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HUMAN HEALTH | ENVIRONMENTAL HEALTH

Migrating GC Methods from Helium to Other Carrier Gases

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Content

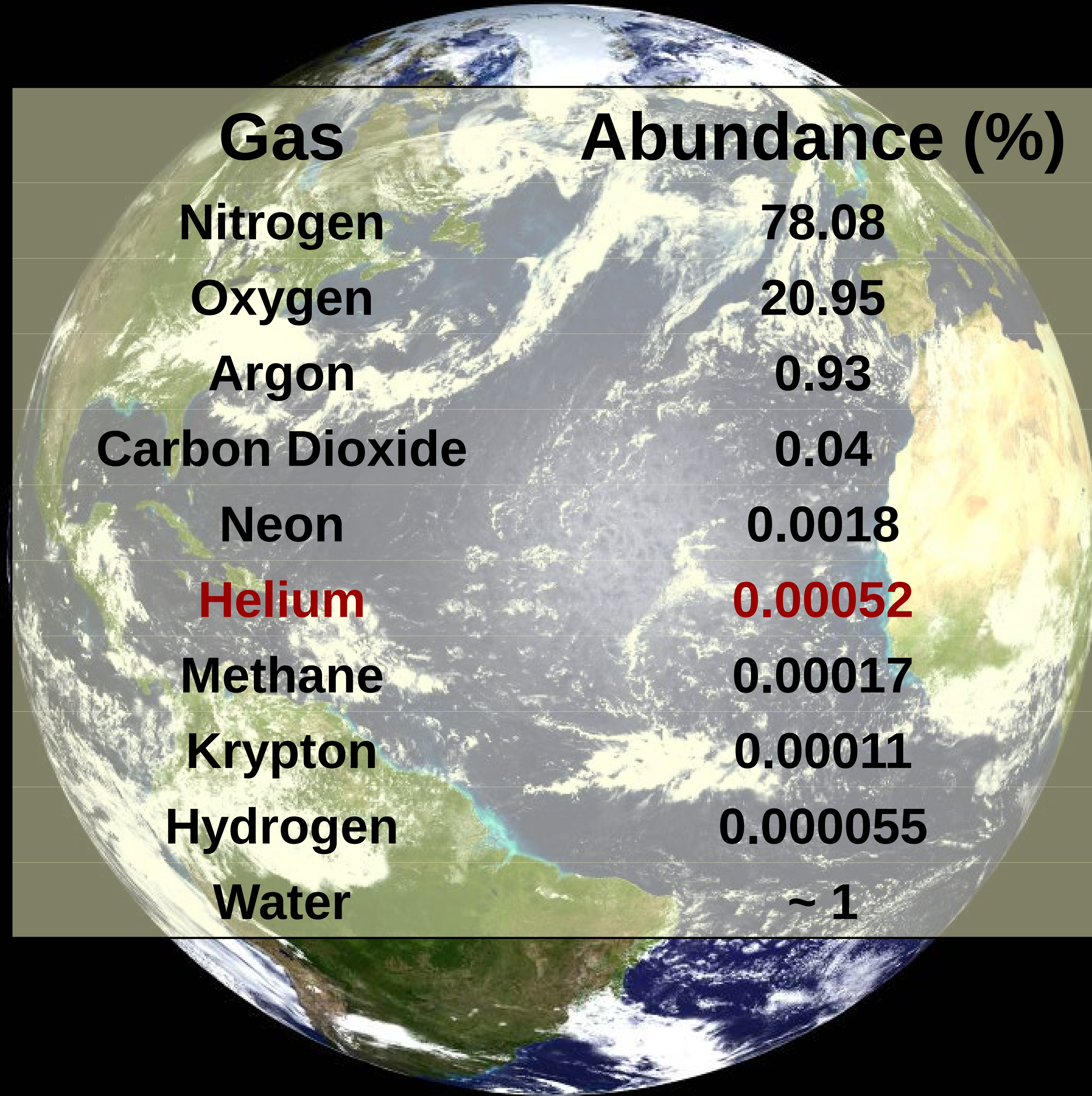
- Increasing concerns in the continued use of helium
- Practical aspects of using hydrogen
- How hydrogen compares with helium as a carrier gas
- Minimizing the risks in using hydrogen

Helium is constantly being formed in stars by thermonuclear fusion of hydrogen at ~15,000,000°K

NASA

Element	Abundance (%)
Hydrogen	73.90
Helium	24.00
Oxygen	1.07
Carbon	0.46
Neon	0.13
Iron	0.11
Nitrogen	0.10
Silicon	0.07
Magnesium	0.06
Sulfur	0.04
Others	0.07

NASA



Gas	Abundance (%)
Nitrogen	78.08
Oxygen	20.95
Argon	0.93
Carbon Dioxide	0.04
Neon	0.0018
Helium	0.00052
Methane	0.00017
Krypton	0.00011
Hydrogen	0.000055
Water	~ 1

NASA

Helium is able to Escape the Confines of Gravity

Helium Formation on Earth

- Produced by the radioactive decay of isotopes of uranium and thorium
- This is a very slow reaction
- Current natural reserves have been generated over the last 4.5 billion years!
- The earth's crust contains 0.0008% helium
- Some natural gas contains up to 7% helium

