Comprehensive two-dimensional gas chromatography (GC×GC): General background and application

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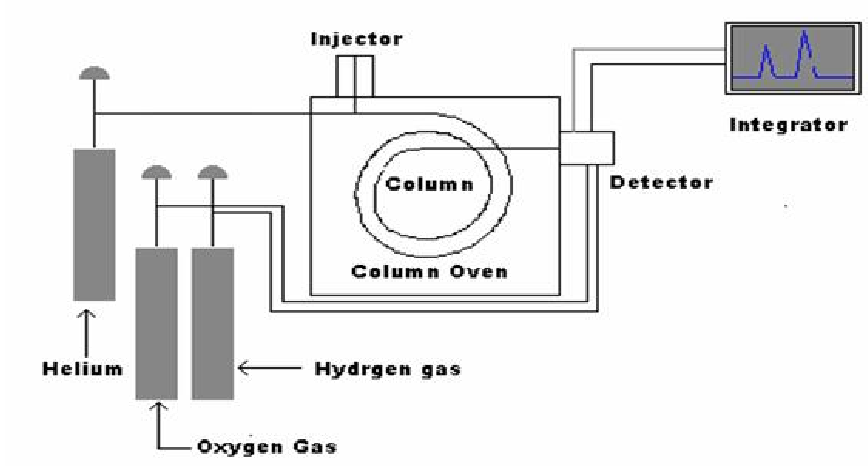
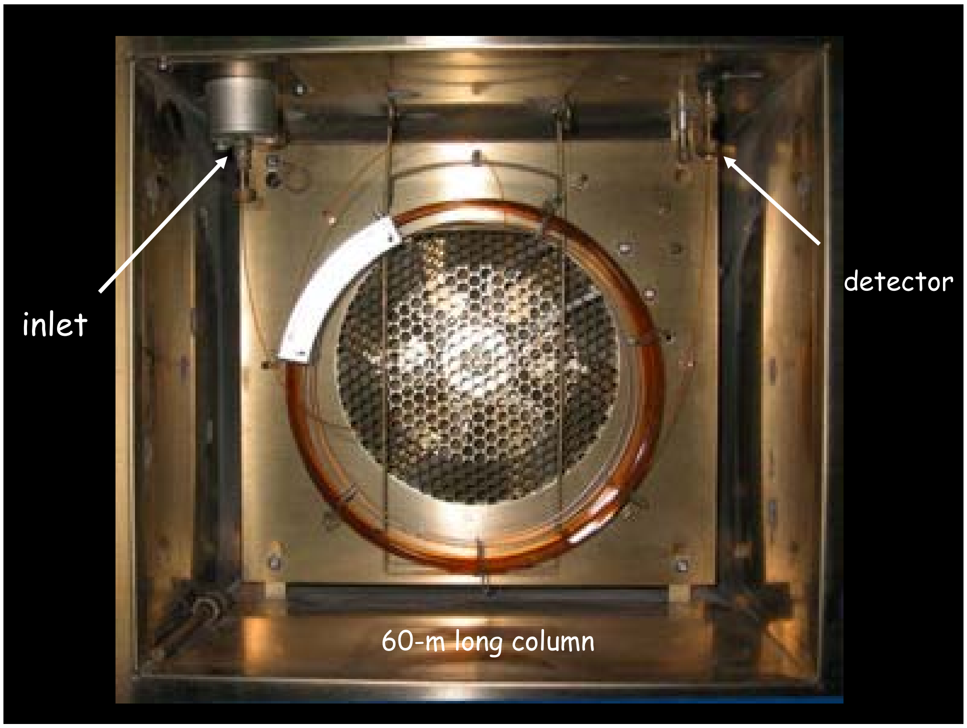
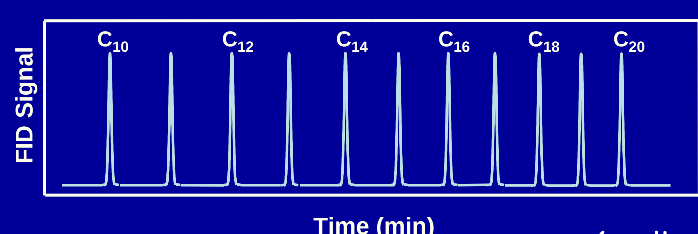
1D gas chromatography





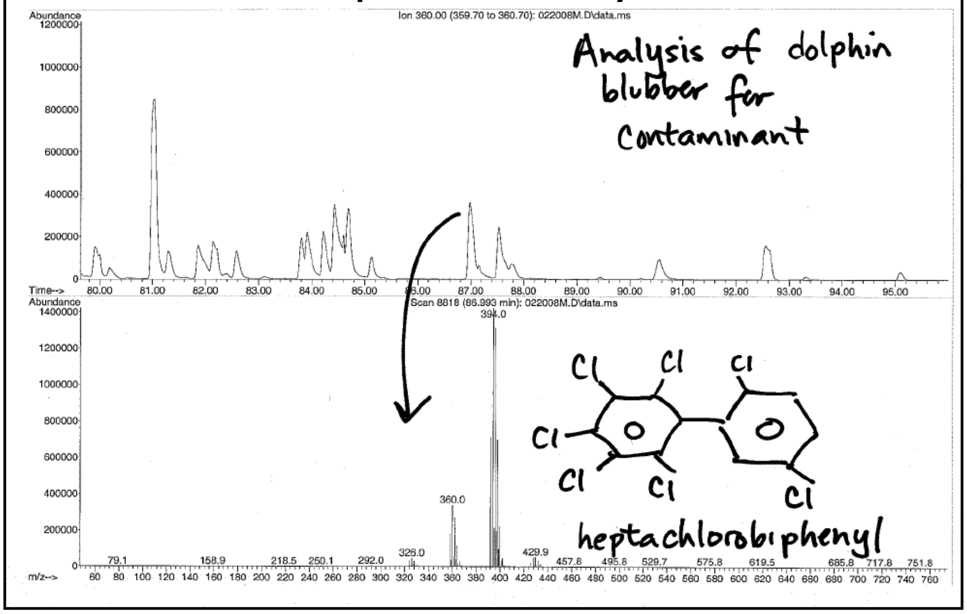
Typical gas chromatogram

- *components vary in some molecular property that can be used by a GC stationary phase to separate them from one another*
- *GC column has sufficient separation power to separate a small number of components*

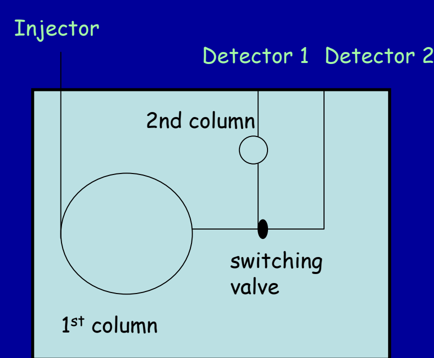


(*n*-alkanes)

1D gas chromatography-mass spectrometry

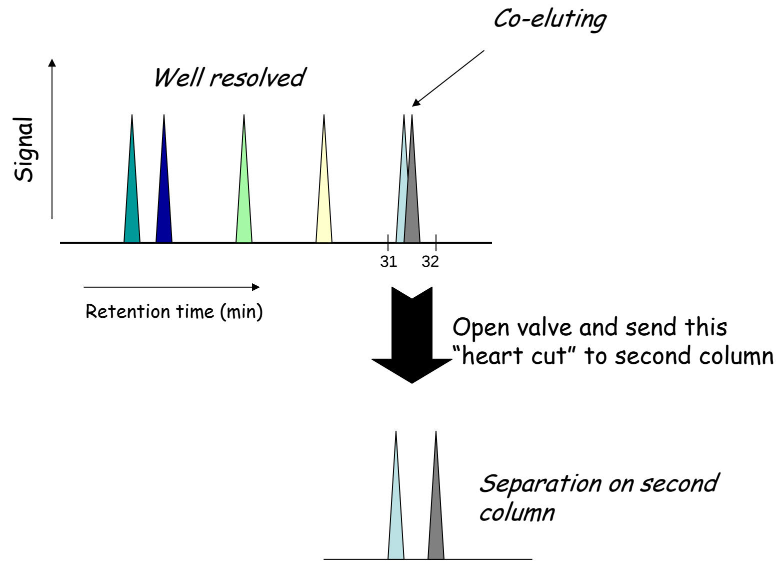


Heart cut 2D GC

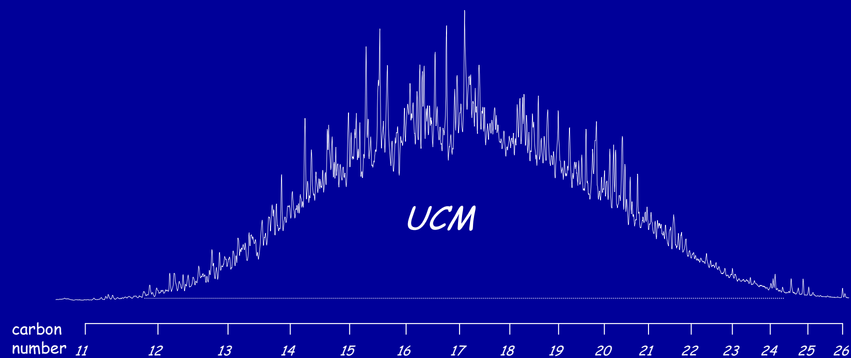


-Stationary phases are not the same in the first and second columns!

-Only send a select region to the second column by switching valve.



Unresolved Complex Mixture



From a sample collected in 2000 from an oil spill that occurred in 1969

Unresolved complex mixture (UCM)

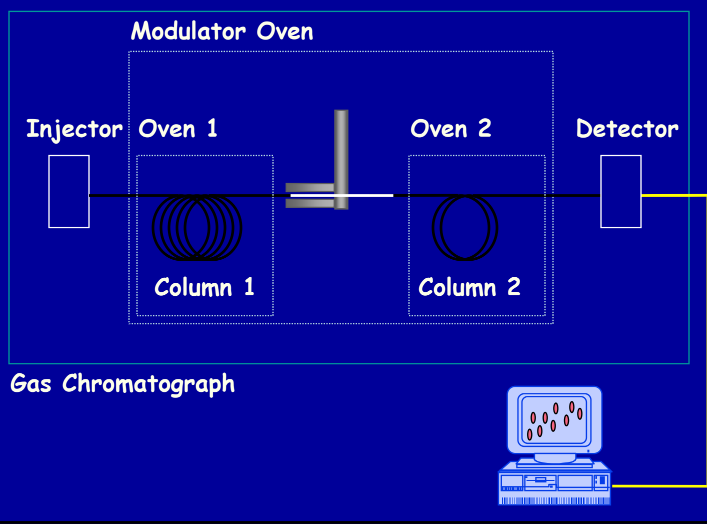
UCM is derived from traditional gas chromatography (GC) and refers to a hump of unresolved and, hence unidentified, hydrocarbons in gas chromatograms.

Too many compounds with very similar GC characteristics (multiple co-elutions) and mass spectral properties (multiple ions).

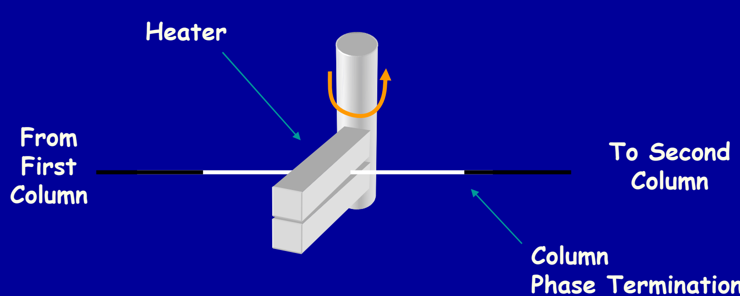
Comprehensive two-dimensional GC (GCxGC)

- Technology capable of separating hundreds to thousands more compounds in complex mixtures.
- Expands our analytical window into the UCM.

