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PerkinElmer Gas Chromatograph / Mass Spectrometer (GC/MS)

Teledyne Tekmar
Purge and Trap (P & T)

Advances of Volatile Organic Compound (VOC) Analysis Including Alternate Carrier Gases

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Region 6 Quality Meeting

October, 2015

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Introduction

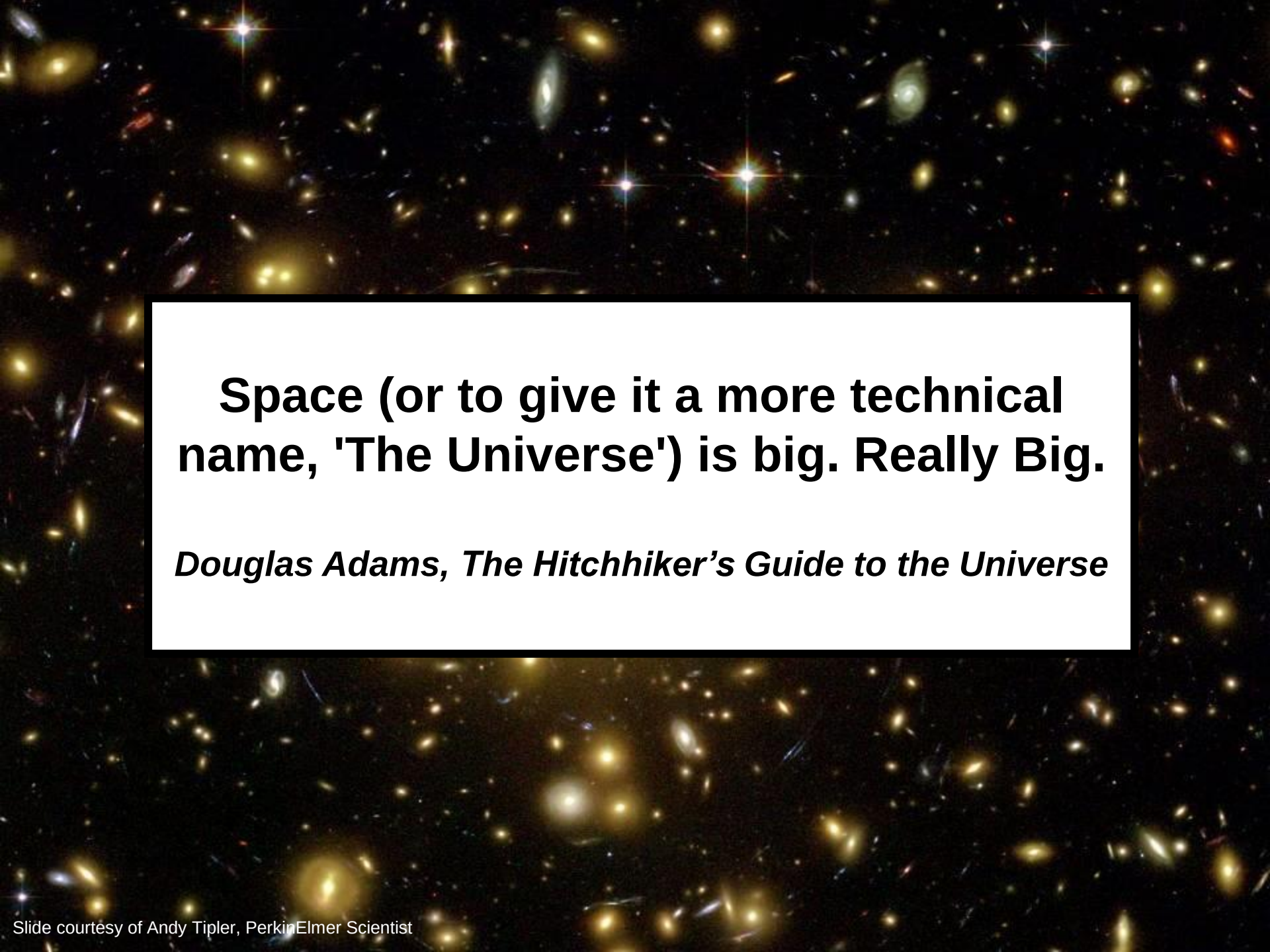
Introduction

- **Method EPA 524.3** covers toxic volatile compounds that may be present in drinking water. The volatile compounds are purged from water and trapped on a concentrator trap using Purge and Trap technology. After the volatiles are concentrated, the trap is heated to volatilize compounds which are eluted onto a GC column where they are separated and detected by mass spectrometry.