Helium Mining

- USA (83%)
- Algeria (11%)
- Canada
- Poland
- Russia
- Qatar

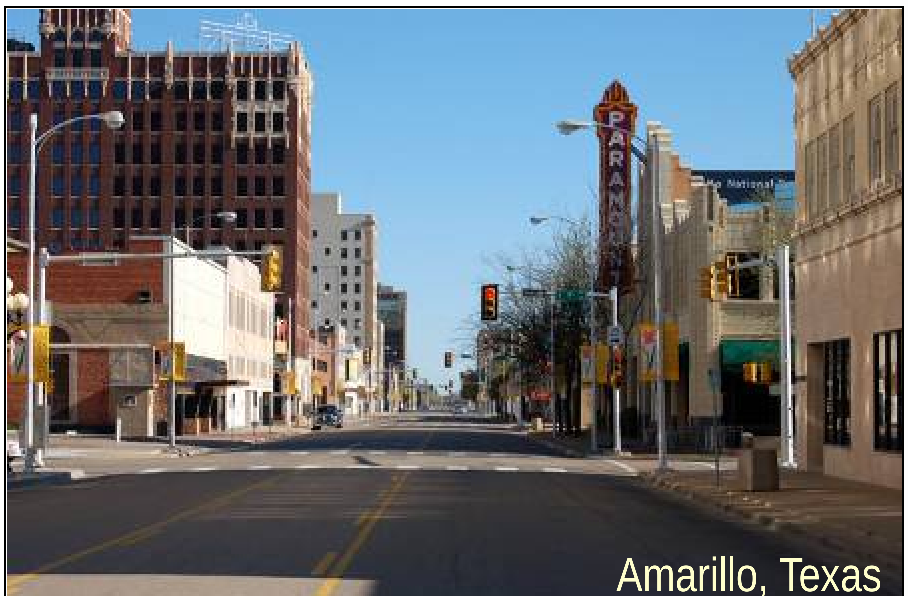
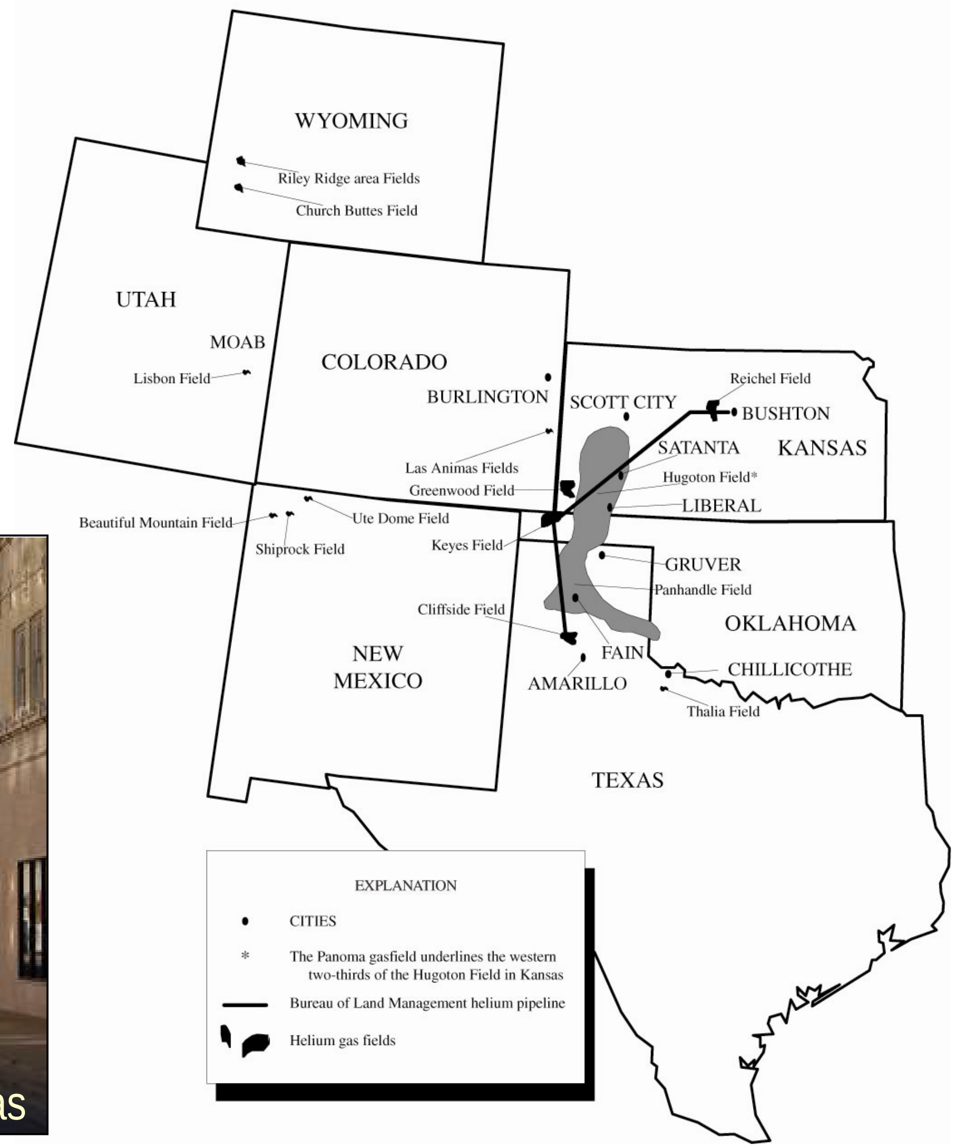
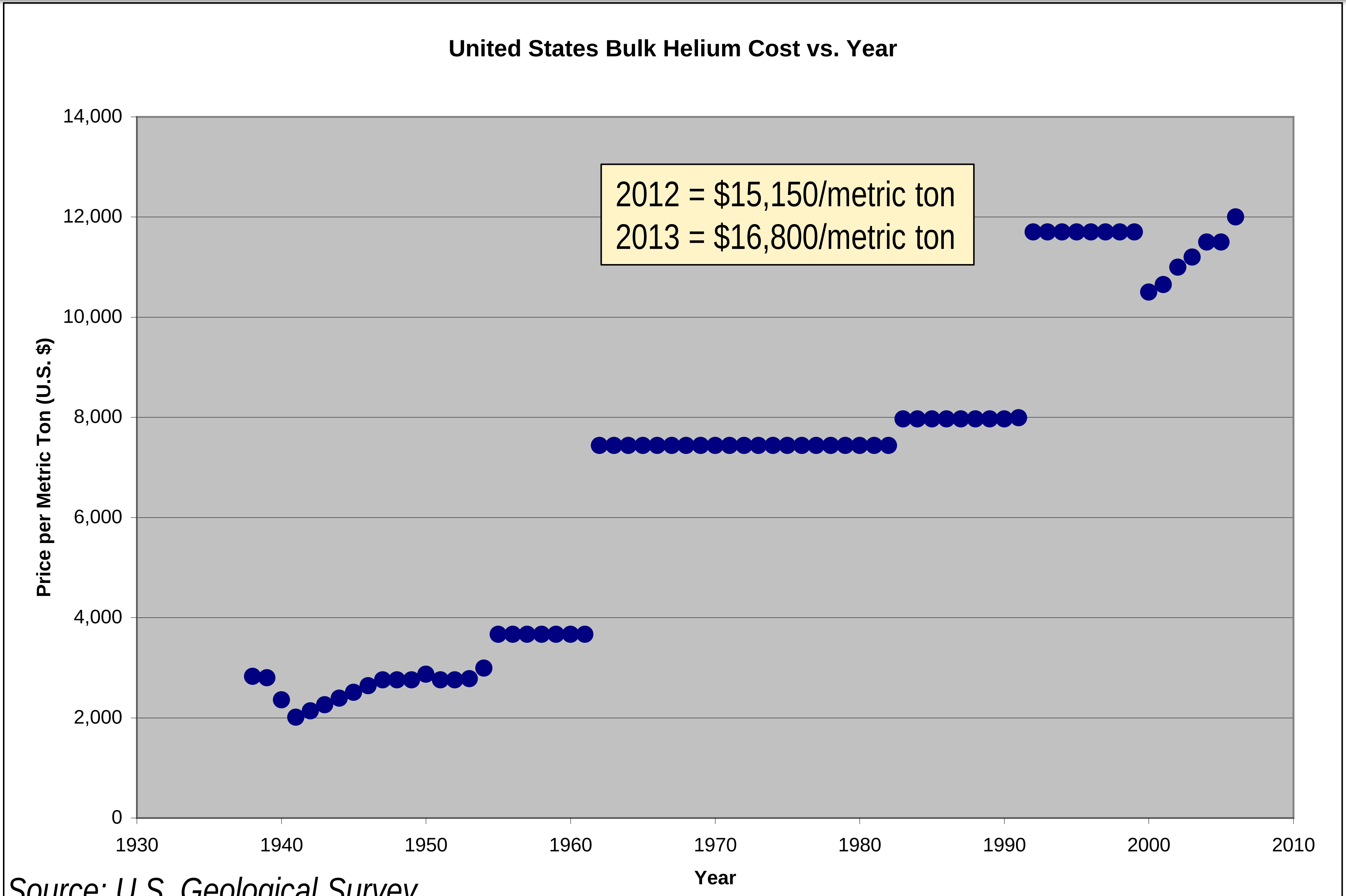