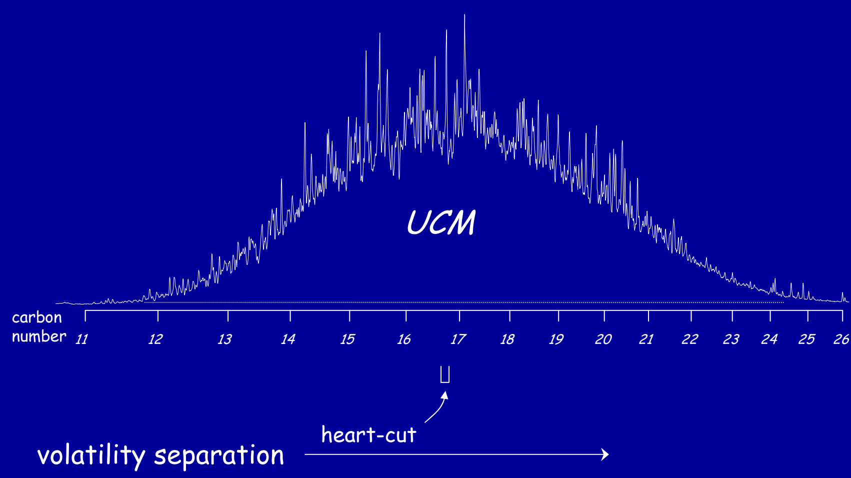
GC×GC



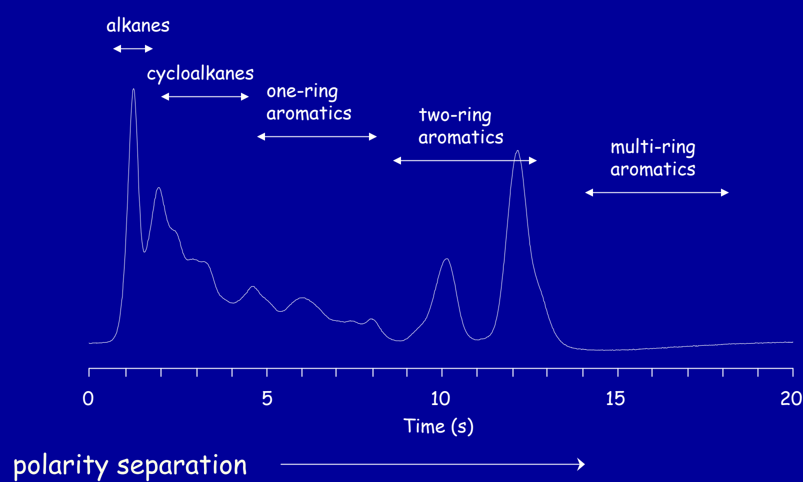
Thermal Modulator



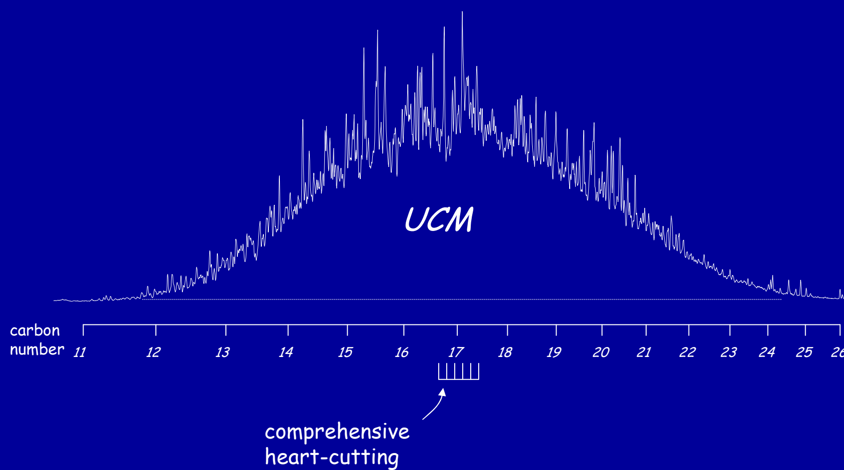
Unresolved Complex Mixture

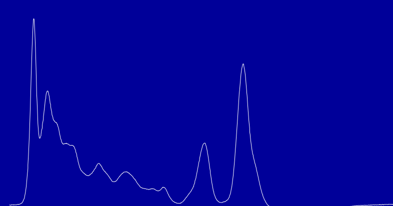


Second-Dimension Separation



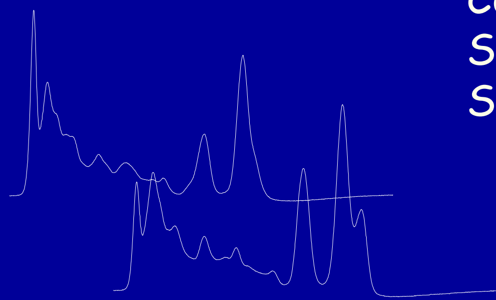
Unresolved Complex Mixture



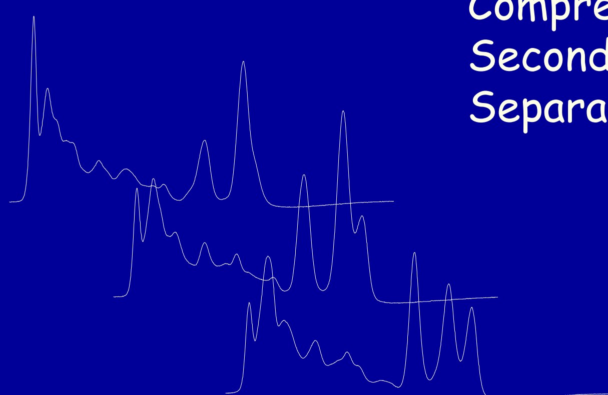


Comprehensive Second-Dimension Separations

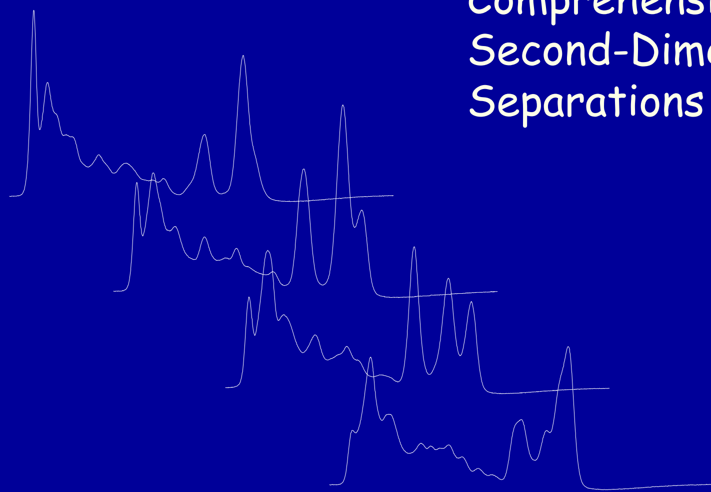
Comprehensive Second-Dimension Separations



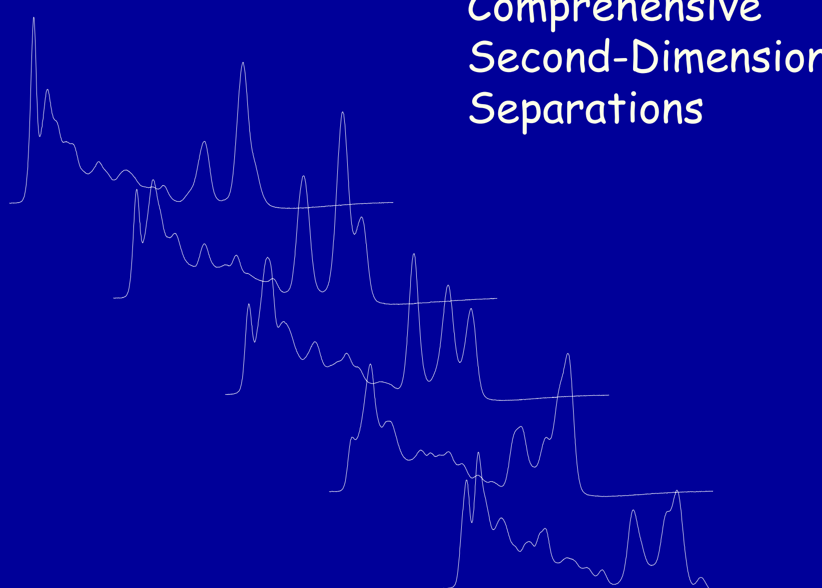
Comprehensive Second-Dimension Separations

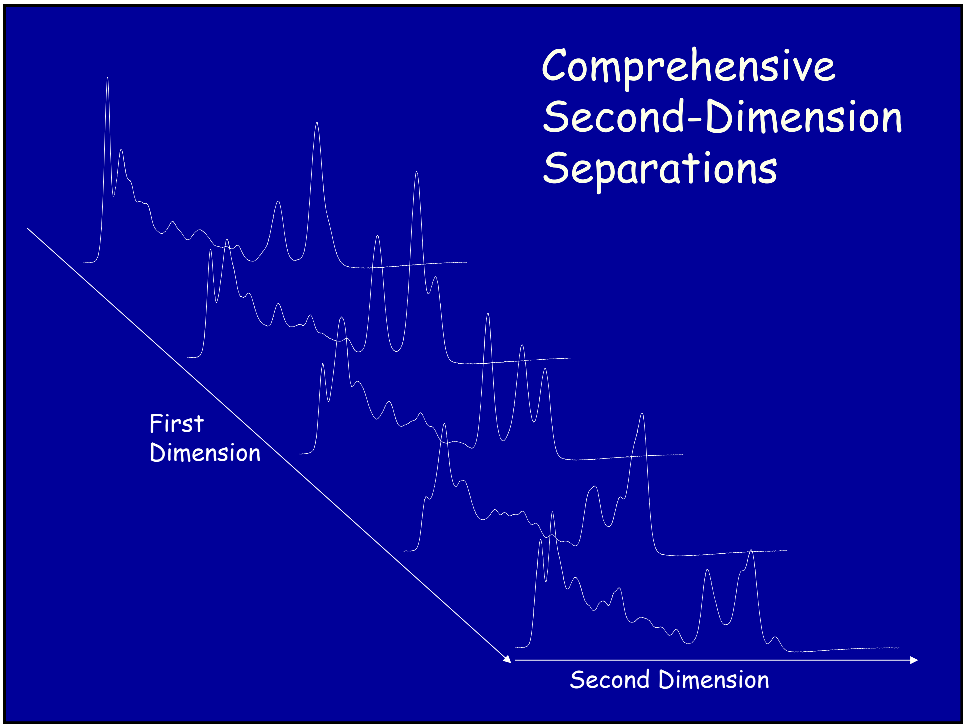


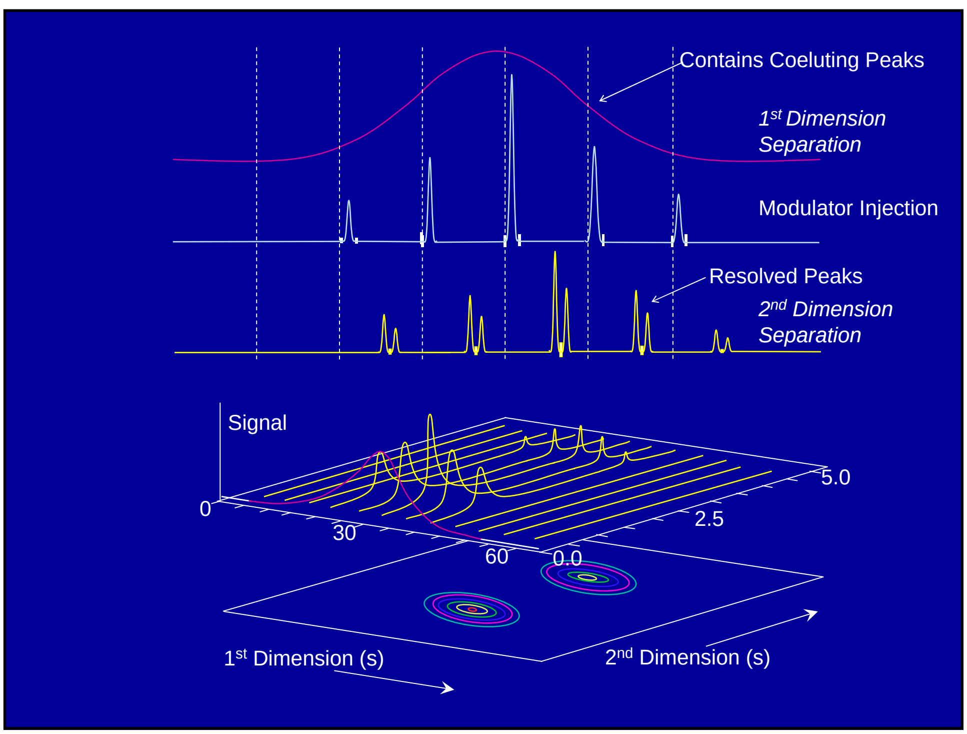
Comprehensive Second-Dimension Separations

