Crown GeoChemistry and Future Geological Technologies

Direct Quadrupole Mass Spectrometer background training
and scope information for clients of mudlogger partners

Prep by Bruce Warren, President – Crown GeoChemistry, Inc.

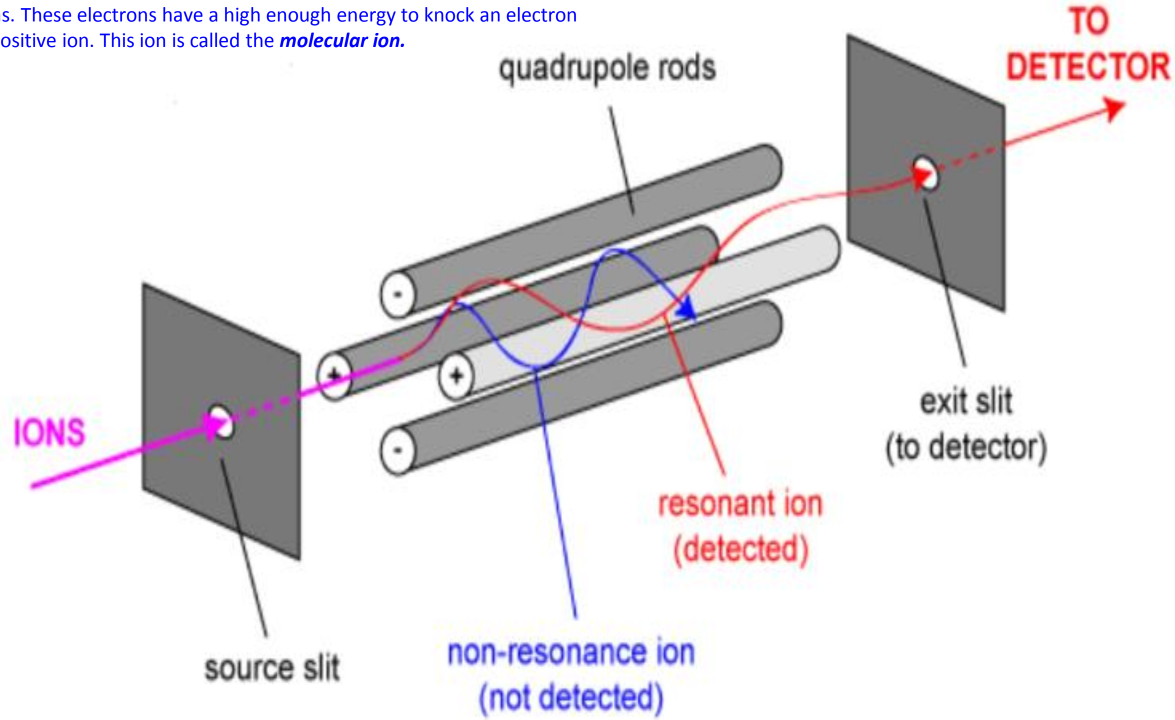
How does DQ Mass Spec work?

The DQMS uses the quad as a mass filter. ONLY ONE MOLECULAR WEIGHT can pass through to be measured.

Source: chemguide.co.uk This is a good resource for those interested in a little further study.

The formation of molecular ions

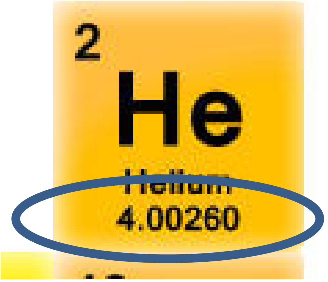
When the vaporised organic sample passes into the ionisation chamber of a mass spectrometer, it is bombarded by a stream of electrons. These electrons have a high enough energy to knock an electron off an organic molecule to form a positive ion. This ion is called the ***molecular ion.***