- This method helps to ensure the safety of our drinking water.

Purpose of Research: Alternative Carrier Gases

- The goal of this research was to investigate the use of alternative carrier gases while meeting method criteria.
- Helium is the referee. Hydrogen and nitrogen were investigated. Nitrogen may be our best choice!


Space (or to give it a more technical name, 'The Universe') is big. Really Big.
Douglas Adams, The Hitchhiker's Guide to the Universe
Slide courtesy of Andy Tipler, PerkinElmer Scientist

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	004
Others	0.07

Slide courtesy of Andy Tipler, PerkinElmer Scientist

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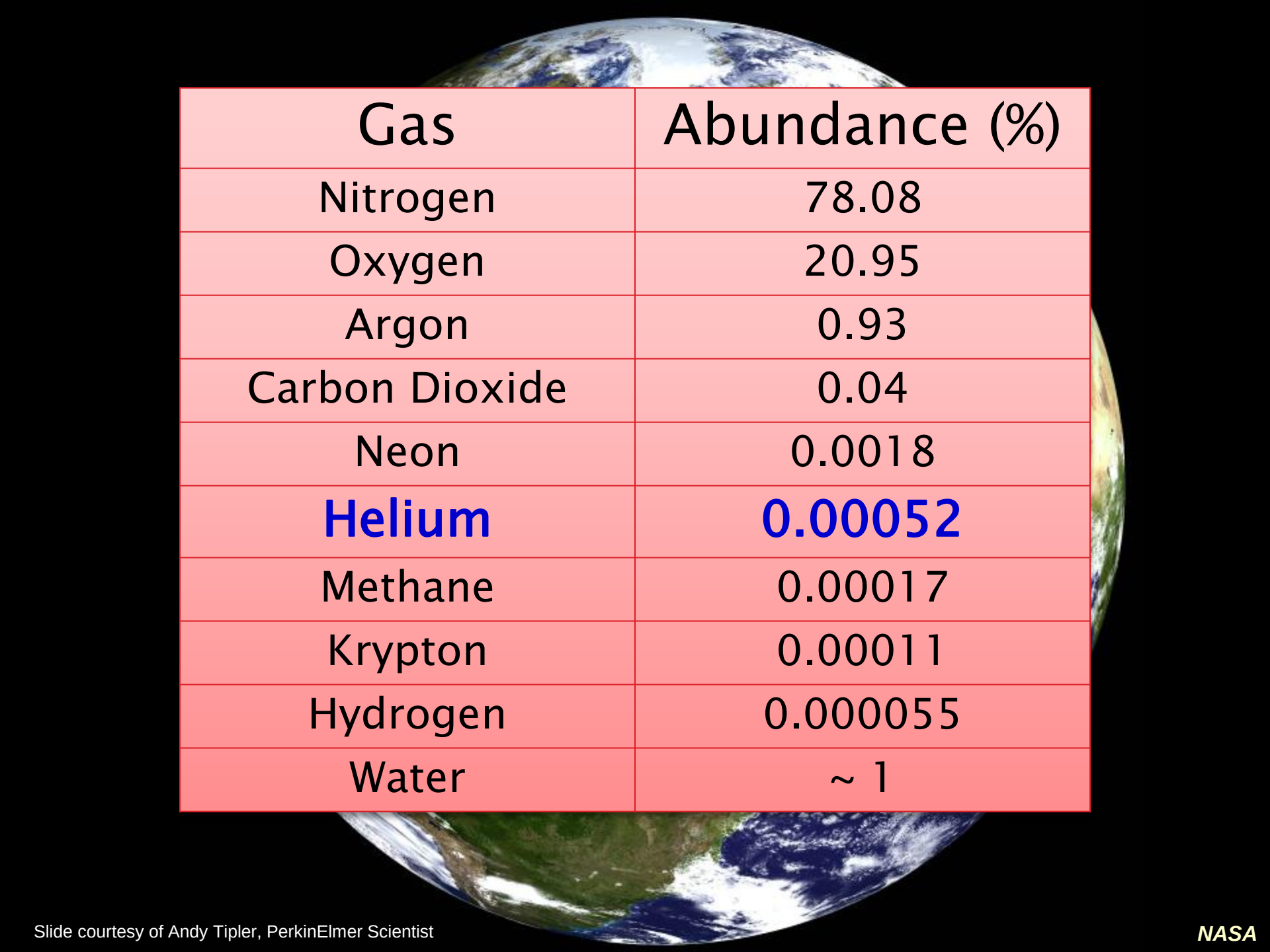
Earth:

Mostly Harmless: a small, blue-green world in one of the less fashionable sectors of the galaxy.

Douglas Adams, The Hitchhiker's Guide to the Universe

Slide courtesy of Andy Tipler, PerkinElmer Scientist

NASA



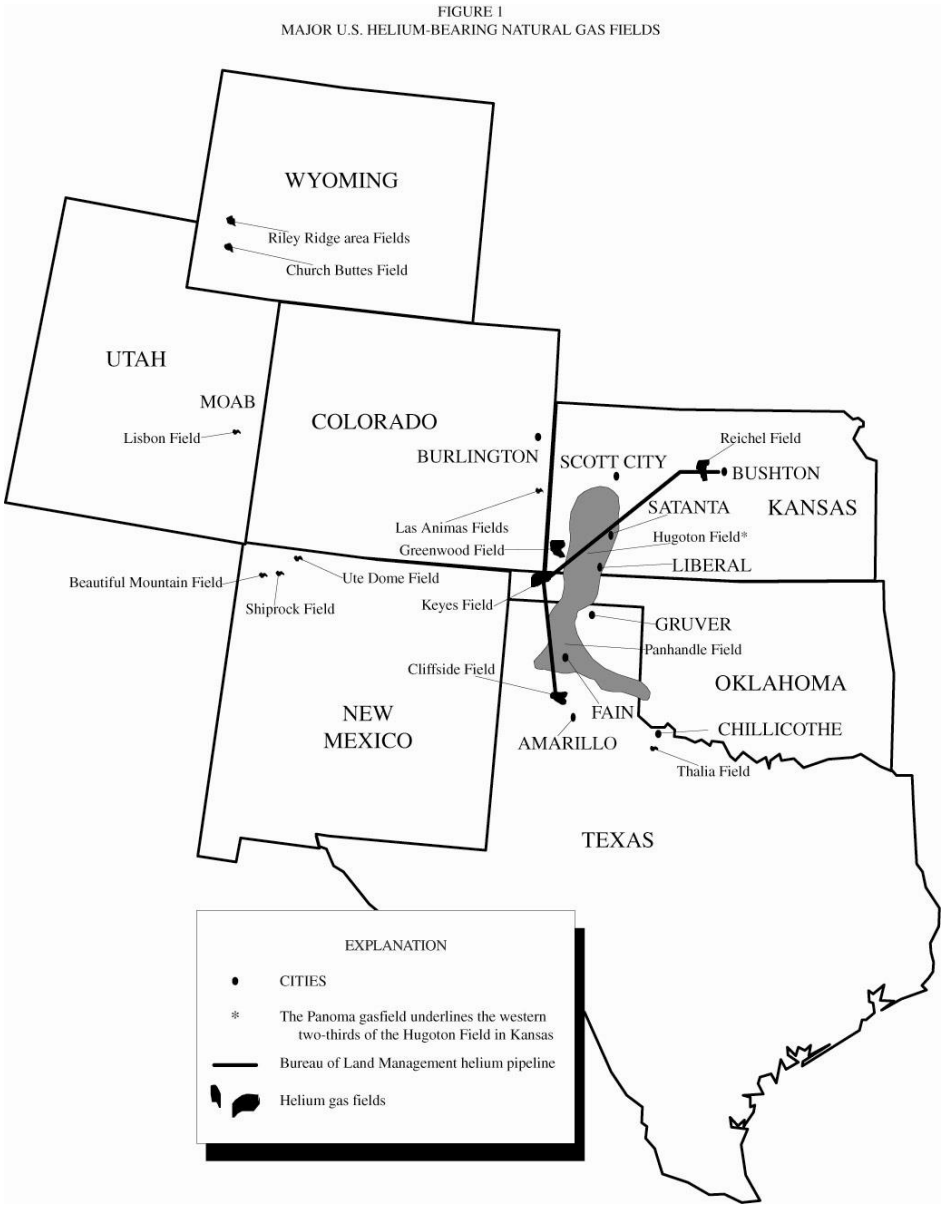
Gas	Abundance (%)
Nitrogen	78.08
Oxygen	20.95
Argon	0.93
Carbon Dioxide	0.04
Neon	0.0018
Helium	**0.00052**
Methane	0.00017
Krypton	0.00011
Hydrogen	0.000055
Water	~ 1