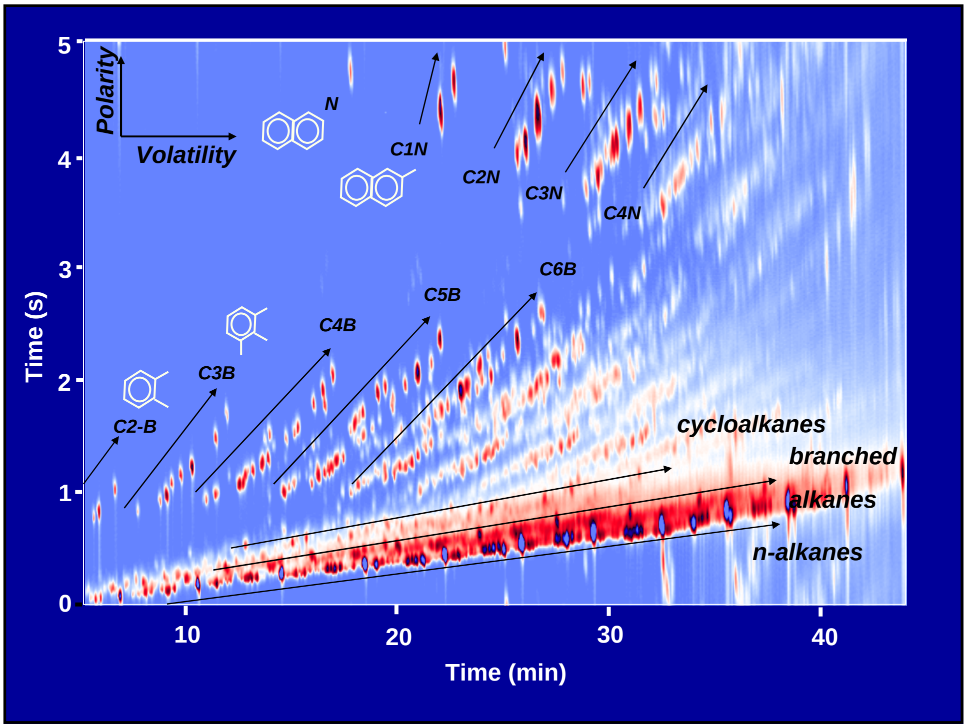


Comprehensive Second-Dimension Separations




Comprehensive Second-Dimension Separations
First Dimension
Second Dimension

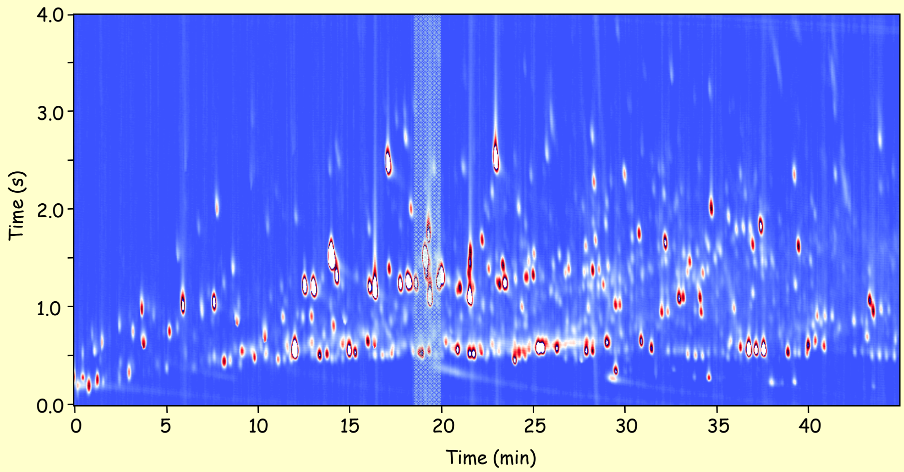

Contains Coeluting Peaks
1st Dimension Separation
Modulator Injection
Resolved Peaks
2nd Dimension Separation
Signal
0
30
60
0.0
2.5
5.0
1st Dimension (s)
2nd Dimension (s)



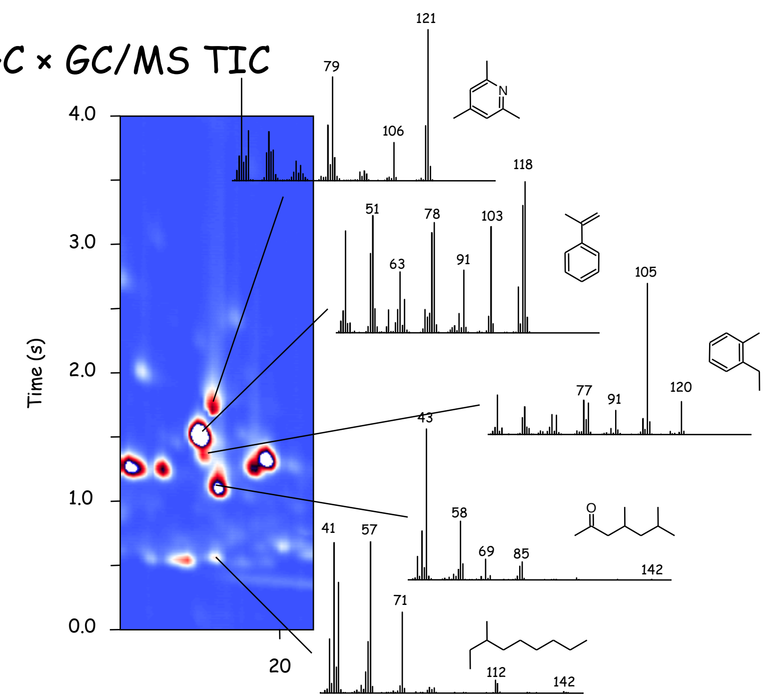
Five things cool about GCxGC

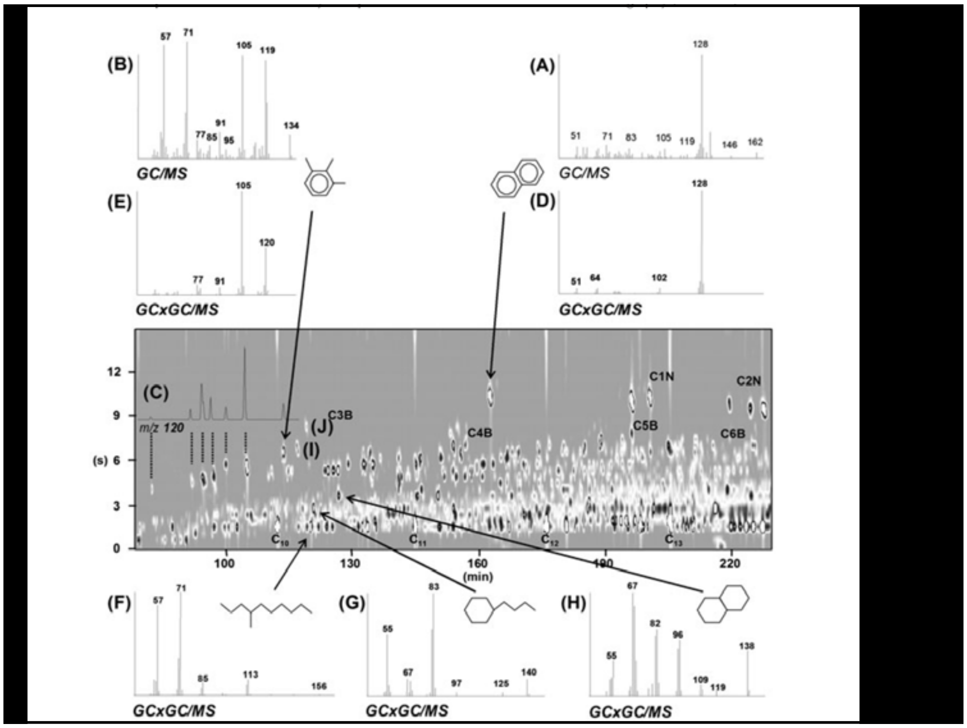
- Increased resolution (more separation)
- Chemical ordering
- Increased signal to noise
- With FID, same response factor (great for oils
- With MS, cleaner mass spectra

GC × GC/MS TIC of Fire Debris



GC × GC/MS TIC





Factors Influencing GC × GC Resolution

- Selection of Chromatographic Stationary Phases
- Stationary Phase Film Thickness
- Column Dimensions
- Mobile Phase Head Pressure / Flow Rate
- Duration of Modulation Period (Trap & Release Cycle)
- Oven 1 & 2 Temperature Ramp Profiles
- Hot Jet Temperature Ramp Profile
- Cold Jet Flow Rate
- The Analyte

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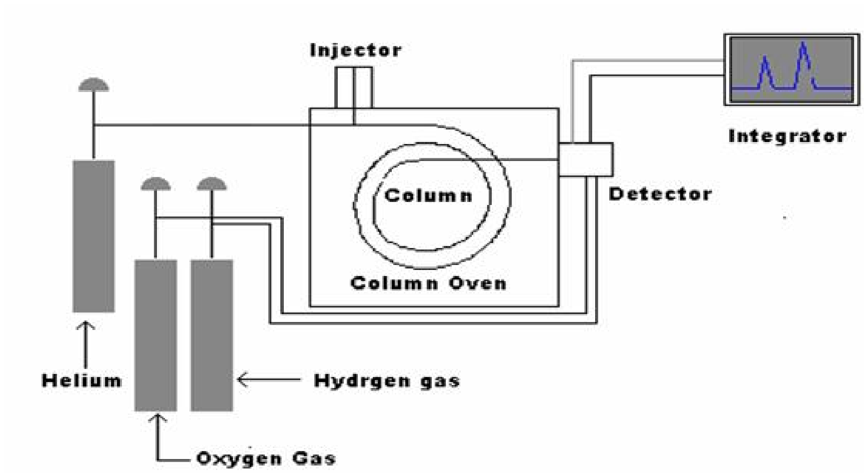
1D gas chromatography



There are newer modulators

GCxGC/TOF-MS Modulator Region

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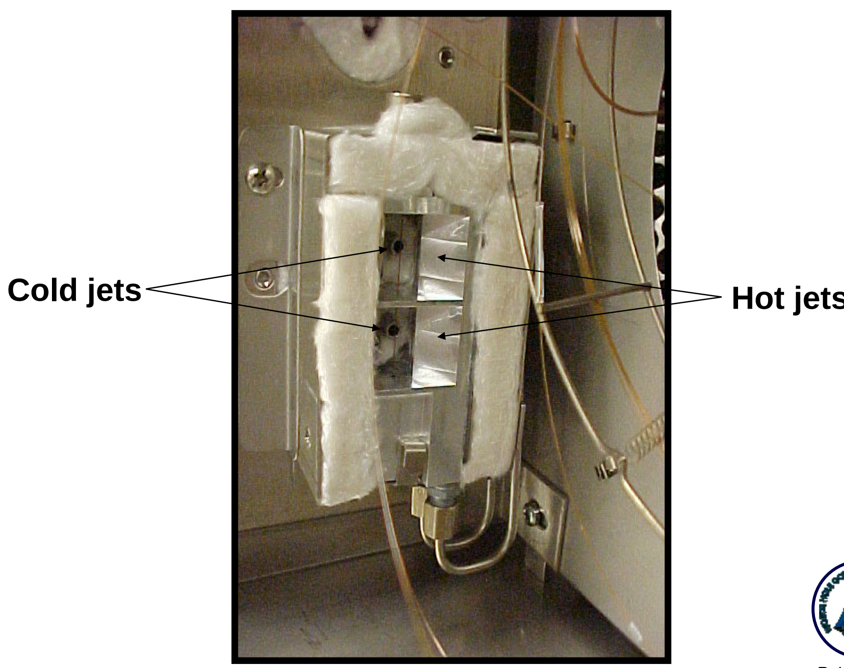