FIGURE 1
MAJOR U.S. HELIUM-BEARING NATURAL GAS FIELDS

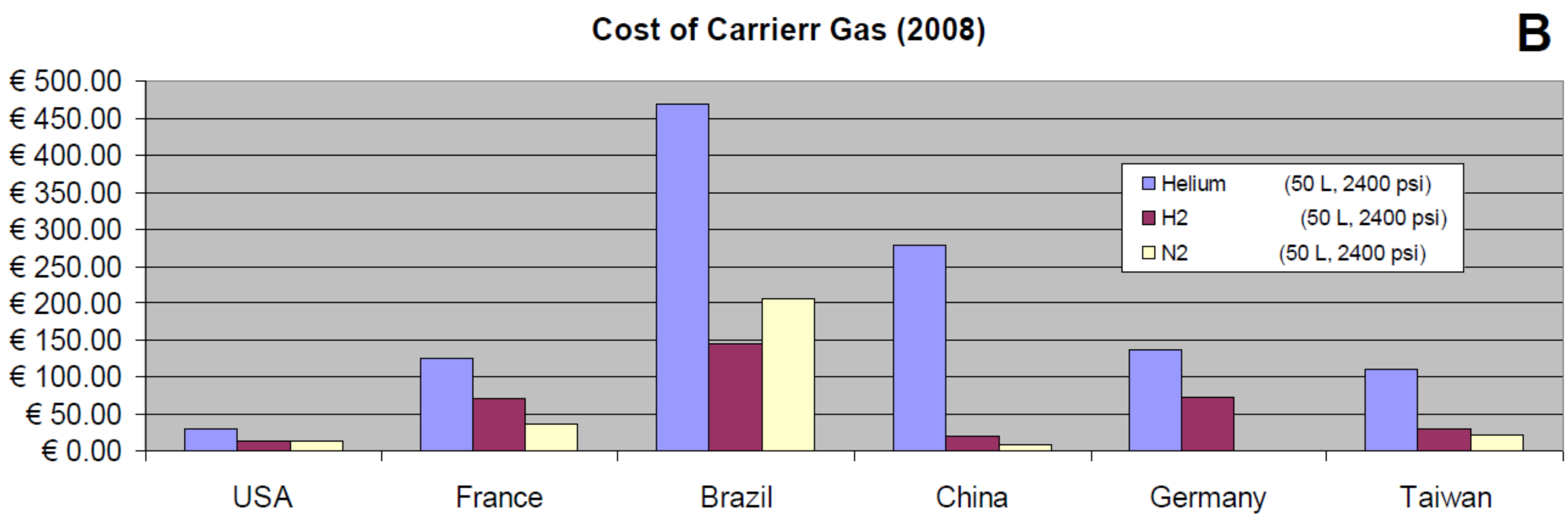


The Price of Helium in the USA



Source: U.S. Geological Survey

Global Supply Bulk Costs



Applications of Helium

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Application	Usage (%)
Lifting	15.1
Magnetic Resonance Imaging (MRI)	15.0
Welding	14.9
Chromatography	7.6
Heat Transfer	6.4
Leak Detection	5.6
Pressurizing	5.5
Fibre Optics	4.1
Diving Mixtures	4.0
Superconductors	2.9
Inert Atmospheres	2.7
Nuclear Magnetic Resonance (NMR)	1.3
Other	14.9

Review of Carrier Gases

Gas	Helium	Hydrogen	Nitrogen
Cost	Expensive	Low cost	Low cost
Speed of chromatography	Medium	Fast	Slow
Chromatographic efficiency	Low	Medium	High
Flow permeability	Low	High	Low
Supply	Pressurized tank	Pressurized tank or electrolytic hydrogen generator	Pressurized tank or nitrogen generator
Safety concerns		Highly explosive	
			

Hydrogen cylinders

Pros

- Can keep up with substantial demand if necessary
- Can usually get spare cylinder quickly

Cons

- Safety concerns with flammability especially with large leaks or catastrophic failures
- Need to ensure adequate supply on hand
- Inconvenient (and can be dangerous) to move and exchange

Hydrogen generator

Pros

- No heavy high pressure cylinders to lug around
- Low internal volumes at low pressure means small hazard potential
- Intelligent shutdown in the event of a fault

Cons

- High initial cost
- May not have spare generator on hand for backup
- Need to assess demand accurately

Injector and Column Compatibility

- Injector Considerations
  - Hydrogen – Very low viscosity requires low inlet pressure.
    - Potential problems with short (30 m or less), wide bore columns (530 µm).
    - MS further limits column dimensions
    - Potential Problems with splitless and pressure pulse injections.
  - Nitrogen - Optimal linear velocity requires low inlet pressure.
    - Potential problems with short (30 m or less), wide bore columns (530 µm).
    - MS further limits column dimensions
    - Potential Problems with splitless and pressure pulse injections.

Injection Method Considerations with MS

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One major consideration when choosing an alternate carrier gas in GC/MS is that the column outlet is at vacuum rather than ambient pressure as it is with traditional detectors. This dramatically reduces the column head pressure required to provide a given column flow/ linear velocity.

Table 2: Comparison of column head pressure at specific flow rates with each carrier.

Carrier Gas Type	Column Length (m)	Column Diameter (µm)	GC Start Temperature (˚C)	Outlet Pressure	Flow (mL/min)	Velocity (cm/sec)	Inlet Pressure (psig)
Helium	30	250	37	Vacuum	1	36.3	7.1
Hydrogen	30	250	37	Vacuum	2	76.1	6
Nitrogen	30	250	37	Vacuum	1	38.2	6
Helium	60	250	37	Vacuum	1	25.7	16.2
Hydrogen	60	250	37	Vacuum	1.5	46.6	10.8
Nitrogen	60	250	37	Vacuum	0.5	19.1	6
Helium	20	180	37	Vacuum	0.75	38.5	15.1
Hydrogen	20	180	37	Vacuum	0.75	57.1	5.4
Nitrogen	20	180	37	Vacuum	0.5	33.1	8.4
Helium	30	250	37	Ambient	1	25.1	11.6
Hydrogen	30	250	37	Ambient	2	51.3	10.8
Nitrogen	30	250	37	Ambient	1	25.7	10.7
Helium	60	250	37	Ambient	1	20.5	19.5
Hydrogen	60	250	37	Ambient	1.5	34.6	14.7
Nitrogen	60	250	37	Ambient	0.5	12.9	10.7
Helium	20	180	37	Ambient	0.75	30.4	18.5
Hydrogen	20	180	37	Ambient	0.75	37.8	10.2
Nitrogen	20	180	37	Ambient	0.5	23.5	12.7

Detector Compatibility

- Combustion Detectors (i.e. FID, FPD)
  - Constant flow mode is preferable
  - Baseline may change in constant pressure or velocity type operation.
- NPD
  - Requires constant flow of hydrogen at ~1 mL/min
  - Hydrogen is not a good choice for a carrier gas
- Single Quad MS
  - Hydrogen potential reduces sensitivity by 2x
  - High vacuum column outlet may constrain injector pressure settings

MS System Performance

Following the optimization of the GC parameters, it is necessary to consider the effect of alternate carrier gas on the MS system. The most notable difference is with nitrogen as carrier. Changes must be made to the instrument tuning to achieve maximum sensitivity (Table 3). The tuning of the MS for helium and hydrogen was similar.

Table 3: Comparison of optimized tune conditions with the use of helium and hydrogen as carrier and nitrogen carrier.

