Alternative carrier gases for process natural gas analysers

Dr Paul Holland

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Global Leaders in Gas Measurement

Overview

- Use of helium for Chromatography
- Why has the price of helium risen so much?
- Investigation: Nitrogen
- Investigation: Argon
- Investigation: Hydrogen
- Summary & Conclusions

Background

Composition analysis of natural gas by gas chromatography for the purpose of physical property calculation is very important.

Usual carrier gas is *helium* as it is deemed to have the optimum properties for this application.

The Great Helium Shortage

Can we change the carrier gas?

- It's not just a straight swap, need to think about the optimum parameters.

Requirements of a suitable carrier gas...

- inertness
- availability
- not a significant component in the sample

So what are the other choices?

Technical details

Investigation: Part 1 Nitrogen

Compare the performance of nitrogen as carrier gases with that when using helium

Investigation: Part 2 Argon

Compare the performance of argon as carrier gases with that when using helium

Investigation: Part 3 Helium

Compare the performance of hydrogen as carrier gases with that when using helium

1 H Hydrogen

Summary

Argon can be used as a carrier gas
Not recommended as an alternative to helium because of poor limits of detection and measurement precision.

Nitrogen would give very similar performance to helium. However won't be able to measure nitrogen in the sample, therefore unable to normalise.

Hydrogen gives very similar chromatographic behaviour to helium with increased detection sensitivity. However the response characteristics when using hydrogen, particularly for measurement of methane, are less consistent, and cause errors and biases which are outside the accepted tolerance.

Conclusions

Helium is a finite resource and it is so light that once it is released it cannot be contained by the Earth's atmosphere.

We will have to find an alternative to helium

Hydrogen is the best alternative and further work is needed to establish it's optimum operating parameters.

There are additional risks when using hydrogen due to it's flammability.

Hydrogen requires different ATEX rated equipment. This is not an easy retrofit and really needs to be purpose built.

Instrument manufacturers are taking this on board and we are seeing increasing numbers of instruments that are running on hydrogen carrier.

Hydrogen generators are an option and keep the volume of stored hydrogen to a minimum.

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In 2013 and again in 2019, there were concerns about helium shortage.

The scarcity of the gas led to significant price rises and uncertainty of availability. Some experts suggest that supplies could be depleted by the middle of the century.

What has caused this?

US HPA (Helium Privitisation Act) - In 1996, the US started selling off their helium store at rock bottom prices, now stocks are low hence prices are increasing.
Helium production has now moved towards the Middle East and Algeria.

Can an alternative carrier gas be used?

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Nitrogen

- ✔ *inertness* characteristic met
- ✔ readily available (78 % of atmosphere)
- ✘ normal component of natural gas (typically 1-10 % range), therefore we couldn't measure the nitrogen in the sample.

Argon

- ✔ *inertness* characteristic met
- ✔ readily available (0.93 % of atmosphere). So will be available in the foreseeable future.

Hydrogen

- ✘ does not fulfill the inertness criterion, however if safety requirements can be met, this potentially could be a good choice.
- ✔ Hydrogen will also never run out.

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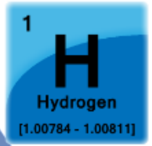

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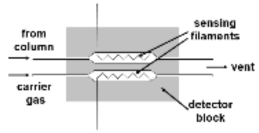
Detection

The principle detector used for process natural gas measurement is the **Thermal Conductivity Detector (TCD).**

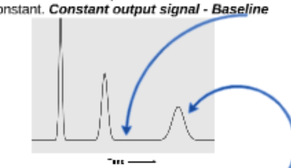


- Two gas flows:
  - Reference gas (carrier gas)
  - From column (carrier gas OR carrier gas + component)
- Two sensing filaments:
  - Reference filament
  - Detector filament

How does TCD work?