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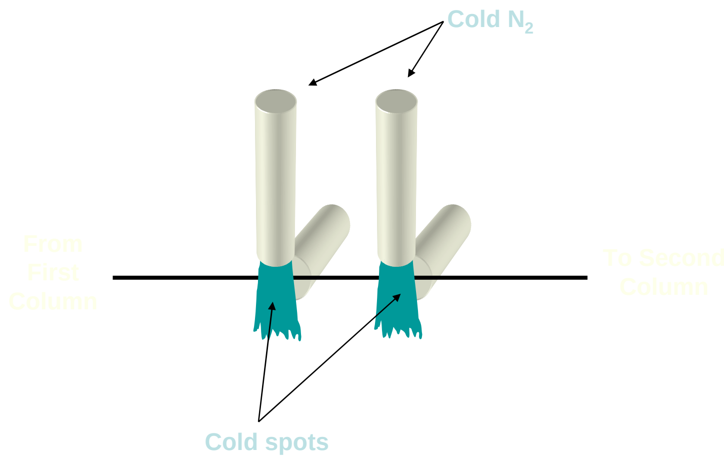
Quad Jet Modulator



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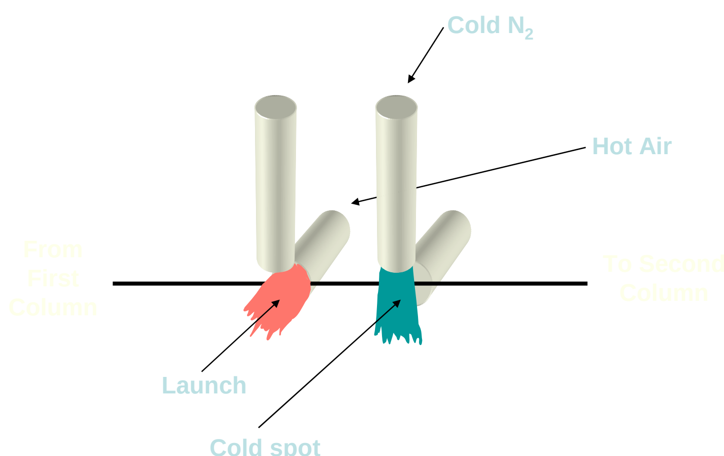
Quad Jet Modulator



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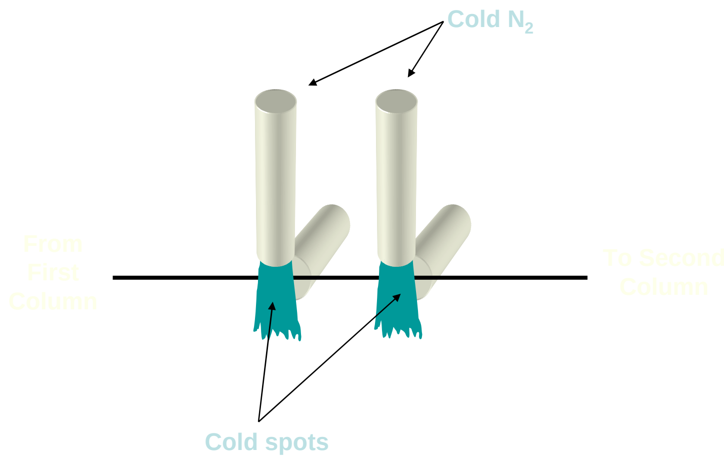
Quad Jet Modulator



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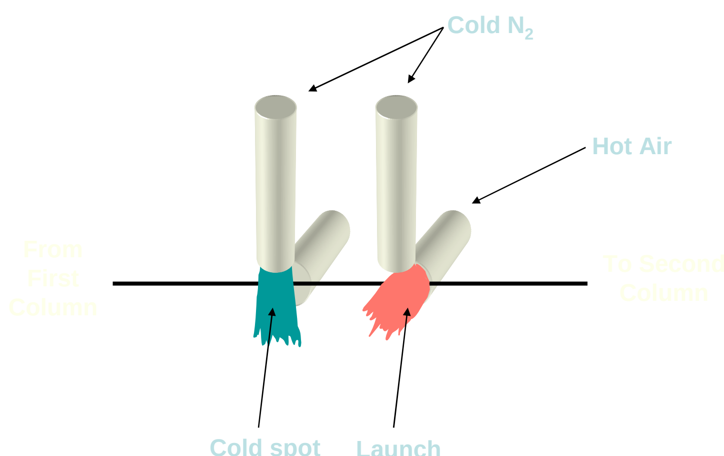
Quad Jet Modulator



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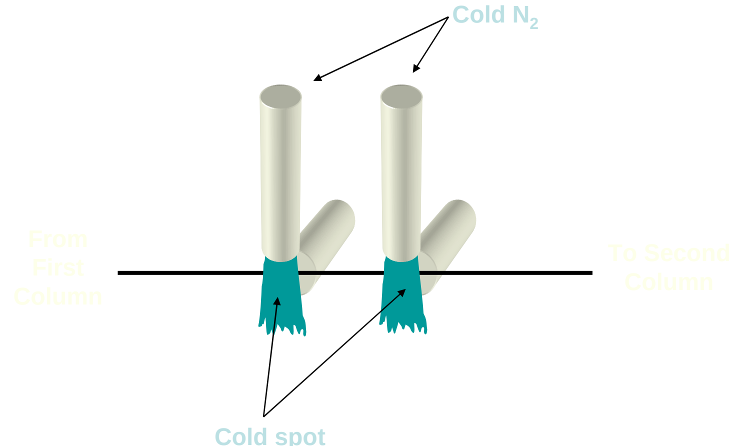
Quad Jet Modulator



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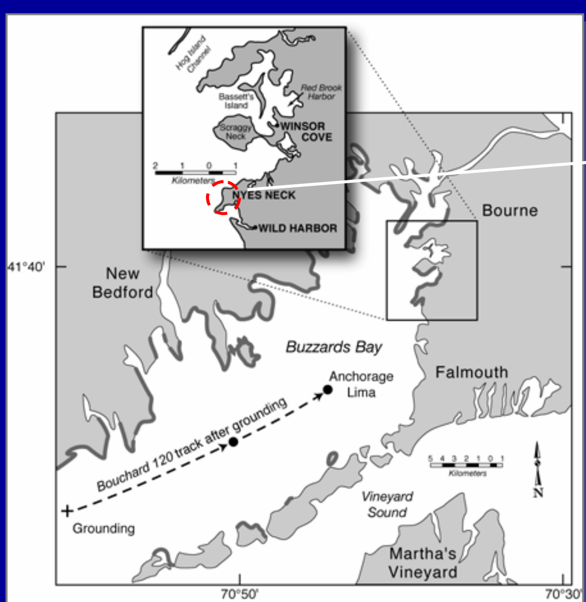
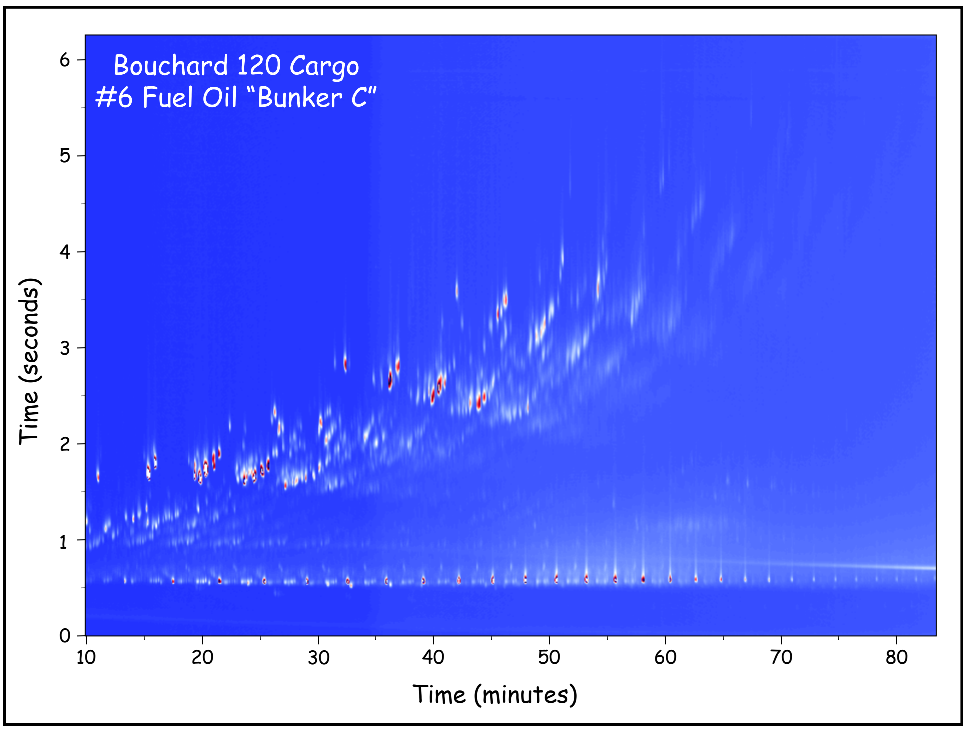