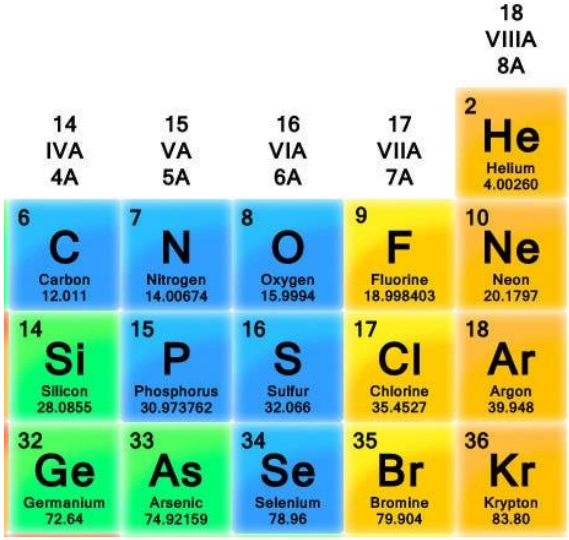


The gas sample is ionized creating positively charged molecules. The flight of the charged molecules is such that only the one m/z makes it through the “tube” created by the rods.

DQMS measures the mass to charge, or *m/z*.

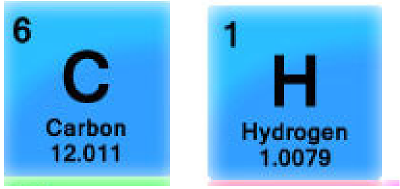
The molecular weight (AMU) for Helium is 4.00260 – *m/z* 4. That m/z phrase is the symbol for **Mass to Charge Ratio**. AMU stands for **Atomic Molecular Unit**. Think of AMU as the actual molecule weight and *m/z* as the machine response.





14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
				2 He Helium 4.00260
6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80

Methane molecular ion = *m/z* 16



1 Carbon + 4 Hydrogen = 16

12 + 4 = 16

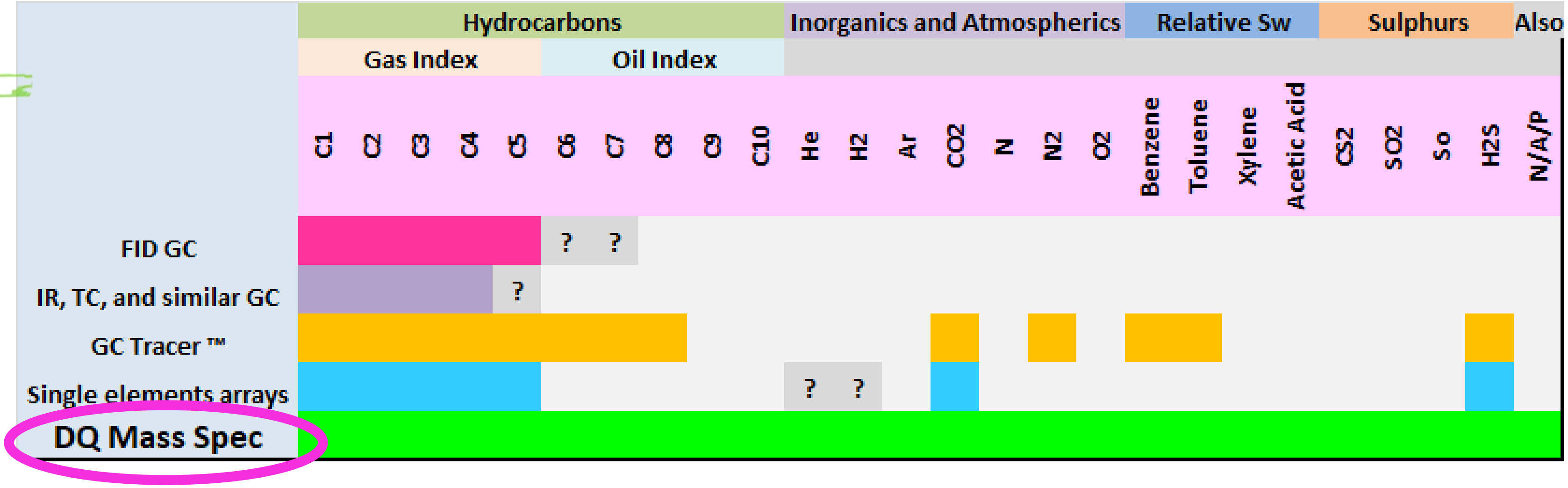
(Because of interference with other species at that unit we use a daughter of C1 for most C1 measurements)