	Helium/ Hydrogen	Nitrogen
Polarity	EI+	EI+
Source Temp (C)	250	250
GCLine Temp (C)	320	320
Electron Energy	70	70
Trap Emission	100	100
Repeller	1	1
Lens 1	5	1
Lens 2	100	100
LM Resolution	10.5	14
HM Resolution	11.5	11
Ion Energy (V)	1.5	0.5
Ion Energy Ramp	1	1
Multiplier (V)	400	400

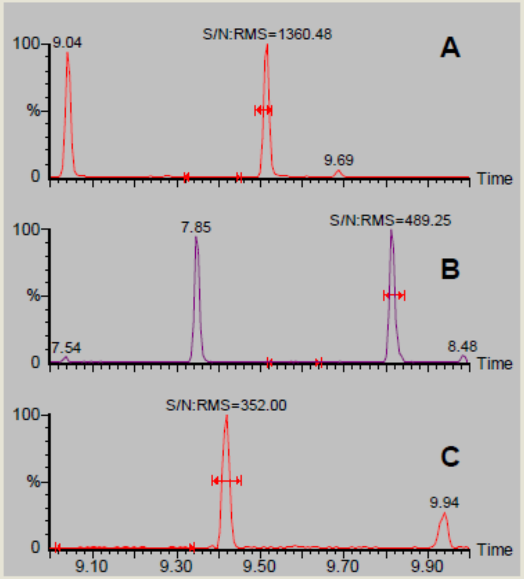


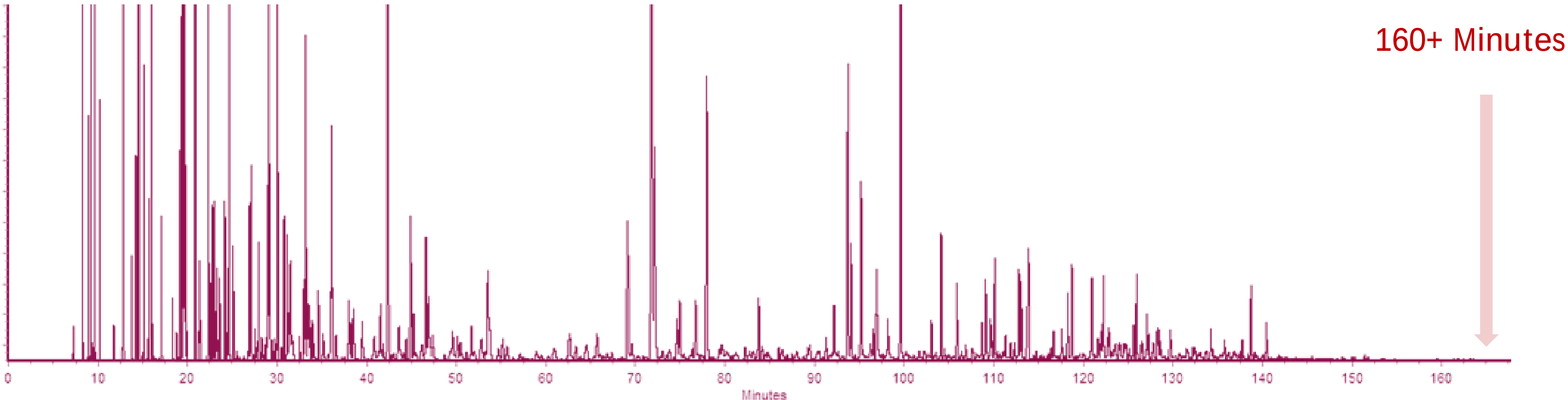
Figure 4: Comparison of the phthalate response of the GC/MS system with each carrier gas. Carrier gas and MS tune parameters were optimized in each example: chromatogram A, helium; chromatogram B, hydrogen; and chromatogram C, nitrogen.

GC Sample Handling Devices

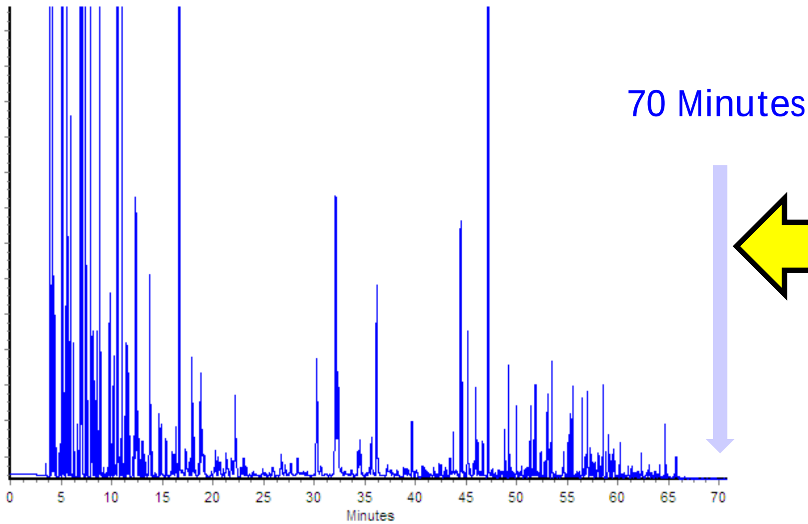
- Hydrogen is not an acceptable carrier gas for thermal desorption type sample introduction.
- Hydrogen is not an acceptable carrier gas for pyrolysis sample introduction, since a heated wire glows red hot in the injector.
- Hydrogen is an acceptable carrier gas for headspace sample introduction when using appropriate safety measures (including a special hydrogen needle).

