
  • It is used APCI
  • In quadrupole it is also used
  • MS systems become more sensitive, so…

• Leak detection is for Nitrogen more challenging
Changing carrier gas from Helium to Nitrogen

If peaks are well resolved:
- Nitrogen at higher velocity, keep conditions the same, loose some separation, deal with shorter column life;

If peaks are just resolved:
- Nitrogen at optimum speed: accept longer analysis time;
- Nitrogen and smaller bore capillary; very interesting concept, many advantages, needs very little method development;
Thank you for your kind attention