Slide courtesy of Andy Tipler, PerkinElmer Scientist

NASA

Helium Mining

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



Slide courtesy of Andy Tipler, PerkinElmer Scientist

Applications of Helium

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

Slide courtesy of Andy Tipler, PerkinElmer Scientist

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The question?

Should chromatographers be investigating other suitable carrier gases?

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Comparisons of Carrier Gases

Criteria

Chromatographic Efficiency

Detection Limits

Quick Look: He, H2 and N2

Parameter	Helium	Hydrogen	Nitrogen
Safety	Safe	Caution	Safe
Source	Cylinder	Cylinder or Generator	Cylinder or Generator
Cost	Expensive	Cost Effective	Cost Effective
Supply	Concern	n/a	n/a
Column choices	Wide to narrow bore	Narrow bore	Narrow bore
Inertness	Inert	Highly Reactive	Inert
BFB/DFTPP	Passes	Passes	Passes

Concerns

- Hydrogen:
  - Possible protonation
  - 2 to 4 times reduction in response.
- Nitrogen:
  - Chromatography efficiency
  - 15 times reduction in response

Research for Nitrogen and Hydrogen: Establish Parameters …

- Meet tune criterion
- Chromatographic efficiency
- 0.2ppb requirements
  - Signal to noise above 30 to one or better for all targets
  - Ensuring quantification meets method requirements
  - Linear to 0.2 ppb (reporting limit)
- Additional Initial Demonstration of Capability (IDC)
  - Precision at mid-point
  - MDL
  - LPIR and UPIR