It works by measuring the difference in thermal conductivity between the two sensing filaments

- When **pure carrier gas** is flowing there will be no difference in TC between the two sensing filaments. Element temperature and resistance will be constant. ***Constant output signal - Baseline***



- When **carrier gas + component** are flowing there is a difference in TC. ***Change in output signal***

Thermal conductivity of a carrier gas is really important - Why?

- It determines the sensitivity of the carrier gas and detector.
- Which way the peak will appear on the chromatogram. (negative values give inverted peaks)

	Thermal conductivity $W.m^{-1}.K^{-1}$ @ 400 K	Thermal conductivity difference		
		from helium	from argon	from hydrogen
helium	0.191	0.000	-0.168	0.038
hydrogen	0.230	-0.039	-0.207	0.000
argon	0.023	0.168	0.000	0.207
nitrogen	0.032	0.159	-0.009	0.198
carbon dioxide	0.025	0.165	-0.002	0.205
methane	0.049	0.142	-0.026	0.181
ethane	0.035	0.156	-0.012	0.195

Helium and **hydrogen** have similar thermal conductivities, therefore will have similar sensitivity.

Argon is an order of magnitude less, therefore it will be less sensitive in comparison. Negative thermal conductivity difference, therefore negative peaks. This can be adjusted for by adjusting the polarity.

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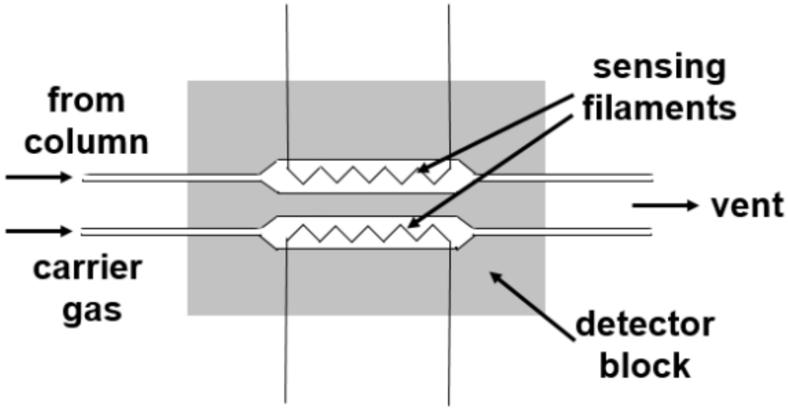

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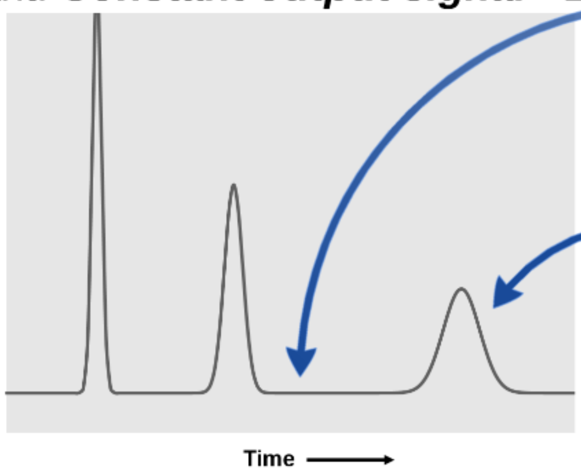

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Investigation: Part 1
Nitrogen

Compare the performance of nitrogen as carrier gases with that when using helium

N 7
Nitrogen

Nitrogen

- ✔ Used as a carrier gas in many GC applications.
- ✔ It is readily available and the *inertness* characteristic is met.
- ✘ It is a normal component of natural gas (typically 1-10 % range), meaning nitrogen would not be measured in the sample.

Normalisation

Complete mixture composition is needed for physical properties calculation (CV, Density, Wobbe Index etc)

Most analyses, while measuring all significant components, do not sum to 100 % due to sample size effects like atmospheric pressure.