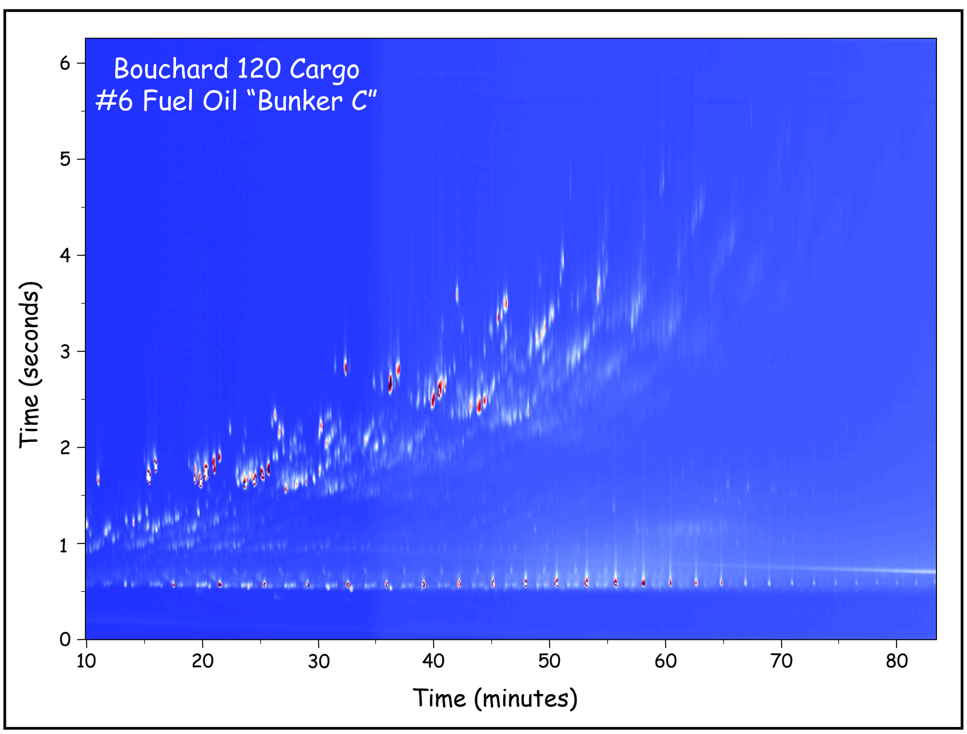
Recent Spill

Bouchard 120
Nyes Neck
April 27, 2003
388000 L of No. 6 fuel oil

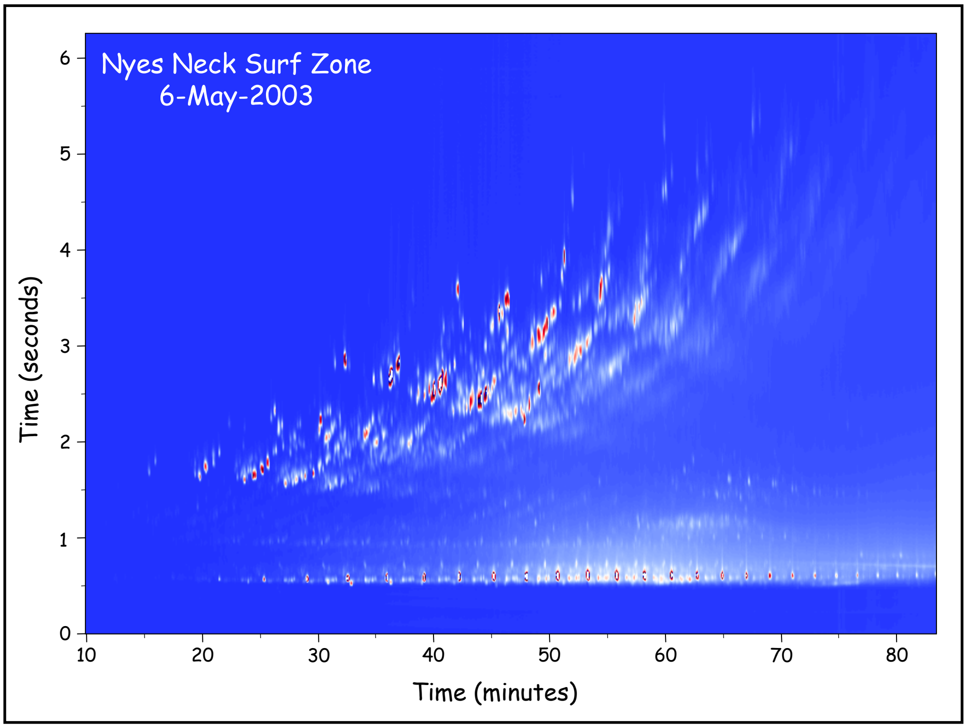
No. 6 fuel oil: *Background*

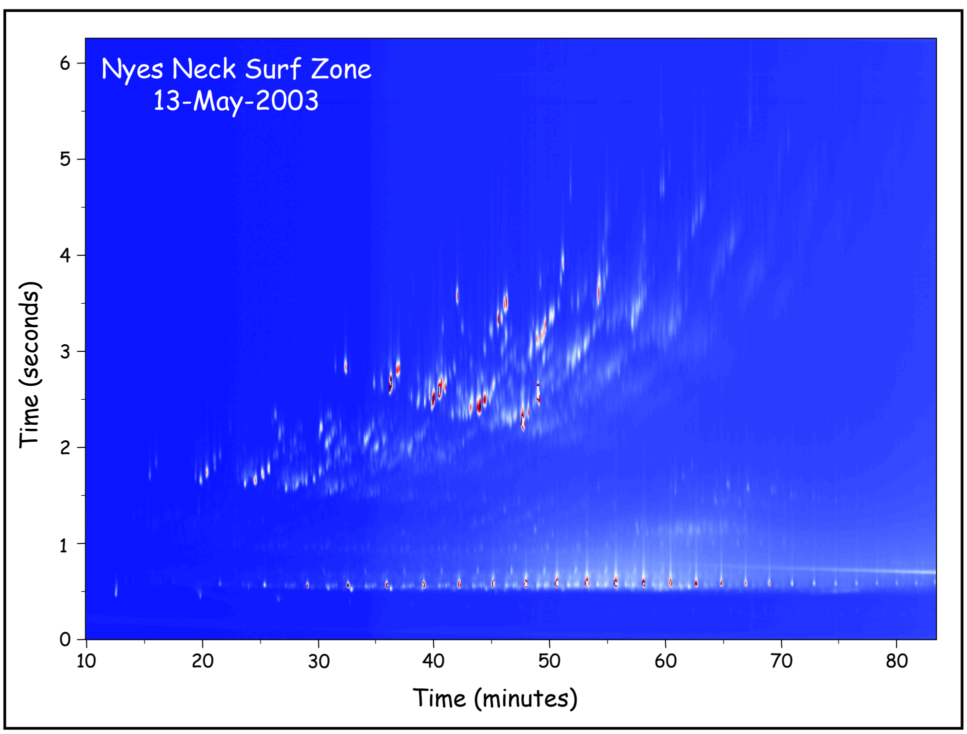
- Petroleum is a complex mixture of organic compounds, which can have different toxicities and long-term fates.
- No. 6 fuel oils are often used in marine diesels or industrial power applications.
- Prepared from the residuum and "cut" with a lighter petroleum product.
- Can vary dramatically in composition.

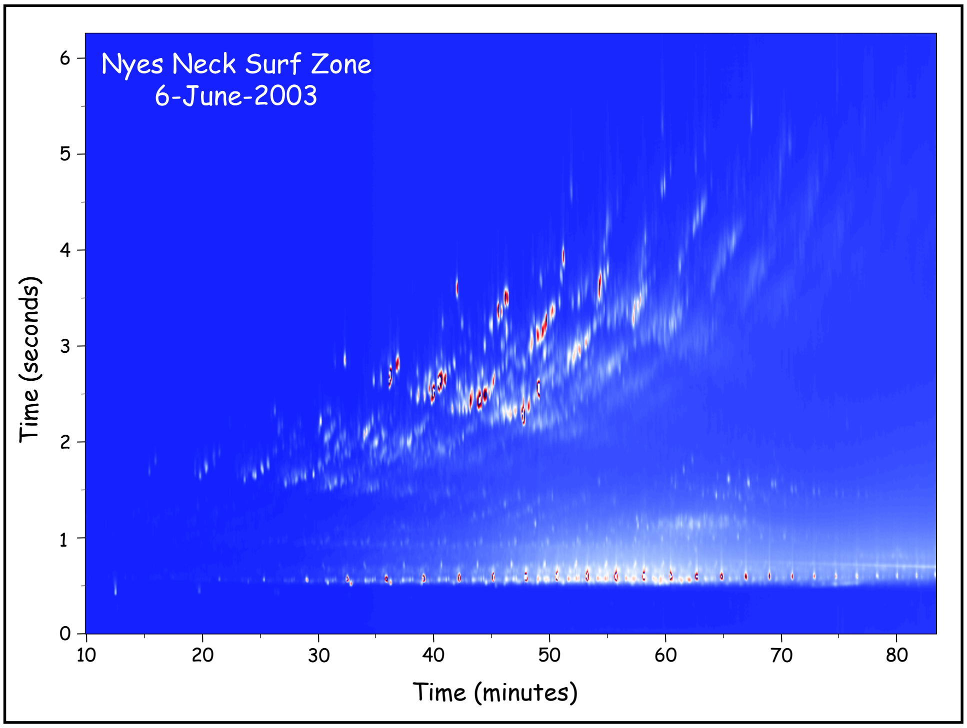


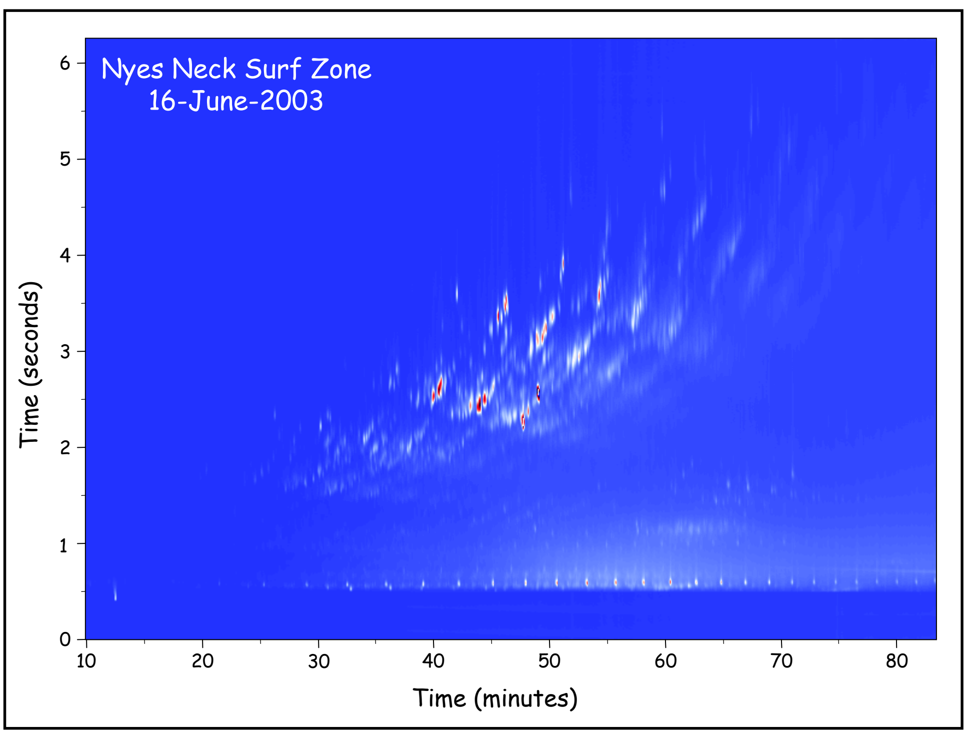


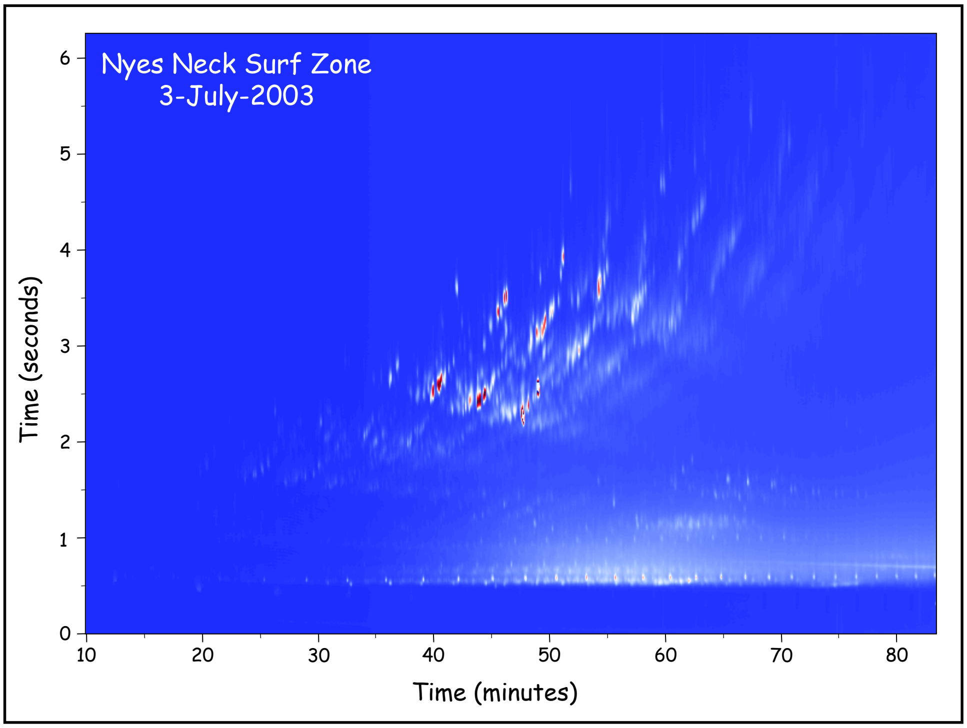
Bouchard 120 Cargo
#6 Fuel Oil "Bunker C"
Time (seconds)
0
1
2
3
4
5
6
Time (minutes)
10
20
30
40
50
60
70
80