Detailed Hydrocarbon Analysis using Helium and Hydrogen

Helium

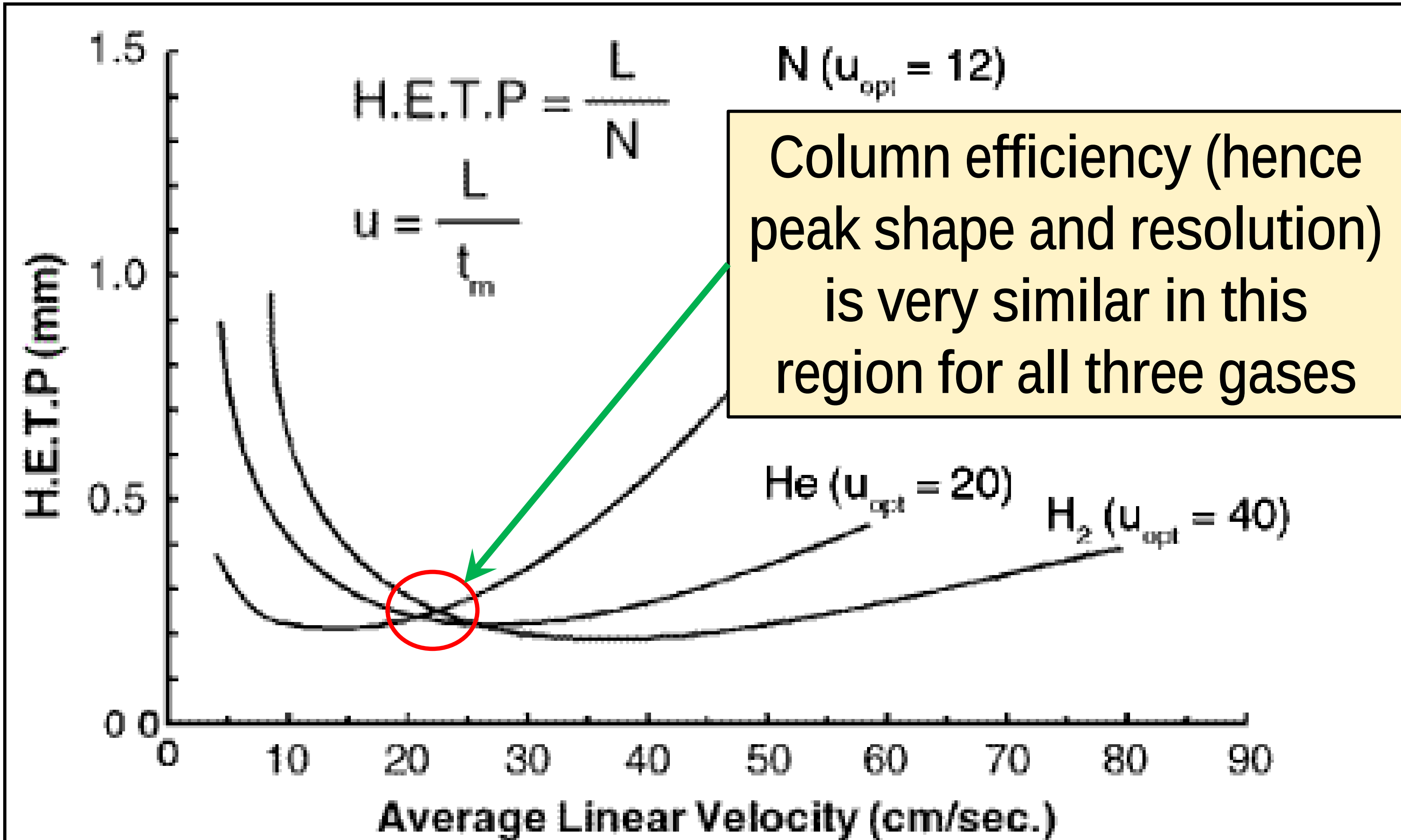


Hydrogen



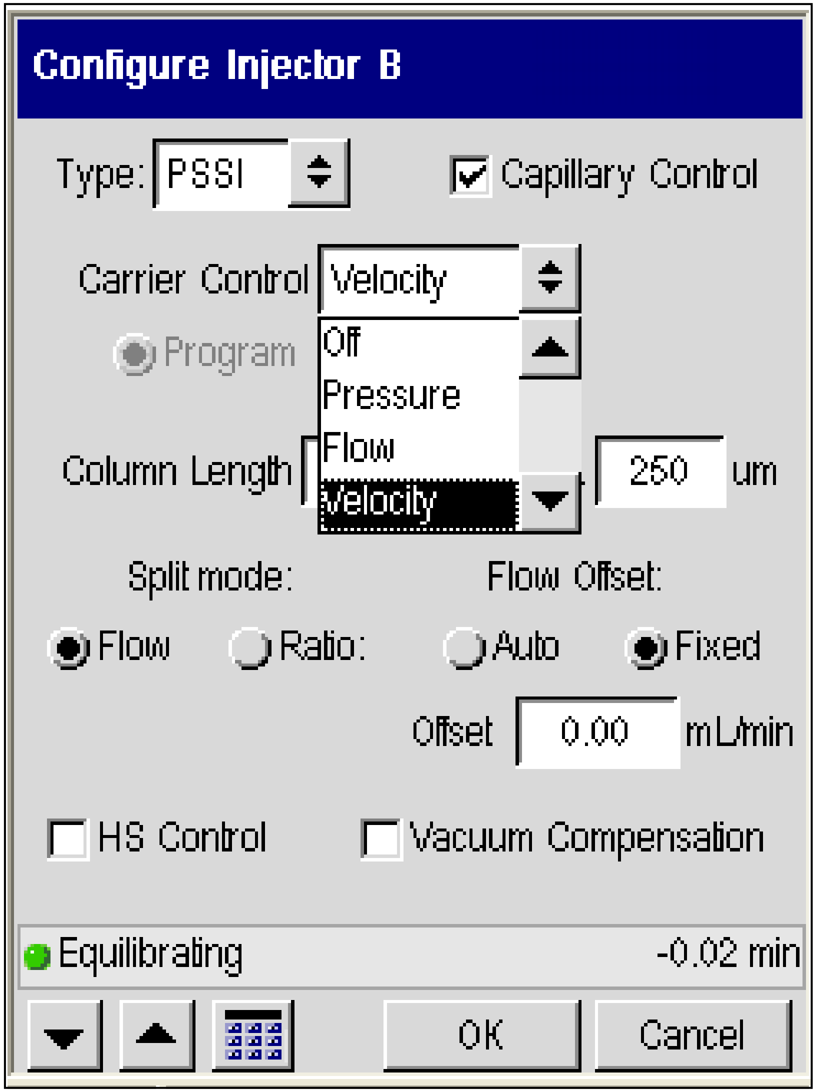
More Available Time

Column Efficiency

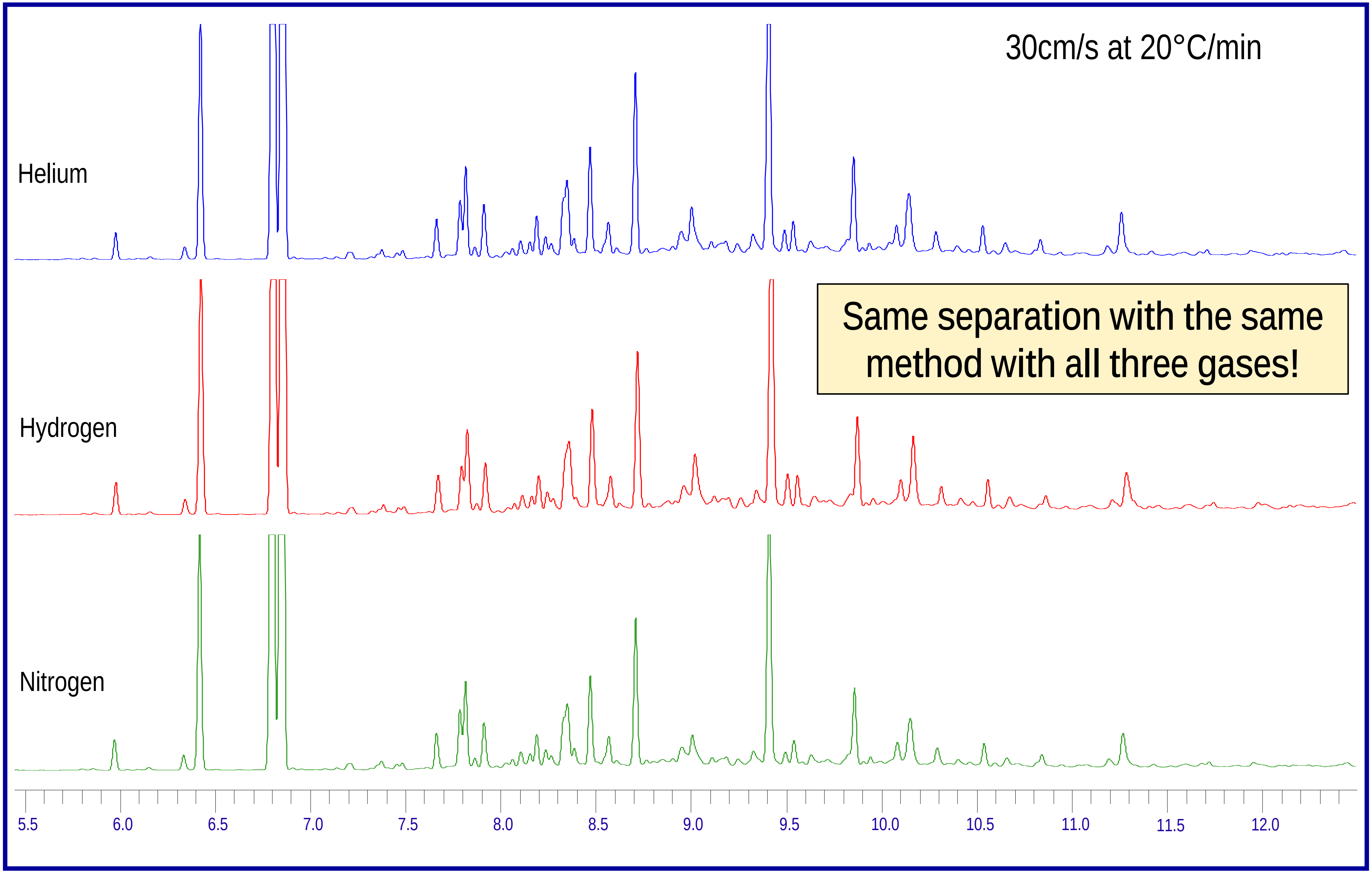