In this case we ***normalise*** the data

Normalisation forces the sum to 100% by applying an adjustment to each of the components.

It reduces uncertainty in calculation of physical properties.

What impact would not measuring nitrogen have

This normalisation correction could not be carried out without the measurement of nitrogen.

Great source of error in calculation of physical properties.

On this basis no further work on nitrogen was carried out.

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Investigation: Part 2
Argon

Compare the performance of argon as carrier gases with that when using helium

The Set Up

Instrument: Daniel model 500

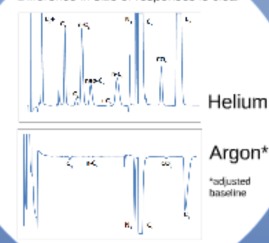
Inlet pressure & flow: Has similar viscosity to helium, therefore the same inlet pressure should give similar carrier gas flows and hence similar analysis times.

Valve switching times were adjusted to ensure all components were correctly allocated to the columns suitable for their measurement.

Reference gas used for this investigation, contained all the significant components found in natural gas.

Comparison

Difference in size of responses is clear



Issues

Sensitivity is the issue when using argon as the carrier gas.

A smaller signal will cause poor **precision of the measurement.**

In the case of argon, the TCD response is less, as is the sensitivity meaning the precision of measurement will be WORSE than when using a helium carrier gas.

Limit of Detection

i-butane, the three pentanes and C6+ are below the limit of detection and are therefore not visible on the argon chromatogram.

component	minimum detectable amount, ppm (mol/mol)		sensitivity improvement
	argon carrier	helium carrier	
propane	[illegible]	[illegible]	[illegible]
n-butane	[illegible]	[illegible]	[illegible]
nitrogen	[illegible]	[illegible]	[illegible]
carbon dioxide	[illegible]	[illegible]	[illegible]

In each case the sensitivity is worse when using argon.
Sensitivity improvement of 18 - 200 times when using helium instead of argon.

Effect on CV

	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
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The bias error arising from failure to measure hydrocarbons below their detection limits is unacceptably high.

No further investigation was carried out as argon is not a suitable carrier gas in this application.

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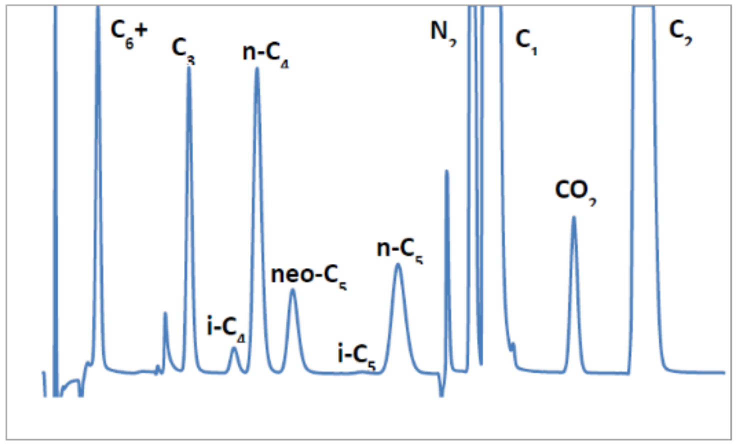
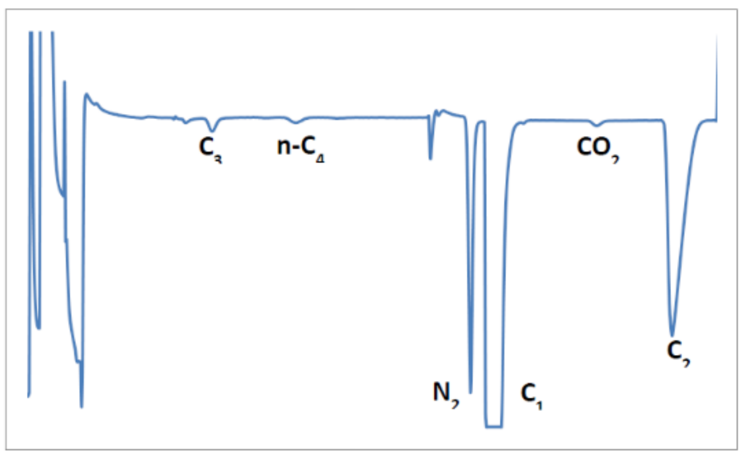