The DQMS is reading Helium when the scan is at the m/z 4 position.
Argon is 40 and Oxygen is 16 – so O2 is 32.

Crown Geochemistry, Inc.

Other detectors vs. DQMS

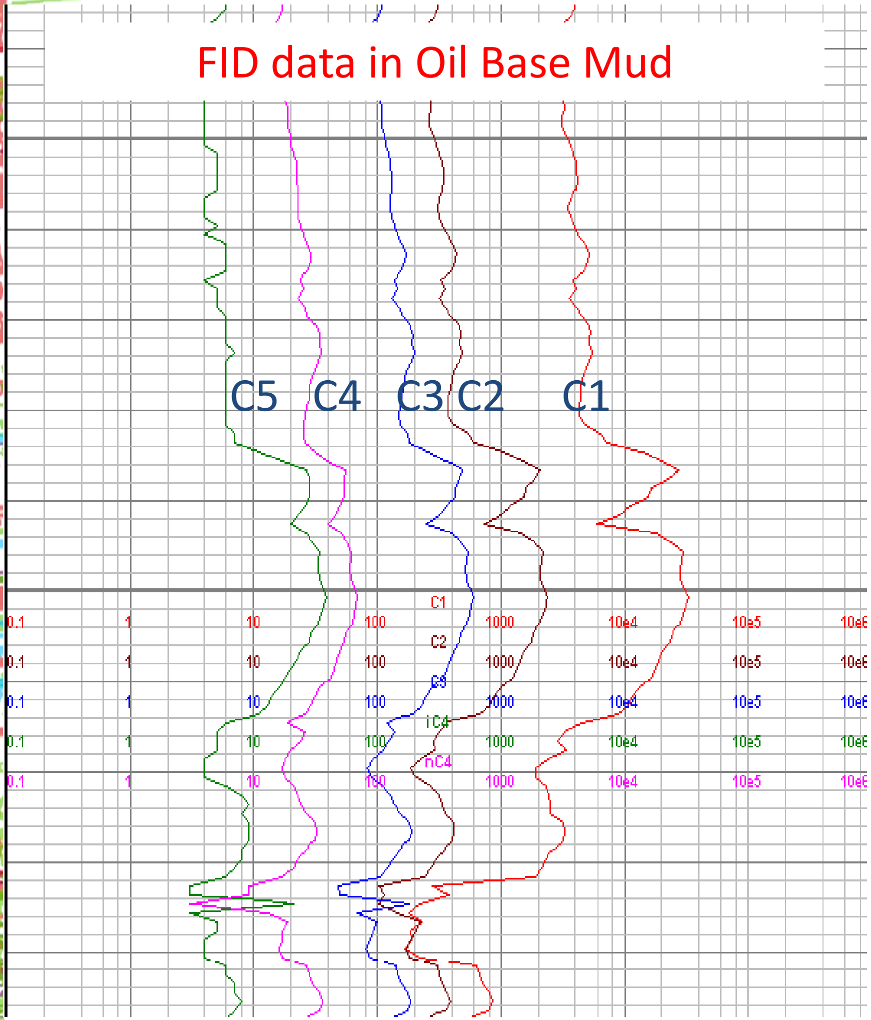
DQMS allows us to look at gobs of analytical inputs.
The relative performance of each to the others can be insightful.
The chart below is actually only a partial list for the DQMS.