Clarus GC PPC Systems Support Velocity Control and Display

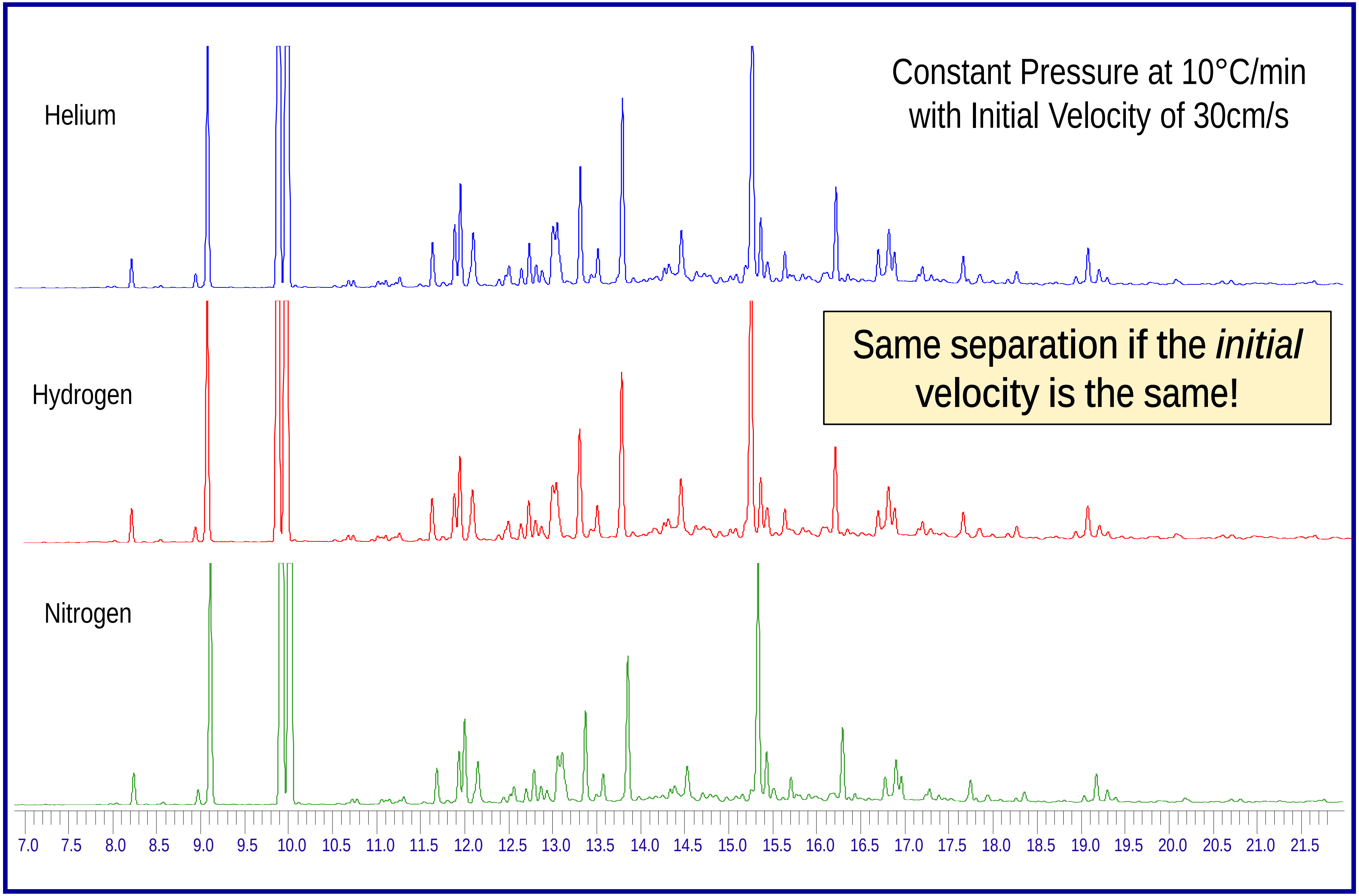
- Capillary column carrier gas may be controlled by setting the pressure, flow or velocity.
- In each mode of control, the current values of all three are displayed in real time