Helium



Argon*

*adjusted baseline

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component	minimum detectable amount, ppm (mol/ mol)		sensitivity improvement
	argon carrier	helium carrier	
propane	900	50	18
n-butane	1930	10	193
nitrogen	370	25	14.8
carbon dioxide	1550	30	51.6

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Effect on CV

	Typical North Sea gas composition	Components below LOD not measured
nitrogen	2.828	2.828
carbon dioxide	1.14	1.14
methane	92.758	92.758
ethane	2.437	2.437
propane	0.436	0.436
i-butane	0.107	0.000
n-butane	0.103	0.000
neo-pentane	0.004	0.000
i-pentane	0.022	0.000
n-pentane	0.030	0.000
C_6+	0.086	0.000
CV MJ/m³	37.586	37.222
CV difference		0.364
CV difference %		-0.97%

The bias error arising from failure to measure hydrocarbons below their detection limits is unacceptably high.

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Investigation: Part 3 Helium

Compare the performance of hydrogen as carrier gases with that when using helium

The Set Up

Instrument: The same Daniel model 500 as previous test.

Inlet pressure & flow: Hydrogen is less viscous than helium, therefore a lower inlet pressure is required to achieve the same flow rate.

An inlet pressure of 37 psi for hydrogen gave comparable retention times and cycle time to helium (89 psi).

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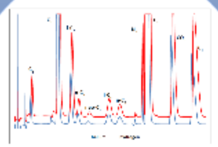
Comparison



- The similarity of the chromatography is evident.
- Hydrogen sensitivity is better by a factor of 1.60 for pentanes and 2.23 for methane.

ISO 10723 - Performance Evaluation of on-line analytical system

- Repeat analyses on 7 certified test gases (N2, CO2, C1 to C5 and n-C6 to represent the C6+ group)
- Each component is measured at seven different concentrations equally spaced over the operating range.
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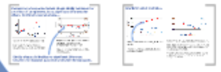
Testing results

- Hydrogen gave better sensitivity than helium
- However the measurement precision was similar to helium
- Limits of detection will be similar whichever of the two carriers is used.



Results of the Performance Evaluation

The results of this different behaviour are shown in the MPE and MPB values calculated for calorific value.

	MPE MJ/m³	MPB MJ/m³
Performance requirements	0.1	0.02
Helium carrier gas	0.046	0.000
Hydrogen carrier gas	0.107	-0.039

With helium carrier MPE and MPB are within tolerance.

Hydrogen exceeds both the MPE and MPE.

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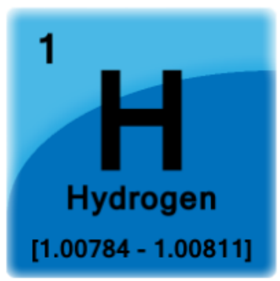

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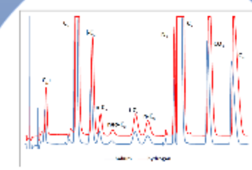