United States Environmental Protection Agency

US EPA Method 524.3

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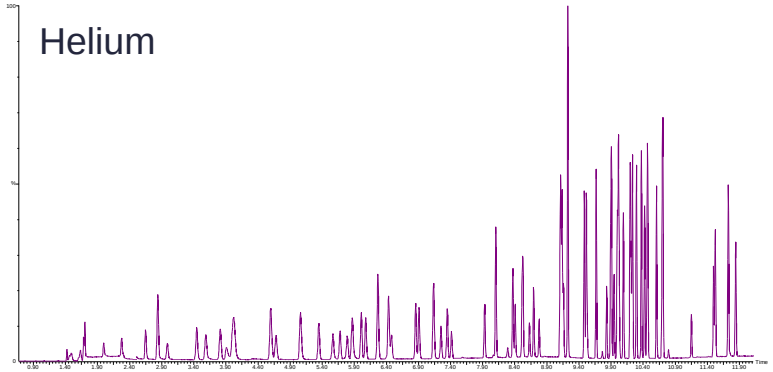
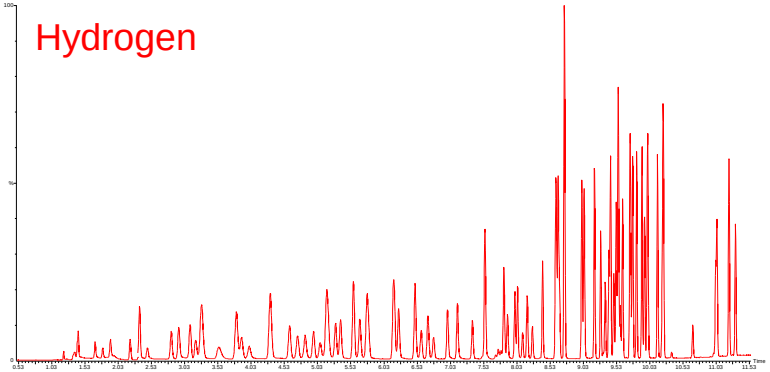
Alternative Carrier Gases:

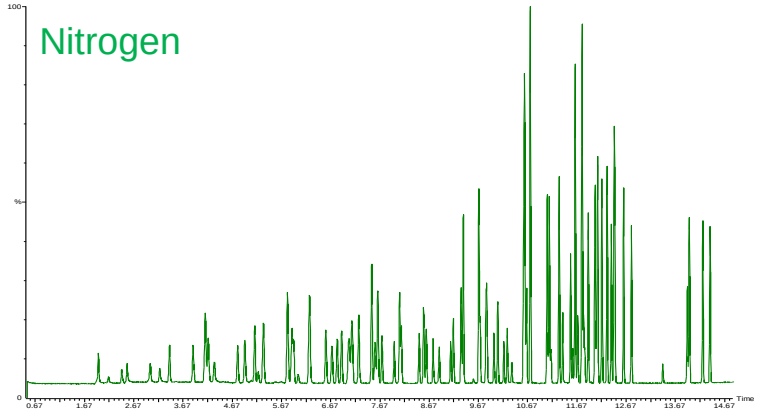
Ensuring peak efficiency

Chromatography



Peak Resolution for Nitrogen is Excellent!





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Meeting Method Criteria and Initial Demonstration of Capability

EPA Method 524.3

Bromofluorobenzene (BFB): Tuning Criteria 524.3

Mass	Ref Mass	Range	Relative Abudance (%)		
			Helium	Hydrogen	Nitrogen
50	BPI	Report only	16.1	15.9	17.1
75	BPI	Report only	45.6	51.7	49.2
95	BPI	100%	100.0	100.0	100.0
96	95	≥ 5% -- ≤ 9%	6.4	6.5	7.5
173	174	< 2%	0.4	0.6	0.8
174	95	>50% -- < 100%	83.9	75.8	83.2
175	174	≥ 5% -- ≤ 9%	6.6	6.2	7.3
176	174	>95% -- <105%	99.8	101.4	97.8
177	176	≥ 5% -- ≤ 10%	6.4	5.4	6.9

… passed tuning criterion in all three carrier gases!