	Hydrocarbons										Inorganics and Atmospherics							Relative Sw				Sulphurs				Also
	Gas Index					Oil Index																				
	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	He	H2	Ar	CO2	N	N2	O2	Benzene	Toluene	Xylene	Acetic Acid	CS2	SO2	So	H2S	N/A/P
FID GC	🟥	🟥	🟥	🟥	🟥	?	?																			
IR, TC, and similar GC	🟪	🟪	🟪	🟪	?																					
GC Tracer ™	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧						🟧		🟧		🟧	🟧						🟧	
Single elements arrays	🟦	🟦	🟦	🟦	🟦						?	?		🟦											🟦	
DQ Mass Spec	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩

The different instruments sometimes claim different limits, hence the question marks, but GCs generally suffer at lower abundances on the heavier elements

So here's what has been a problem



North Sea Methane Show
BTU about 1000

The best Flame-ionization chromatograph (FID) available circa 2003

And it looks like every mud log show you ever saw

This older gear was used in the fifties because it would live at a drilling rig – plain and simple. We would have used a mass spec then if they were smaller, portable, more reliable.

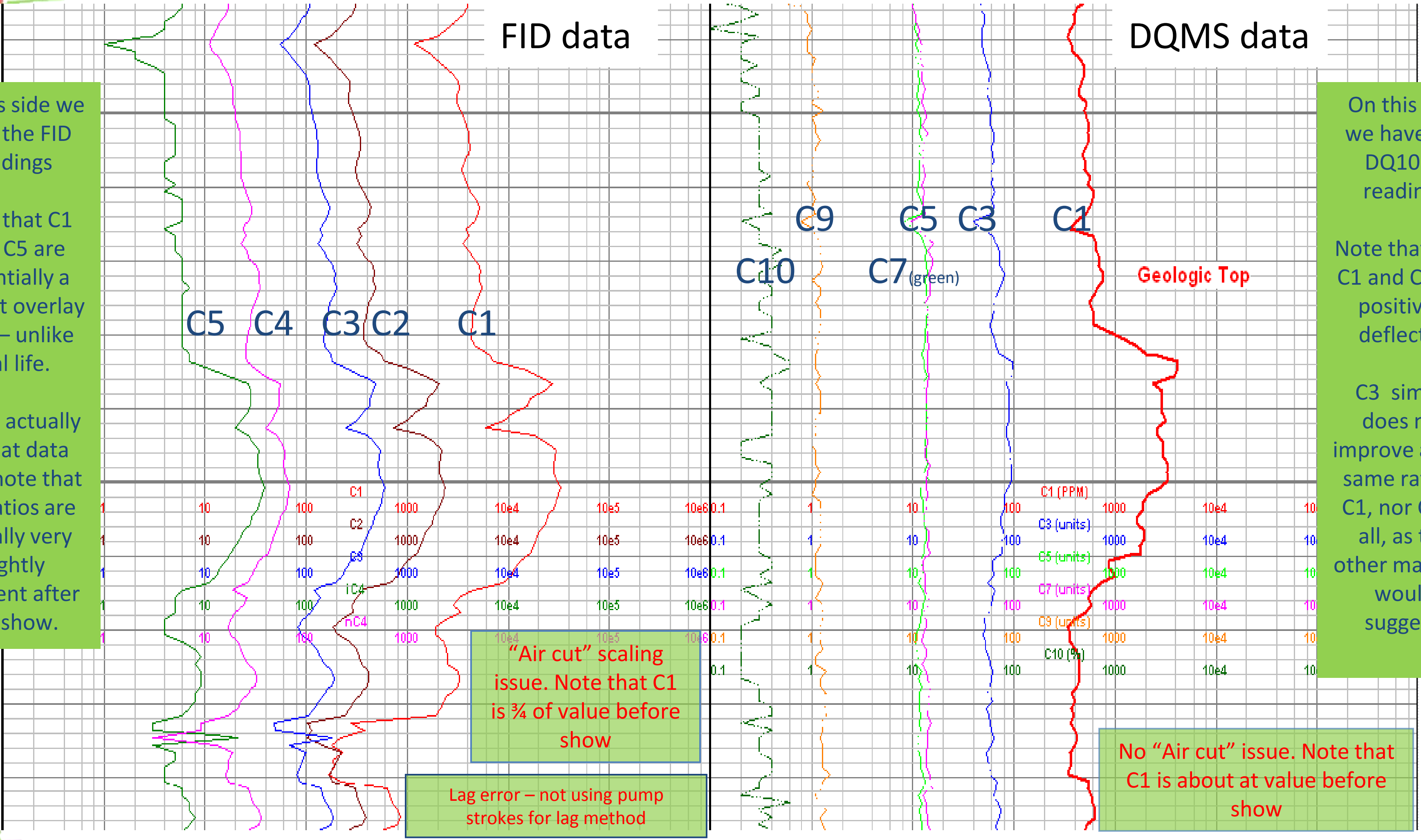
Hydrogen Flame vs. Mass Spec

The older gear does not detect at all for the wetter hydrocarbons which are needed to do critical gas analysis.

On this side we have the FID readings

Note that C1 thru C5 are essentially a perfect overlay here – unlike real life.

This is actually a great data set – note that the ratios are actually very slightly different after the show.



"Air cut" scaling issue. Note that C1 is ¾ of value before show

Lag error – not using pump strokes for lag method

No "Air cut" issue. Note that C1 is about at value before show

On this side we have the DQ1000 readings

Note that only C1 and C3 are positively deflected

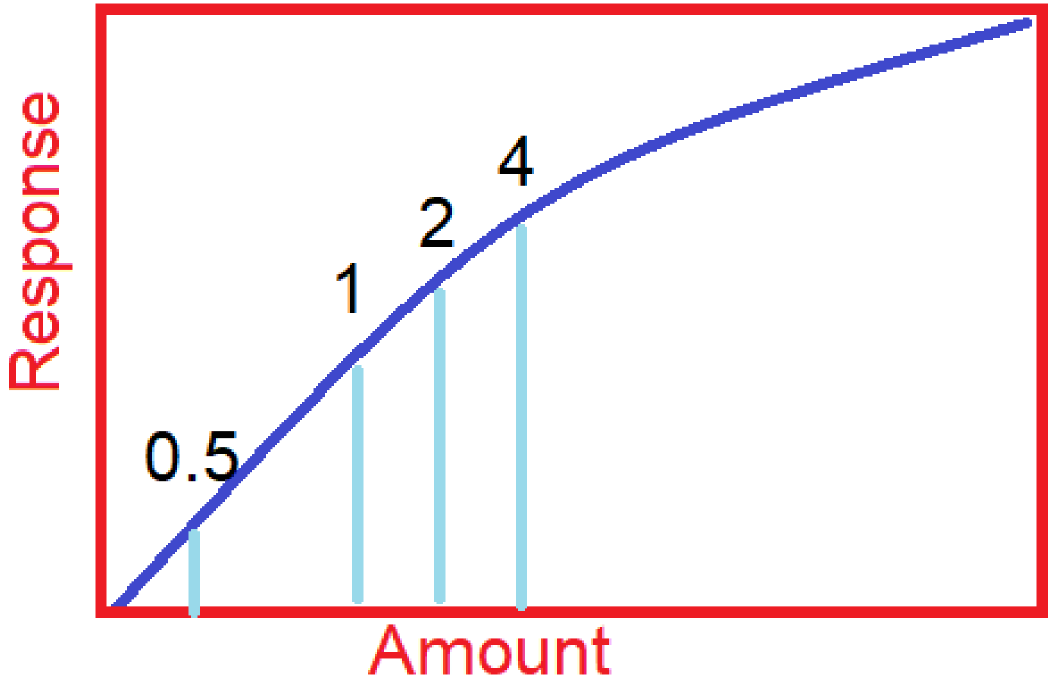
C3 simply does not improve at the same rate as C1, nor C5 at all, as the other machine would suggest.