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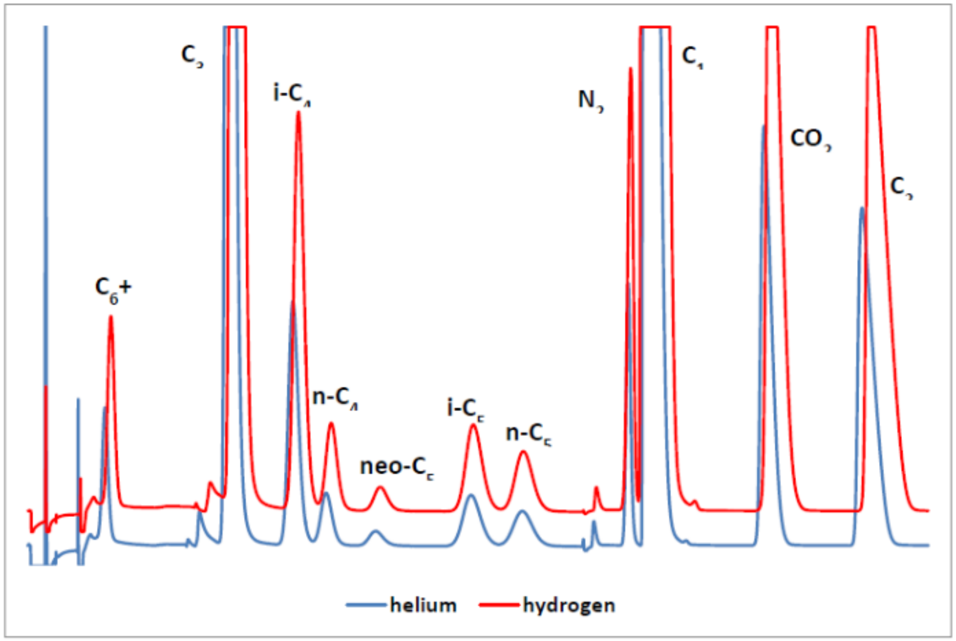

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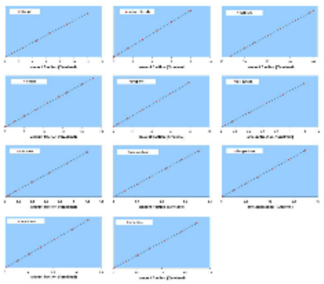
Linearity Plots



What information does an ISO 10723 Performance Evaluation give?

It calculates the errors and bias of the components and these are compared to:

- maximum permissible error (MPE)
- maximum permissible bias (MPB)

of the physical properties:

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- Density
- Wobbe Index

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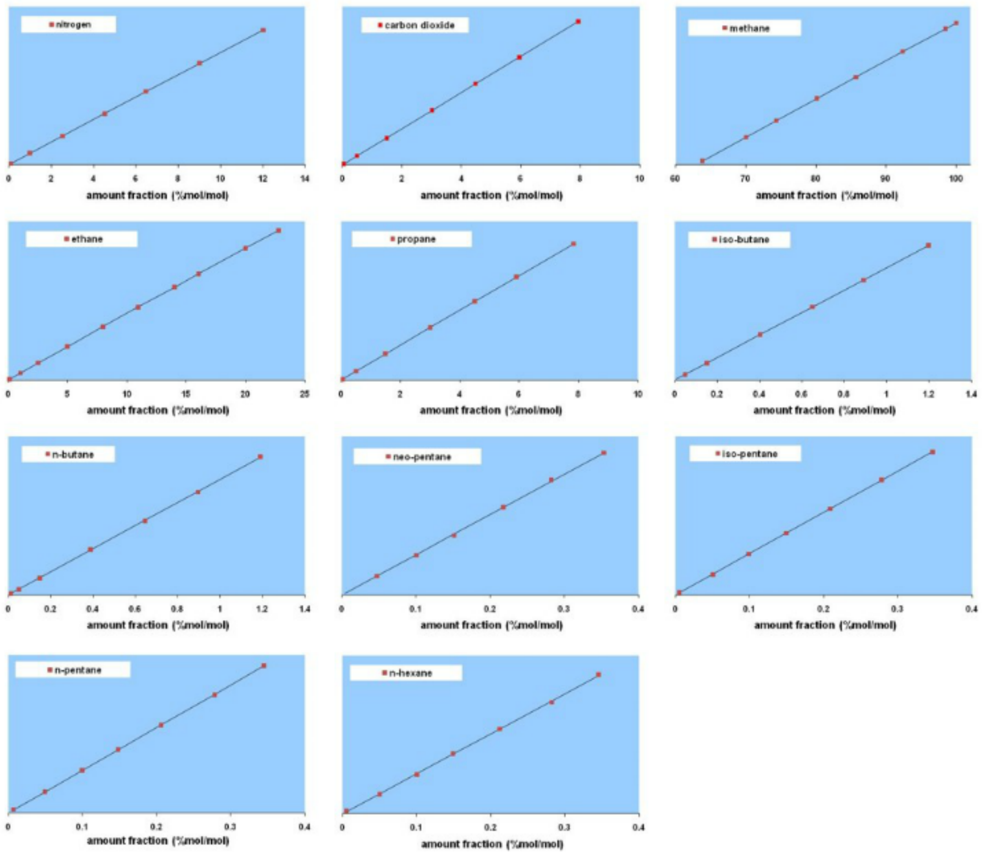