Linearity and Reporting Limit (short list)

Range: 0.2 to 50 ppb

Carrier	Helium			Hydrogen			Nitrogen		
Compound Name	Linearity	0.2ppb std	S:N @ 0.2 ppb	Linearity	0.2 ppb std	S/N @ 0.2ppb	Linearity	0.2ppb std	S/N @ 0.2ppb
Vinyl Chloride	0.9999	0.21	470:1	0.9998	0.21	175:1	0.9998	0.19	55:1
1,3-Butadiene	0.9998	0.23	360:1	0.9996	0.20	73:1	1.0000	0.20	36:1
Carbon disulfide	1.0000	0.21	250:1	0.9999	0.23	222:1	1.0000	0.20	230:1
Methylene chloride	0.9999	0.20	440:1	0.9999	0.20	93:1	1.0000	0.20	480:1
Methyl tert-Butyl Ether	0.9999	0.20	110:1	0.9994	0.21	350:1	0.9999	0.19	68:1
Chloroform	0.9999	0.19	260:1	1.0000	0.22	85:1	1.0000	0.20	308:1
Benzene	0.9998	0.20	120:1	1.0000	0.21	460:1	1.0000	0.21	134:1
Toluene	1.0000	0.20	550:1	1.0000	0.20	454:1	0.9999	0.18	208:1
Chlorobenzene	1.0000	0.22	320:1	0.9999	0.22	845:1	0.9998	0.17	257:1
1,2-Dichlorobenzene	1.0000	0.21	450:1	1.0000	0.20	484:1	0.9999	0.23	186:1
Naphthalene	1.0000	0.21	820:1	0.9996	0.24	367:1	0.9998	0.24	246:1

Precision at Midpoint (20ppb), LPIR and UPIR

The range for LPIR and UPIR is 50 to 150

Carrier Gas	Helium			Hydrogen			Nitrogen		
Compound Name	**%RSD @ midpoint**	**LPIR**	**UPIR**	**%RSD @ midpoint**	**LPIR**	**UPIR**	**%RSD @ midpoint**	**LPIR**	**UPIR**
Vinyl Chloride	3.9	73	126	7.6	78	105	6.9	56	128
1,3-Butadiene	3.7	84	133	2.3	75	100	2.1	67	126
Carbon disulfide	5.1	54	92	3.2	96	115	3.4	88	130
Methylene chloride	3.0	70	112	4.7	87	100	4.6	74	123
Methyl tert-Butyl Ether	1.5	86	116	3.7	97	105	3.3	72	130
Chloroform	1.7	62	111	1.9	93	110	2.2	85	133
Benzene	2.1	77	96	2.3	78	105	2.0	73	111
Toluene	1.7	89	127	4.7	82	100	2.1	67	98
Chlorobenzene	1.5	105	145	2.0	84	133	2.2	68	79
1,2-Dichlorobenzene	1.4	87	131	1.7	82	113	1.2	90	103
Naphthalene	0.6	79	128	1.1	103	120	0.9	107	134

Upper and lower limits for prediction interval of results (UPIR and LPIR)

Purge and Trap Conditions

Purge	
Valve Oven Temp	140°C
Transfer Line Temp	140°C
Sample Mount Temp	90°C
Water Heater Temp	90°C
Sample Vial Temp	20°C
Sample Equilibrate Time	0.00 min
Soil Valve Temp	50°C
Standby Flow	10 mL/min
Purge Ready Temp	40°C
Condensate Ready Temp	45°C
Presweep Time	0.25 min
Prime Sample Fill Volume	3.0 mL
Sample Volume	5.0 mL
Sweep Sample Time	0.25 min
Sweep Sample Flow	100 mL/min
Sparge Vessel Heater	On
Sparge Vessel Temp	40°C
Prepurge Time	1.00 min
Prepurge Flow	0 mL/min
Purge Time	8.00 min
Purge Flow	60 mL/min
Purge Temp	20°C
Condensate Purge Temp	20°C
Dry Purge Time	1.00 min
Dry Purge Flow	100 mL/min
Dry Purge Temp	20°C