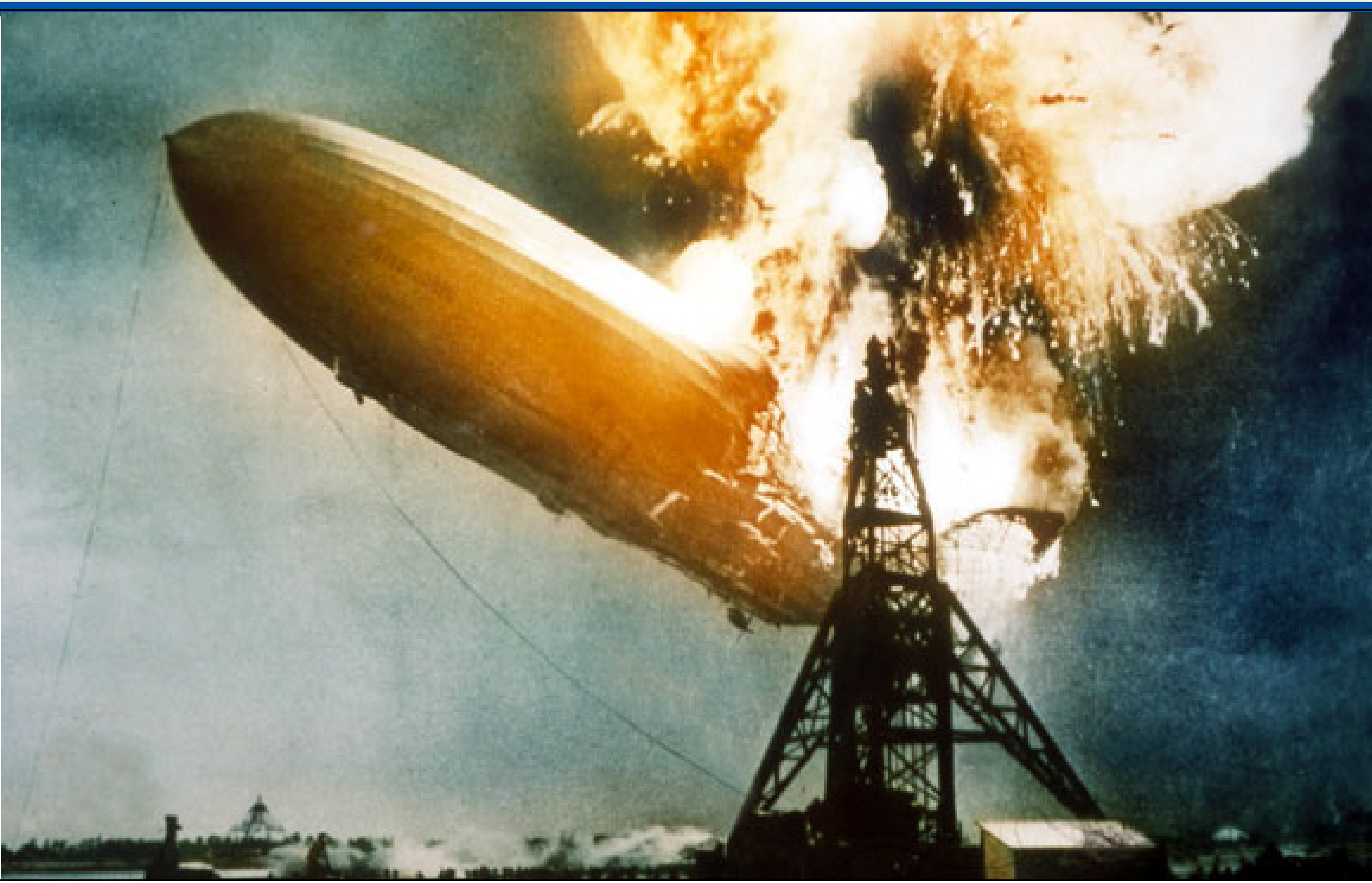
Method migration with carrier gas velocity control



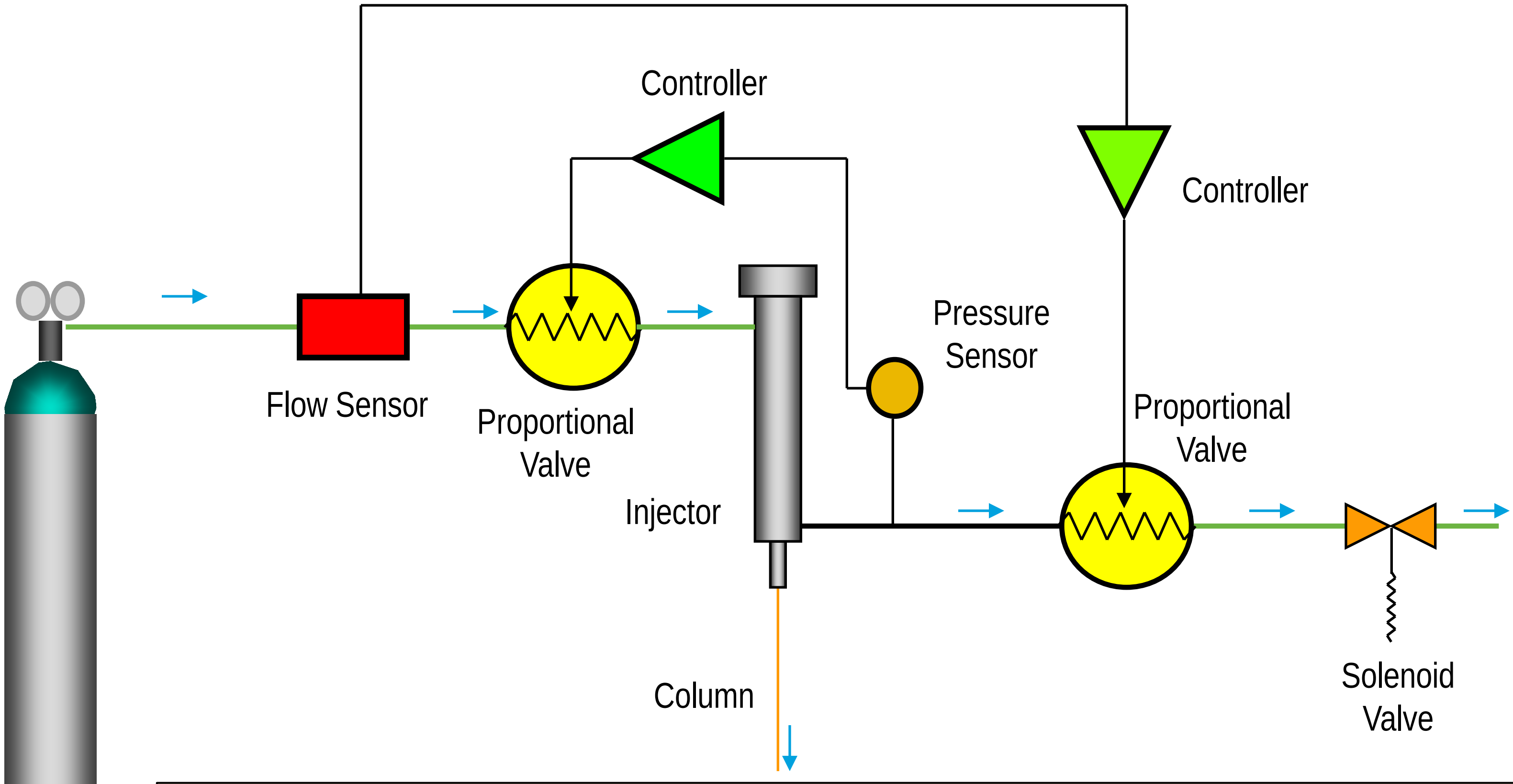
Can I migrate methods with flow or pressure carrier gas control?