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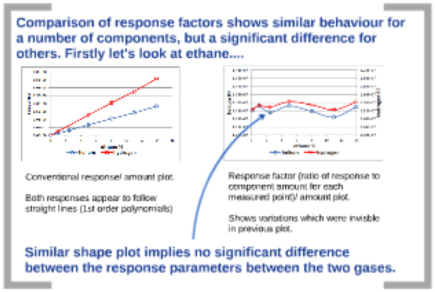
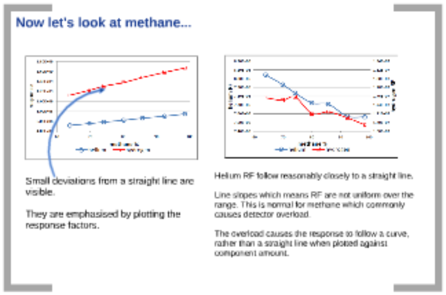
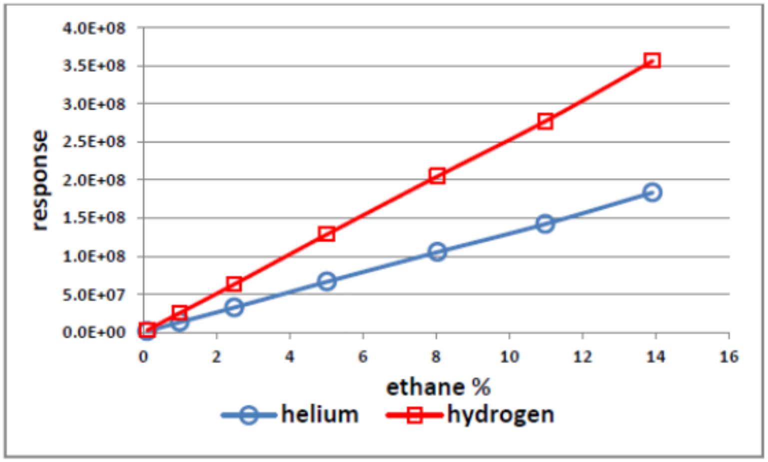