Desorb	
Methanol Needle Rinse	Off
Methanol Needle Rinse Volume	3.0 mL
Water Needle Rinse Volume	7.0 mL
Sweep Needle Time	0.25 min
Desorb Preheat Temp	245°C
GC Start Signal	Start of Desorb
Desorb Time	0.50 min
Drain Flow	300 mL/min
Desorb Temp	250°C
Bake	
Methanol Glass Rinse	Off
Number of Methanol Glass Rinses	1
Methanol Glass Rinse Volume	3.0 mL
Number of Water Bake Rinses	1
Water Bake Rinse Volume	7.0 mL
Bake Rinse Sweep Time	0.25 min
Bake Rinse Sweep Flow	100 mL/min
Bake Rinse Drain Time	0.40 min
Bake Time	3.00 min
Bake Flow	400 mL/min
Bake Temp	270°C
Condensate Bake Temp	200°C
Bake Temp	270°C
Condensate Bake Temp	200°C

GC/MS Conditions

Carrier	Helium	Hydrogen	Nitrogen
GC Conditions			
Oven Parameters	35°C for 4.0min ramp @ 16°C/min to 85°C ramp @ 30°C/min to 210°C hold 1.71min	35°C for 4.0min ramp @ 16°C/min to 85°C ramp @ 30°C/min to 210°C hold 1.71min	35°C for 3.0min ramp @ 10°C/min to 70°C ramp @ 20°C/min to 230°C hold 1min
Run Time	13min (last peak elutes @ 11.5min)	13min (last peak elutes @ 11.5min)	15.5min (last peak elutes @ 14.5min)
Inlet Temperature	220°C	220°C	220°C
Carrier Flow	0.4mL/min	0.2mL/min	0.3mL/min
MS Conditions			
Ionization	EI+	EI+	EI+
Mass Range	35 to 270	35 to 270	35 to 270
Scan Speed	12 to 15 scans per peak	12 to 15 scans per peak	12 to 15 scans per peak
Source Temp	260°C	260°C	280°C
Transfer Line Temp	240°C	240°C	240°C

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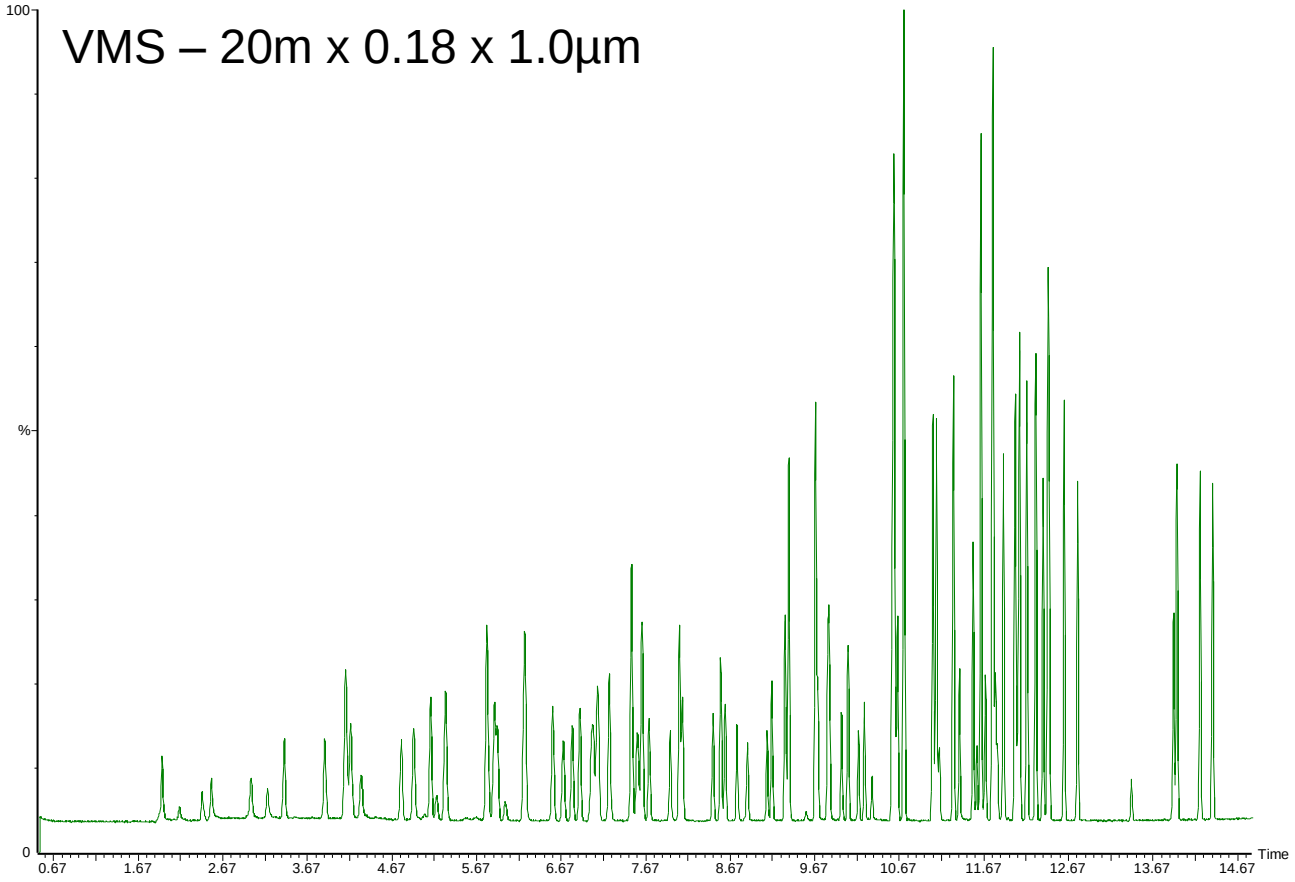
EPA Method 8260