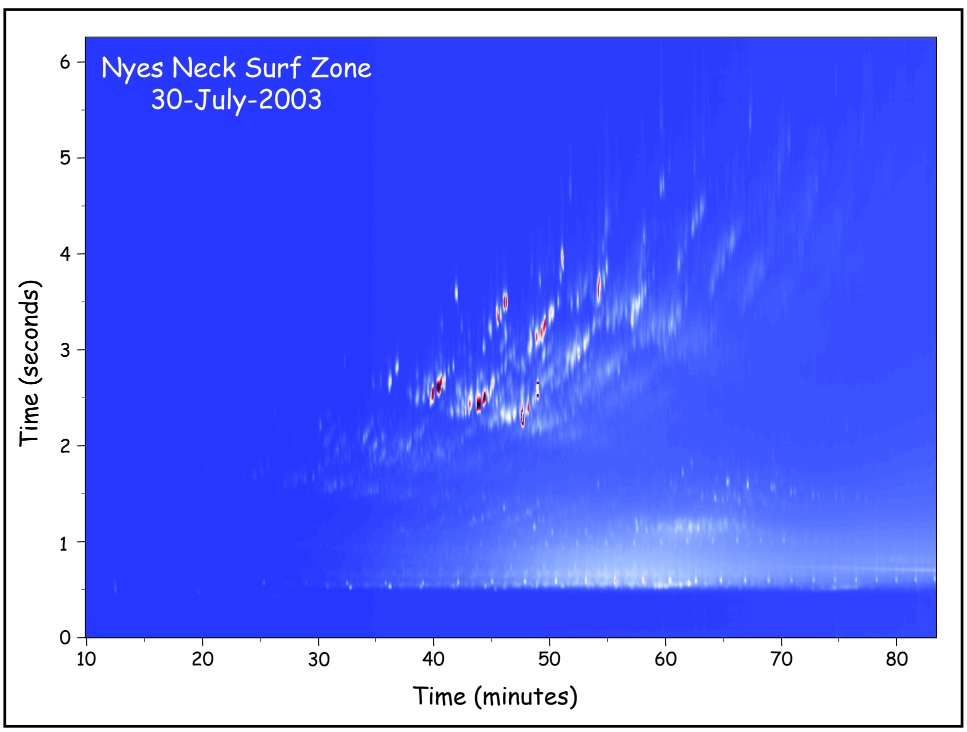

Nyes Neck Surf Zone
6-May-2003
Time (seconds)
Time (minutes)

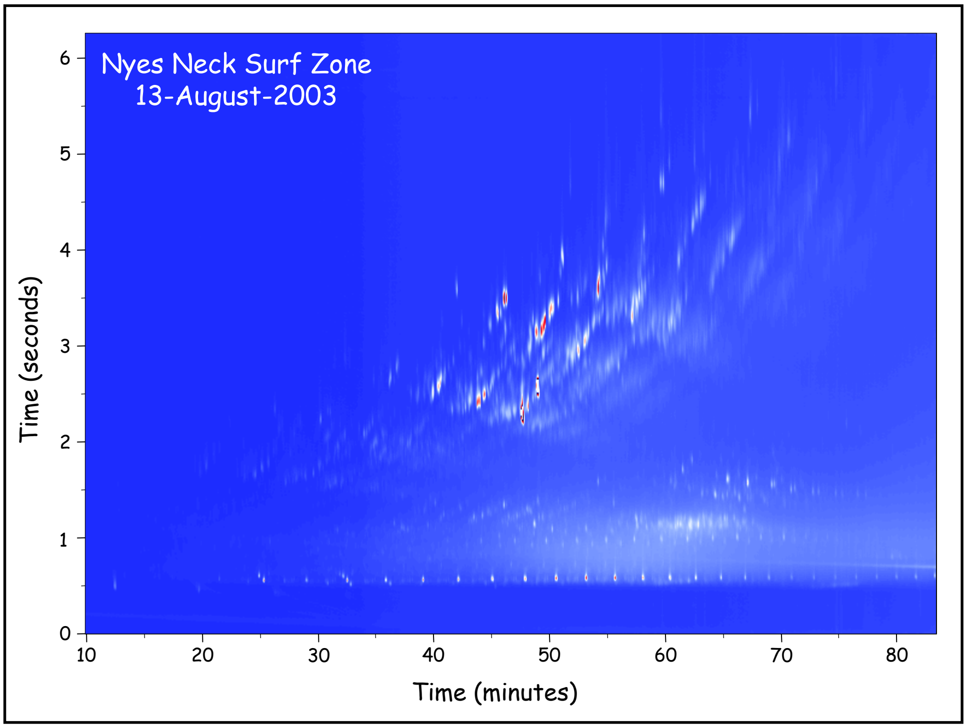

Nyes Neck Surf Zone
13-May-2003
Time (seconds)
Time (minutes)

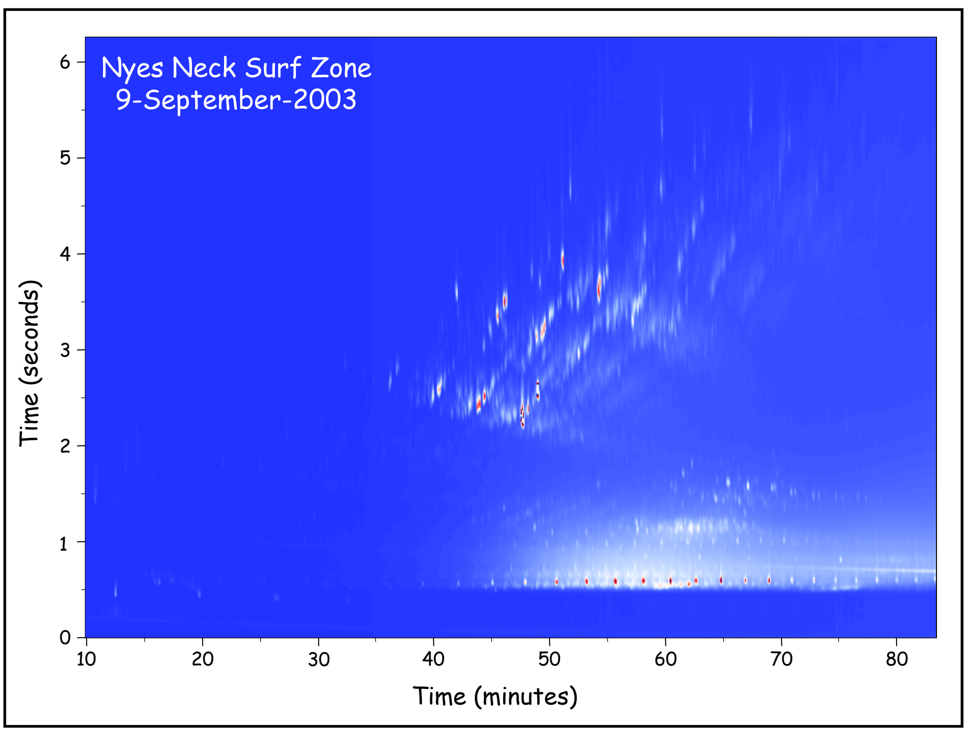

Nyes Neck Surf Zone
6-June-2003
Time (seconds)
Time (minutes)
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80

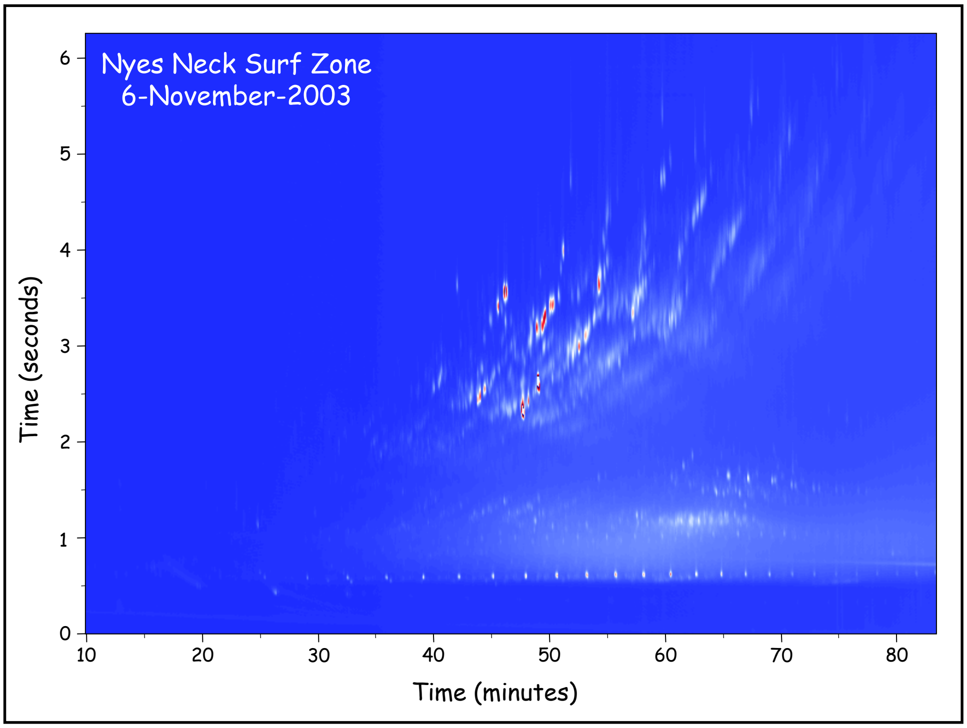

Nyes Neck Surf Zone
16-June-2003
Time (seconds)
Time (minutes)
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80

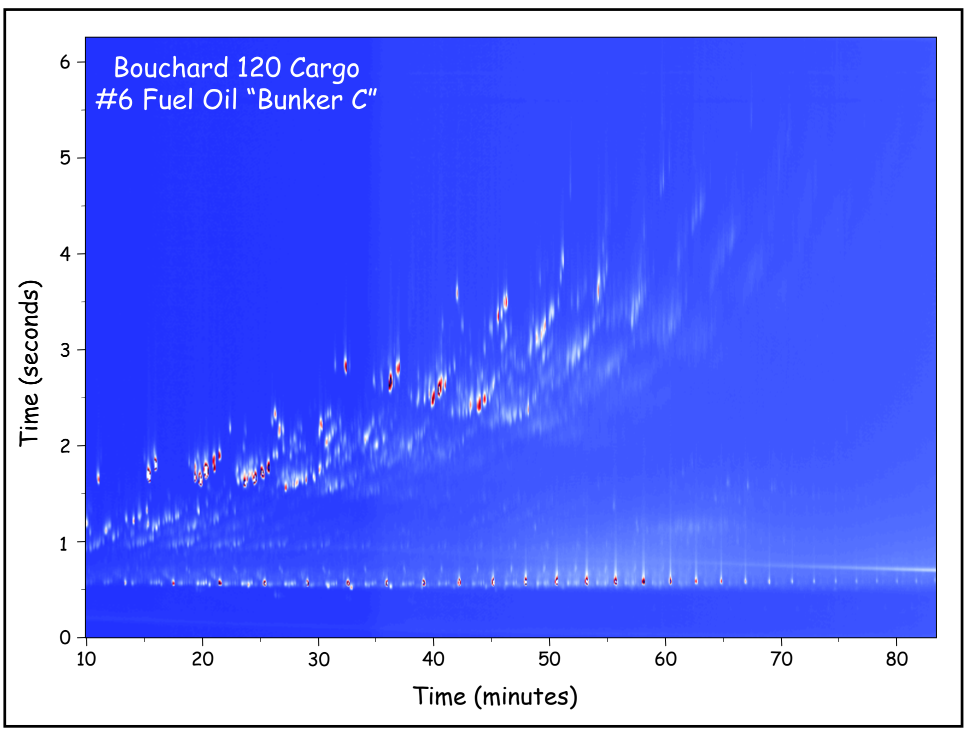

Nyes Neck Surf Zone
3-July-2003
Time (seconds)
Time (minutes)
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80