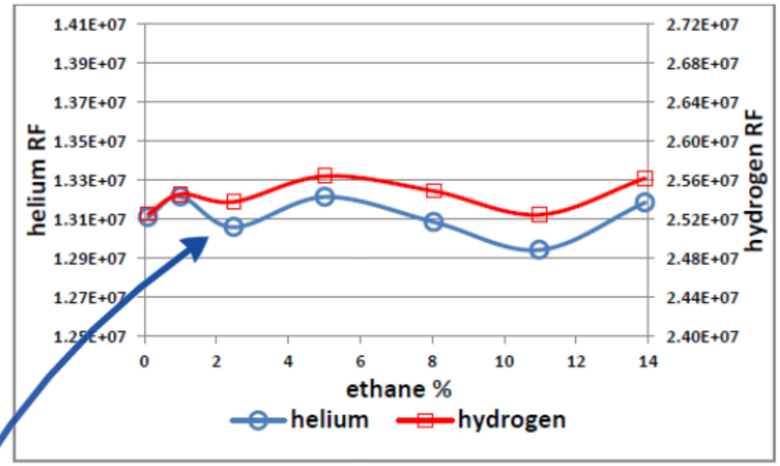


Comparison of response factors shows similar behaviour for a number of components, but a significant difference for others. Firstly let's look at ethane....



Conventional response/ amount plot.

Both responses appear to follow straight lines (1st order polynomials)

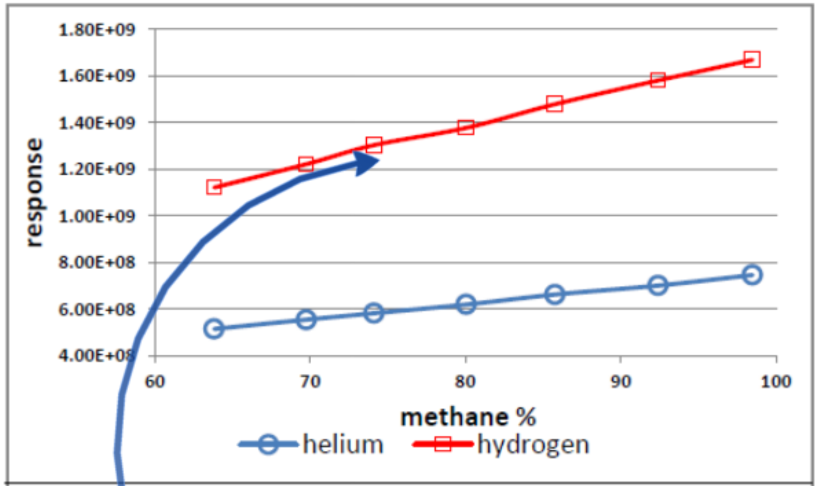


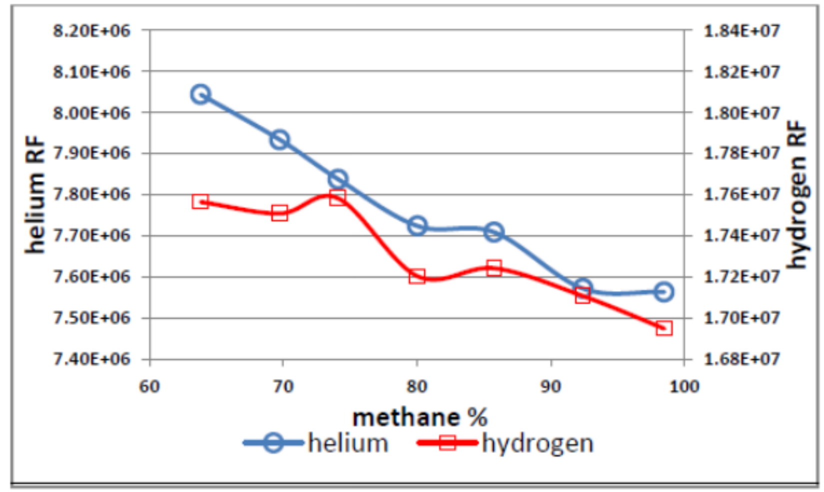
Response factor (ratio of response to component amount for each measured point)/ amount plot.

Shows variations which were invisble in previous plot.

Similar shape plot implies no significant difference between the response parameters between the two gases.

Now let's look at methane...





Small deviations from a straight line are visible.

They are emphasised by plotting the response factors.

Helium RF follow reasonably closely to a straight line.

Line slopes which means RF are not uniform over the range. This is normal for methane which commonly causes detector overload.