using Nitrogen as Carrier Gas

8260 Total Ion chromatogram: Carrier is Nitrogen



BFB: Passing 8260C Criteria (carrier nitrogen)

Mass	Ref Mass	Range	Relative Abudnace
			Nitrogen
50	95	15 to 40 %	17.1
75	95	40 to 60	47.1
95	BPI	100%	100.0
96	95	5 to 9 %	6.8
173	174	< 2%	0.9
174	95	>50%	81.0
175	174	5% to 9%	6.6
176	174	>95% -- <101%	98.6
177	176	5% to 9%	5.6

8260 Meeting Criteria in Nitrogen

Compound Name	%RSD Calibration 0.5 to 200 ppb	Correlation Coefficient 0.5 to 200 ppb	S/N @ 0.5 ppb	%RSD @ 0.5ppb (n=7)
Vinyl Chloride	4.81	0.9999	95:1	4.70
Methylene chloride	6.50	0.9999	100:1	6.28
Methyl tert-Butyl Ether (MTBE)	3.57	0.9991	380:1	6.49
1,1-Dichloroethane	3.24	0.9997	431:1	8.69
Chloroform	3.83	0.9997	225:1	9.25
Carbon Tetrachloride	8.65	0.9995	132:1	11.36
1,1,1-Trichloroethane	3.42	0.9995	225:1	5.69
Benzene	4.36	0.9999	400:1	6.85
Toluene	3.14	0.9998	410:1	8.42
Chlorobenzene	5.16	0.9999	615:1	9.89
Ethylbenzene	8.27	0.9999	506:1	5.89
n-Butyl Benzene	3.00	0.9999	572:1	6.99
1,2-Dichlorobenzene	2.90	1.0000	605:1	5.25
1,2,4-Trichlorobenzene	2.83	0.9999	318:1	7.41
Naphthalene	6.38	0.9999	395:1	8.35

… entire list is available

Summary

- All method criteria for 524.3 was met using all three gases
- Since nitrogen appears to be the favorable alternative, this should be investigated further

- All method criteria for 8260 was met using nitrogen as a carrier gas

- To come – investigation of nitrogen and hydrogen as alternative carrier gases for all methods

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Thank you

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