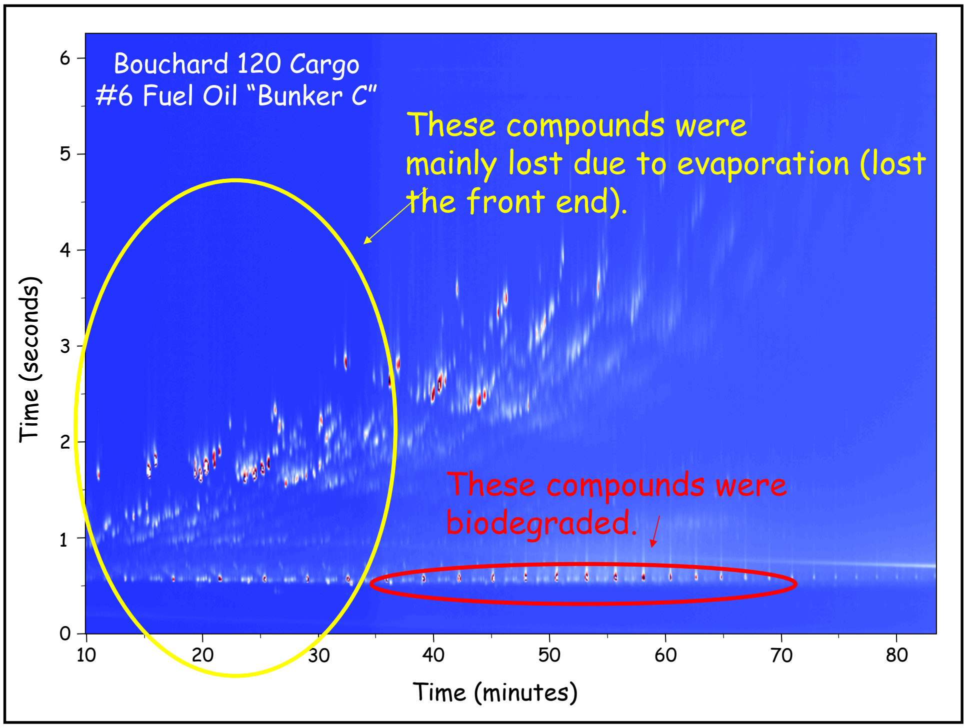

Nyes Neck Surf Zone
30-July-2003
Time (seconds)
Time (minutes)
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80


Nyes Neck Surf Zone
13-August-2003
Time (seconds)
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
Time (minutes)

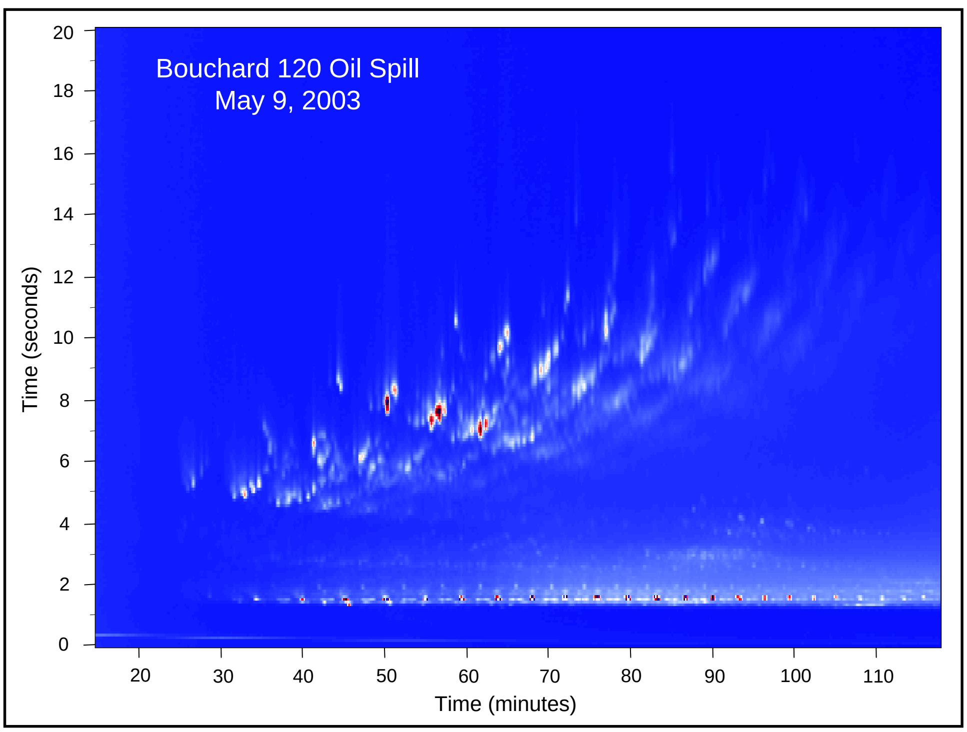

Nyes Neck Surf Zone
9-September-2003
Time (seconds)
6
5
4
3
2
1
0
10
20
30
40
50
60
70
80
Time (minutes)


Nyes Neck Surf Zone
6-November-2003
Time (seconds)
Time (minutes)
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80

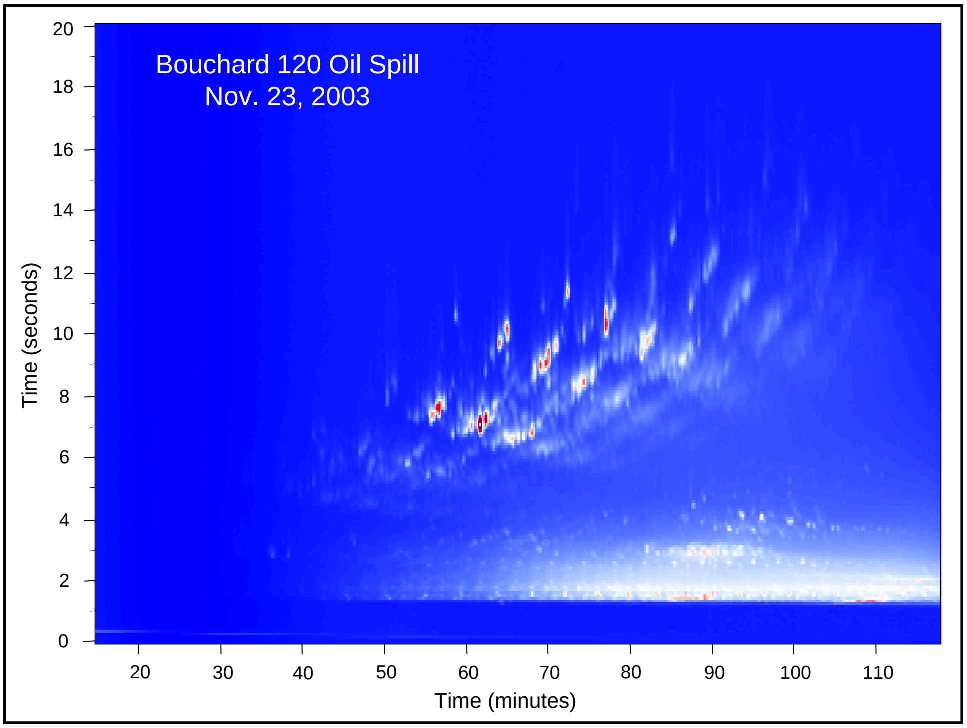

Bouchard 120 Cargo
#6 Fuel Oil "Bunker C"
Time (seconds)
Time (minutes)
0
1
2
3
4
5
6
10
20
30
40
50
60
70
80

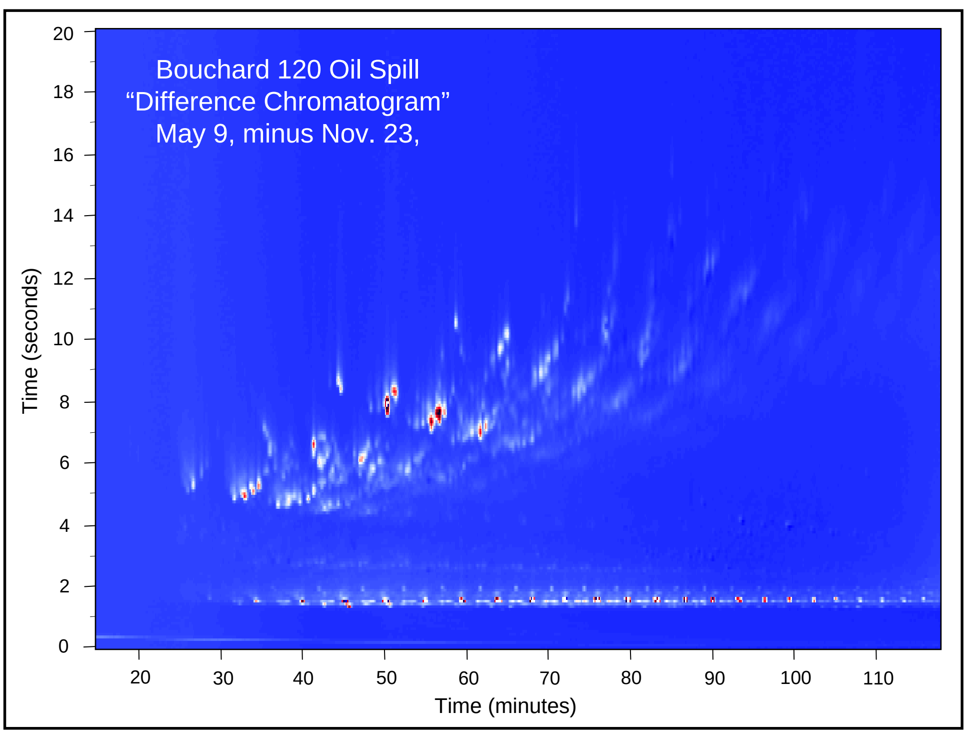


Bouchard 120 Cargo
#6 Fuel Oil "Bunker C"
These compounds were mainly lost due to evaporation (lost the front end).
These compounds were biodegraded.
Time (seconds)
Time (minutes)

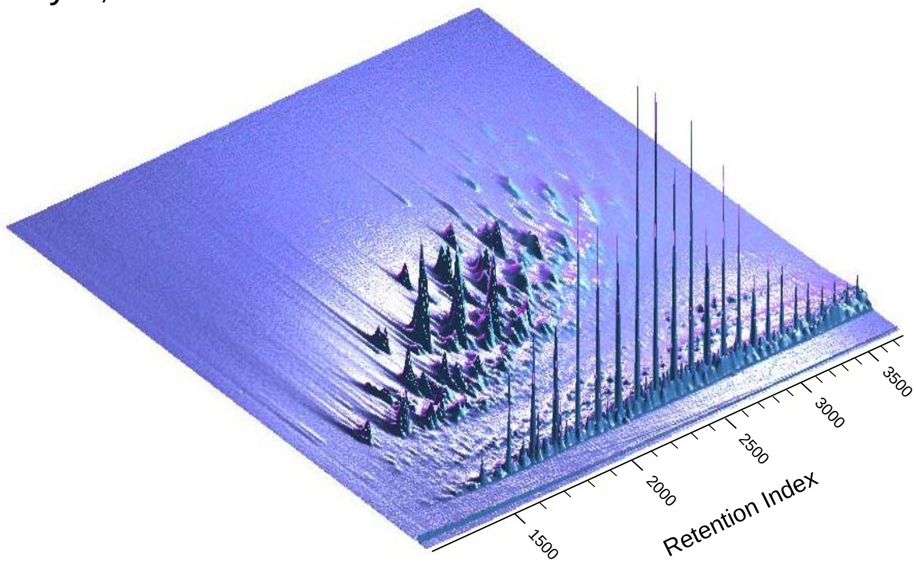


Bouchard 120 Oil Spill
May 9, 2003
Time (seconds)
Time (minutes)