It's not the GC calibration either. The GC is not putting C5 at the wrong value. Simply putting it there at ALL is the problem. No C4 or C5 in the product, as in 0.0 PPM.

Non-Linear Response is part of it.

The better FIDs have a fatter sweet spot for near-linear response but all of them have this problem

The different gas species are at different points along this skew.
Methane might have a population of 100x Butane

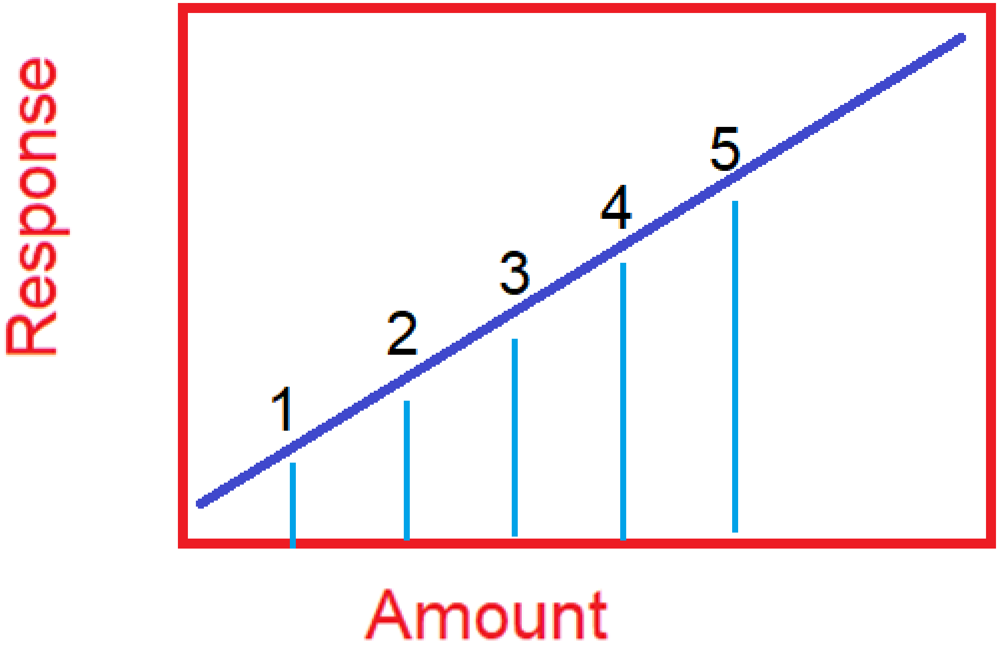


This is simply an artistic example of one of the factors that is part of the GC world. There are methods to account for part of this, but…

DQMS response is nearly perfectly linear.

The DQMS has a different lower working limit for each species depending on the “trash on the floor” of other molecule fragments. For instance the clutter at Helium is such that until about 3 or 4 PPM the Helium data is mixed with these junk fragments, and after that it is all Helium up till 1 million PPM.

Each gas species will exactly double the response when the dose is doubled.

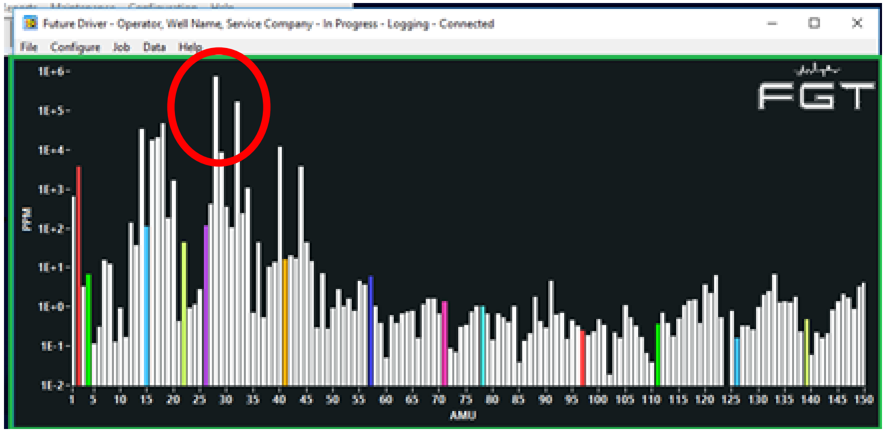


The DQMS results being linear – after the lower detection limit – allows us to use ratios of very low abundance items compared to very high abundance items, which allows the perm and porosity comparisons for example.