The overload causes the response to follow a curve, rather than a straight line when plotted against component amount.

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Not recommended as an alternative to helium because of poor limits of detection and measurement precision.

Nitrogen would give very similar performance to helium. However won't be able to measure nitrogen in the sample, therefore unable to normalise.

Hydrogen gives very similar chromatographic behaviour to helium with increased detection sensitivity. However the response characteristics when using hydrogen, particularly for measurement of methane, are less consistent, and cause errors and biases which are outside the accepted tolerance.

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Conclusions

Helium is a finite resource and it is so light that once it is released it cannot be contained by the Earth's atmosphere.

We will have to find an alternative to helium

Hydrogen is the best alternative and further work is needed to establish it's optimum operating parameters.

There are additional risks when using hydrogen due to it's flammability.

Hydrogen requires different ATEX rated equipment. This is not an easy retrofit and really needs to be purpose built.

Instrument manufacturers are taking this on board and we are seeing increasing numbers of instruments that are running on hydrogen carrier.

Hydrogen generators are an option and keep the volume of stored hydrogen to a minimum.

Alternative carrier gases for process natural gas analysers

Dr Paul Holland

EffecTech

Global Leaders in Gas Measurement

Overview

- Use of helium for Chromatography
- Why has the price of helium risen so much?
- Investigation: Nitrogen
- Investigation: Argon
- Investigation: Hydrogen
- Summary & Conclusions

Background

Composition analysis of natural gas by gas chromatography for the purpose of physical property calculation is very important.

Usual carrier gas is helium as it is deemed to have the optimum properties for this application.

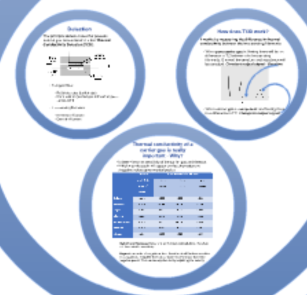
Can we change the carrier gas?

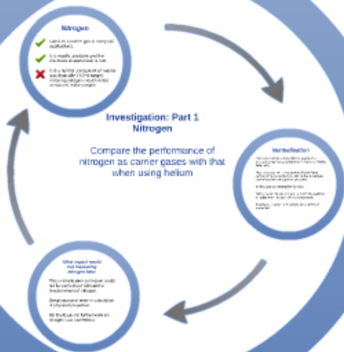
- It's not just a straight swap, need to think about the optimum parameters.

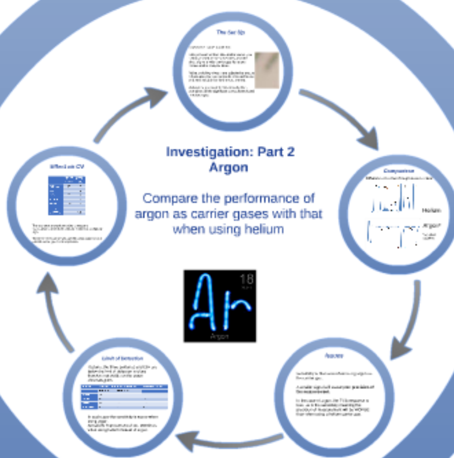
Requirements of a suitable carrier gas...

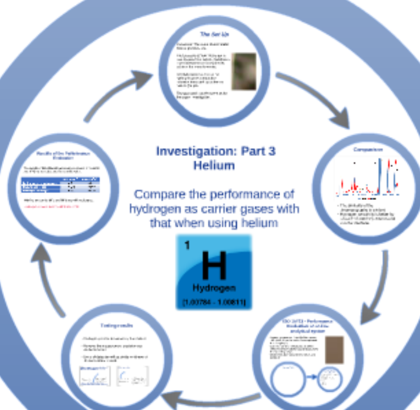
- inertness
- availability
- not a significant component in the sample

Technical details









Summary

Argon can be used as a carrier gas
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