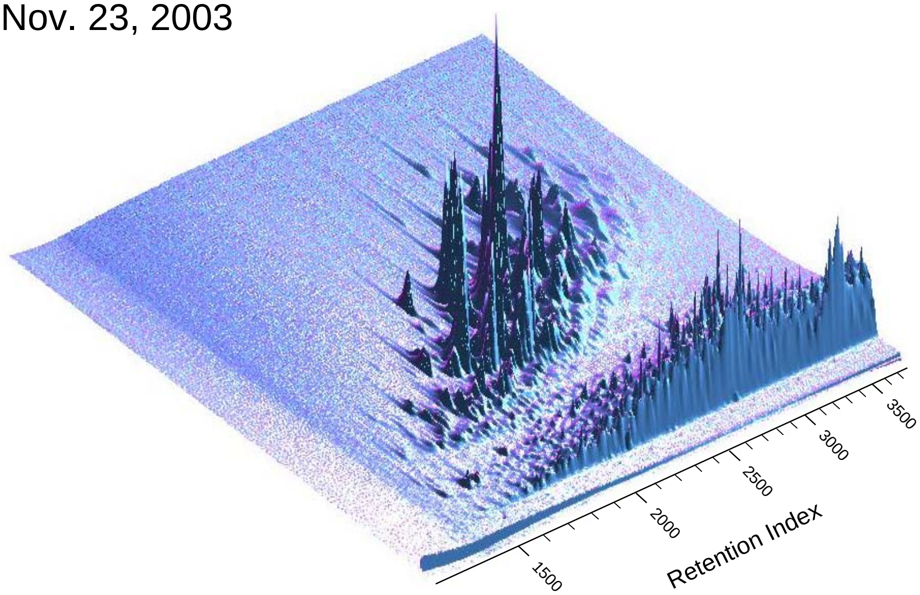

Bouchard 120 Oil Spill
Nov. 23, 2003
Time (seconds)
20
18
16
14
12
10
8
6
4
2
0
20
30
40
50
60
70
80
90
100
110
Time (minutes)


Bouchard 120 Oil Spill
“Difference Chromatogram”
May 9, minus Nov. 23,
Time (seconds)
20
18
16
14
12
10
8
6
4
2
0
20
30
40
50
60
70
80
90
100
110
Time (minutes)

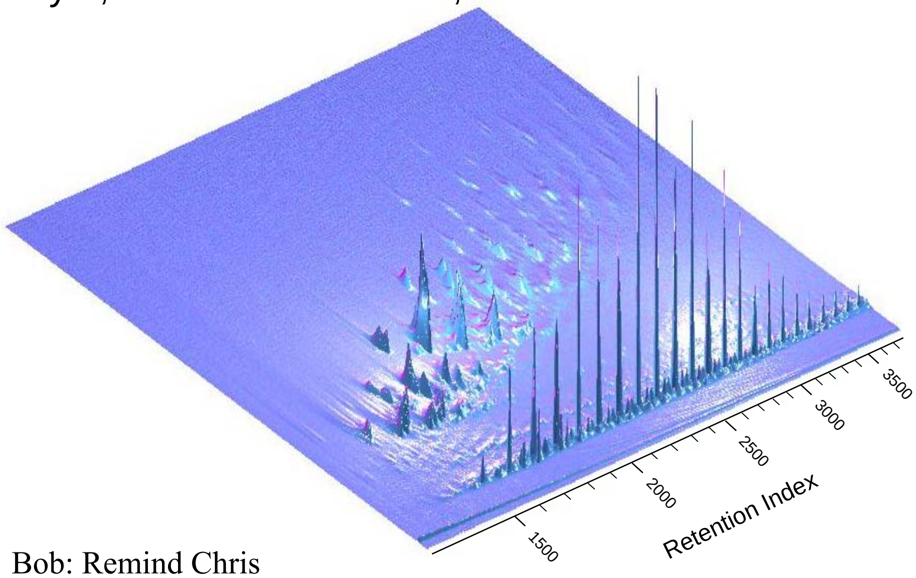
Bouchard 120 Oil Spill
May 9, 2003



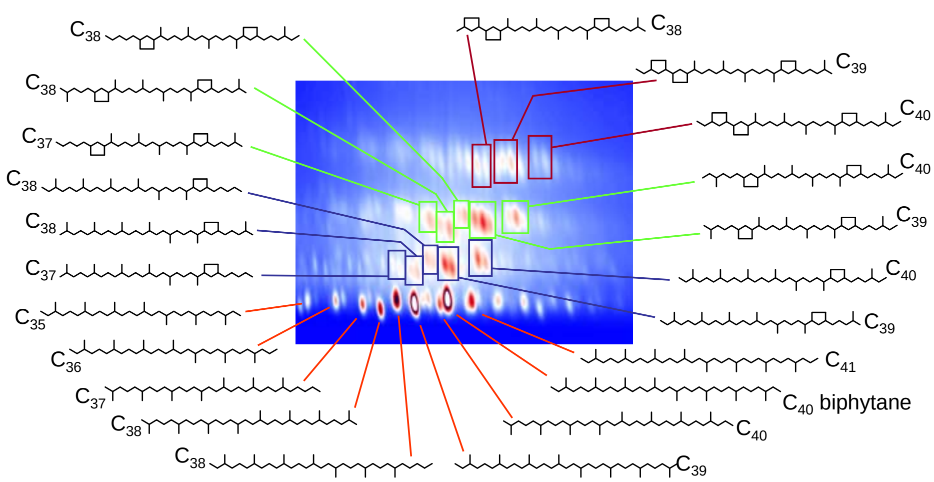
Bouchard 120 Oil Spill
Nov. 23, 2003



Difference Chromatogram
May 9, 2003 minus Nov. 23, 2003



Bob: Remind Chris



Color contour plot of a comprehensive two-dimensional gas chromatogram from the GC×GC-ToF analysis of organic extracts from 2.7 billion year old rocks.

Summary

- Traditional GC can be limited with complex mixtures
- Heart-cutting 2D GC only selective to one region in a chromatogram.
- GCxGC is a new technique, which provides increased separation power and other positive attributes.
  - It is comprehensive as everything from the first column also travels thru the second column.

Van der Waals Interactions Between Molecules

• Interactions between neutral molecules generally result from the combined effects of a number of different forces such as; dipole-dipole electrostatic attraction, hydrogen bonding, and Van der Waals forces. In the case of neutral hydrocarbons interacting with a dimethylpolysiloxane stationary phase, the Van der Waals interaction is the most important.

• The boiling point of a substance is defined as the temperature at which its vapor pressure is equal to the external pressure (usually 1 atmosphere). *The vapor pressure of a substance is inversely related to the energy that causes individual molecules to attract one another.*

weak intermolecular attractive force = low boiling point = high vapor pressure
strong intermolecular attractive force = high boiling point = low vapor pressure

• The Van der Waals attractive force results from an electron correlation effect (also known as London dispersion force) in which the motion of electrons is mutually correlated between molecules to produce a net attraction.

• Van der Waals attractive forces are extremely sensitive to distance and varies as $1/r^6$.

• Van der Waals attractive forces are only significant for molecules that are close to each other - but not too close – if electron charge clouds overlap, an electron repulsion occurs and the molecules push apart.

• The magnitude of Van der Waals attraction depends upon the volume of contact area between two molecules. Large contact area = large attractive force.

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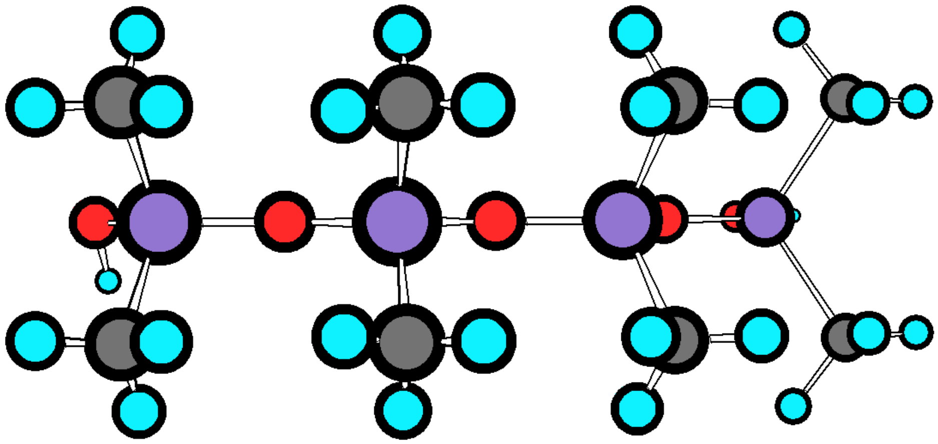
Restek Rtx-1 (100% Dimethylpolysiloxane) 3D View: Looking down along polymer backbone



Red = Oxygen
Purple = Silicon
Gray = Carbon
Light Blue = Hydrogen

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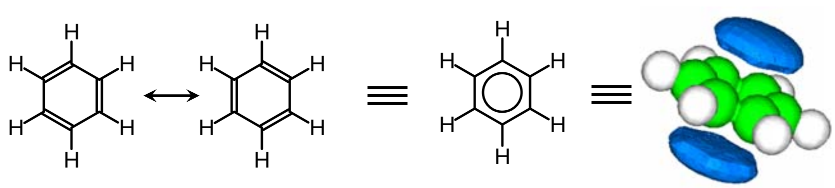
Electrostatic Interactions

- A dipole-dipole interaction is the product of an electrostatic attraction between the electron cloud of a polarized bond and a nucleus that bears a positive charge as a result of bond polarization.



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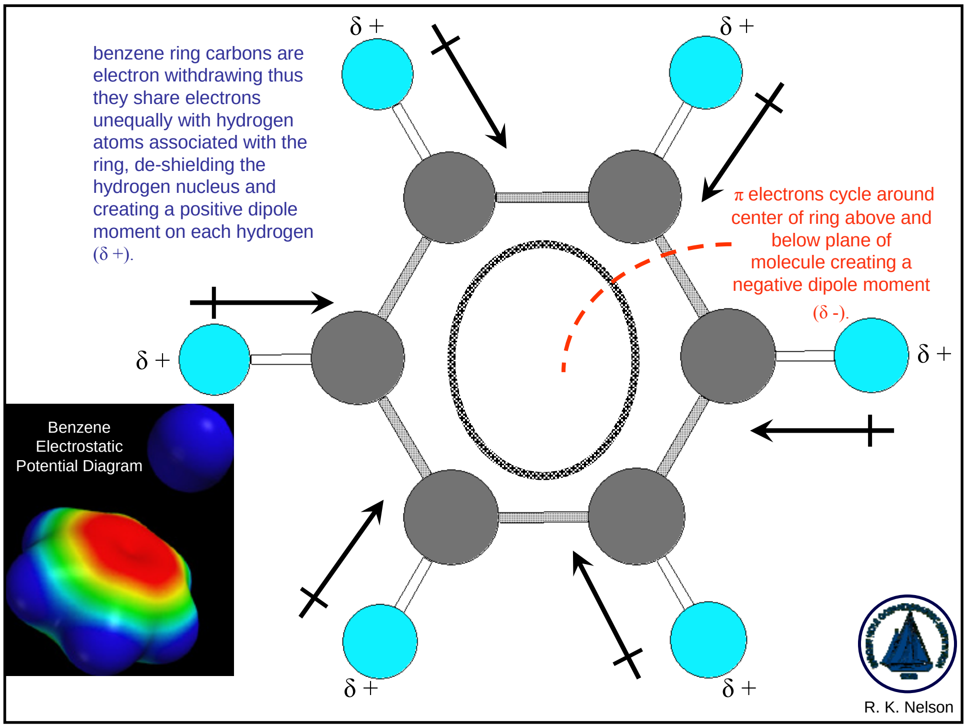
benzene ring carbons are electron withdrawing thus they share electrons unequally with hydrogen atoms associated with the ring, de-shielding the hydrogen nucleus and creating a positive dipole moment on each hydrogen (δ +).
δ +
δ +
δ +
δ +
δ +
δ +
π electrons cycle around center of ring above and below plane of molecule creating a negative dipole moment (δ -).
Benzene Electrostatic Potential Diagram
R. K. Nelson