Don’t Forget that Hydrogen is Explosive



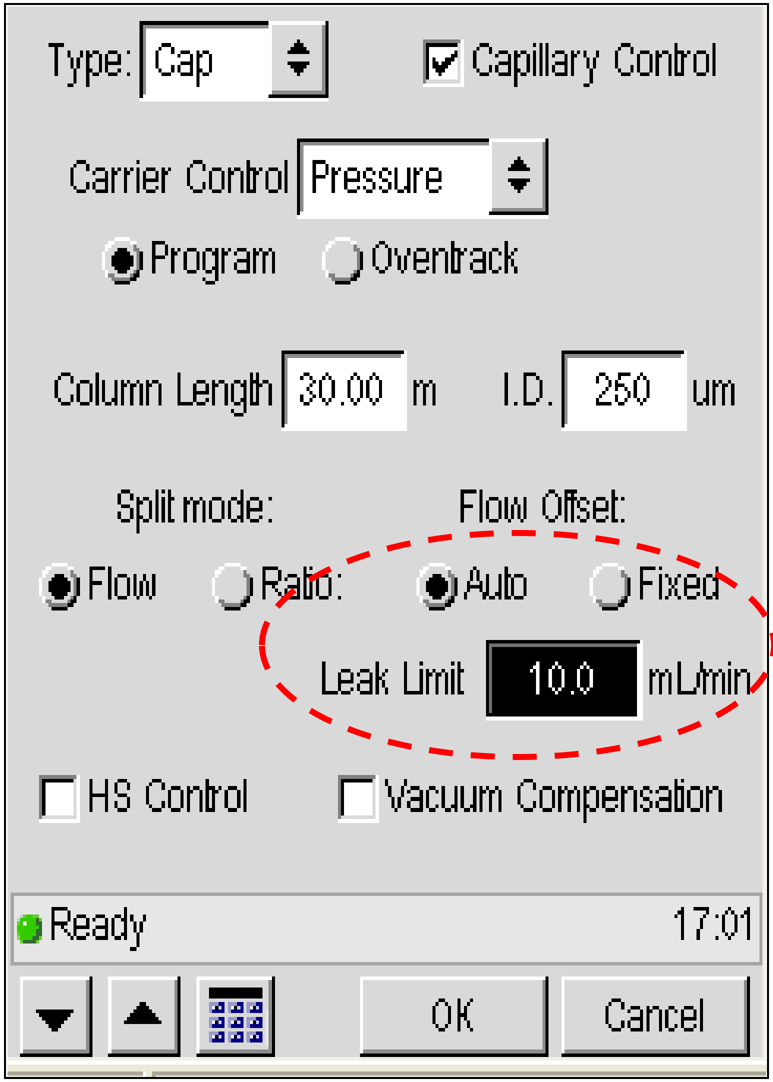
Clarus GC PPC Split Pneumatics – Split Mode



- Leaks are detected by a sudden loss in pressure and the system is subsequently shutdown after 2 minutes
- An automatic system leak-check may be performed at the start of each run – again the system is shutdown after 2 minutes if a fault is detected
- In split mode, the PPC controller regulates the gas-flow *into* the injector so leakage will never exceed this rate.

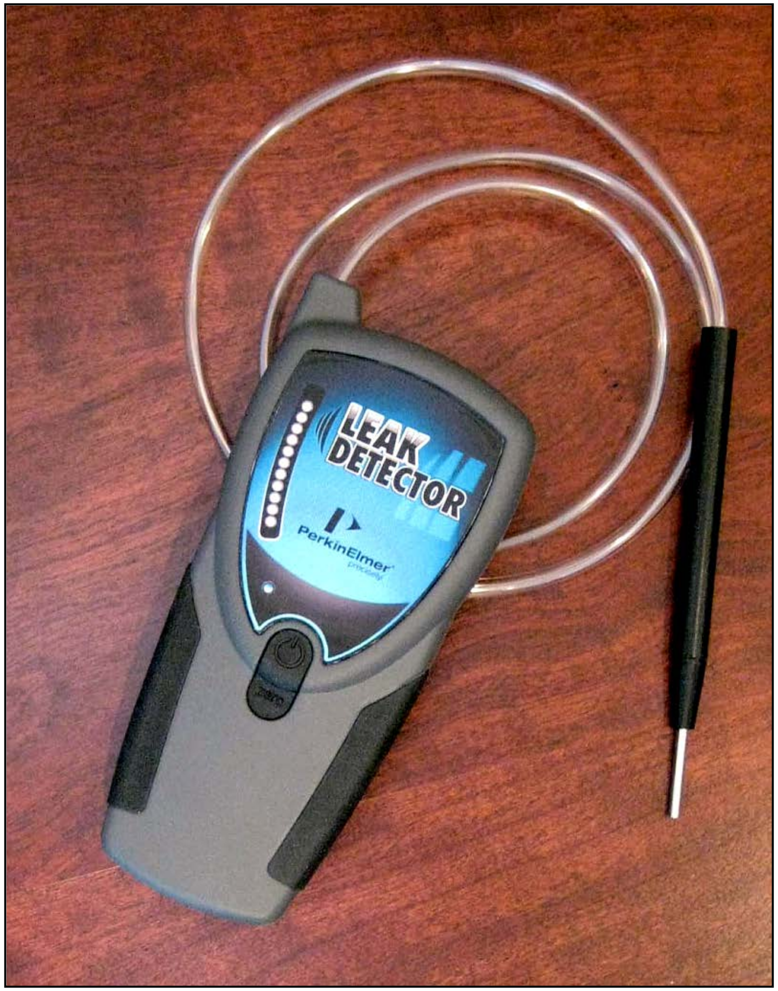
Automatic Leak Checking with PPC

- Flow rate into injector checked as a pre-run event
- If flow rate exceeds limit, GC will shutdown
- Prevents major loss of carrier gas
- Also reduces explosion risk with hydrogen carrier gas



Things the user can do to minimize risks in using hydrogen

- Ensure systems are leak free (and re-check them periodically)
- Use an in-line snubber if you are using high pressure cylinders
- Use a hydrogen generator rather than a high pressure cylinder
- Route gas vents away from the instrument
- Use PPC pneumatic systems to limit and detect leakage and to shutdown the system if necessary
- Install capillary columns so that they don't rub against other surfaces



Special considerations for GC/MS

- Use caution when venting
  - Shut down carrier gas before MS pumps

- Use extra caution after a power failure or unexpected failure of vacuum system
  - Shut down carrier flow
  - Do not turn MS system on immediately
  - Allow hydrogen to dissipate
  - Use a nitrogen purge accessory

GC/MS Drinking Water Tuning_Example

				Helium		Hydrogen
Mass	**525.1**	**525.2**	**525.3**	DFTPP Helium		DFTPP Hydrogen
51	10-80% of base peak	10-80% of base peak	n/a	46.6		43.9
68	<2% of 69	<2% of 69	<2% of 69	1.3		1.6
69	n/a	n/a	present	52.0		45.6
70	<2% of 69	<2% of 69	<2% of 69	0.1		0.5
127	10-80% of base peak	10-80% of base peak	n/a	56.6		47.1
197	<2% of 198	<2% of 198	<2% of 198	0.2		0.7
198	base peak or >50% of 442	base peak or >50% of 442	present	100.0		100.0
199	5-9% of 198	5-9% of 198	5-9% of 198	5.4		6.3
275	10-60% of base peak	10-60% of base peak	n/a	23.2		24.3
365	>1% of base peak	>1% of base peak	>1% of base peak	1.9		2.5
441	Present and < 443	Present and < 443	<150% of 443	79.5		78.8
442	base peak or >50% of 198	base peak or >50% of 198	present	64.7		75.3
443	15-24% of 442	15-24% of 442	15-24% of 442	19.7		17.7

Summary

- There is a compelling need to switch GC methods away from using helium
  - Cost
  - Sustained supply
  - Free up helium supplies for ‘more important’ purposes (e.g. MRI)

- There are feasible alternative carrier gases
  - Hydrogen
  - Nitrogen

- Chromatography equivalent to that obtained with helium carrier is possible with hydrogen or nitrogen on GC systems that control and monitor gas velocity through the GC column.

- Although there is risk of an explosion when using hydrogen, this will be very small if the following are followed:
  - Use a hydrogen generator
  - Use PPC pneumatic controllers
  - Ensure that systems are leak-free
  - Route split vents etc. to the instrument exterior
  - Use a hydrogen sensor in the GC oven