DQMS calibration.

The DQMS as we employ it shows the response amplitude for every molecular weight from *m/z* 2 through *m/z* 150.

Among the peaks available are atmospheric compounds including Nitrogen, Oxygen, and Argon. Atmospheric peaks are used for calibration of the instrument. Each is able to have the current reading compared to the known amount in atmosphere.



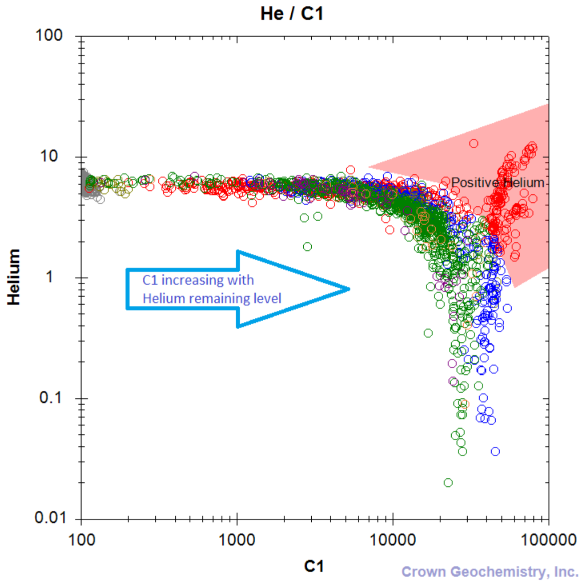
The DQMS scan showing m/z 2 through m/z 150 left to right.

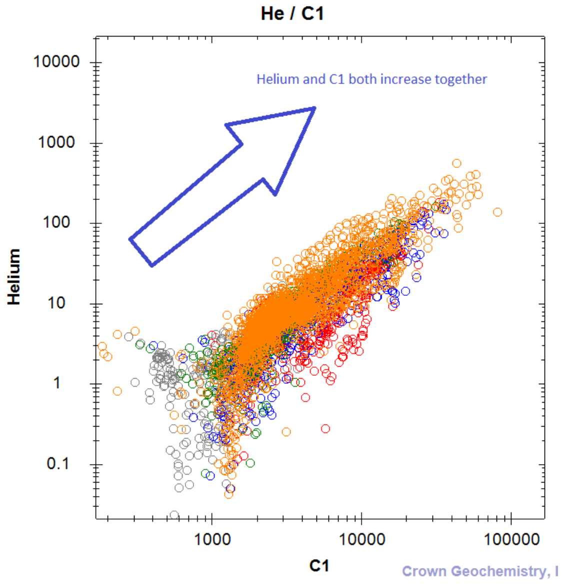
Within the circled inset are the instrument peaks for Nitrogen at *m/z* 28 and Oxygen at *m/z* 34

The DQMS software compares the peaks for these compounds and uses their response strength to set the response range of the instrument. Using a high quantity element and a low quantity element it then sets the gain from high to low. This is done for minor adjustments every instrument cycle. Periodically a more robust calibration occurs for which the instrument takes a short break from regular duty to run a fuller calibration.

Since we see literally parts per MILLION…

We can do a lot, but garbage in – garbage out will always be in play. By comparing Helium which is at low PPM and is very high volatility to hydrocarbons we can gain valuable insight. But not if the sample line is so far from the extractor to the trailer that it allows Helium and light HCs to equilibrate.

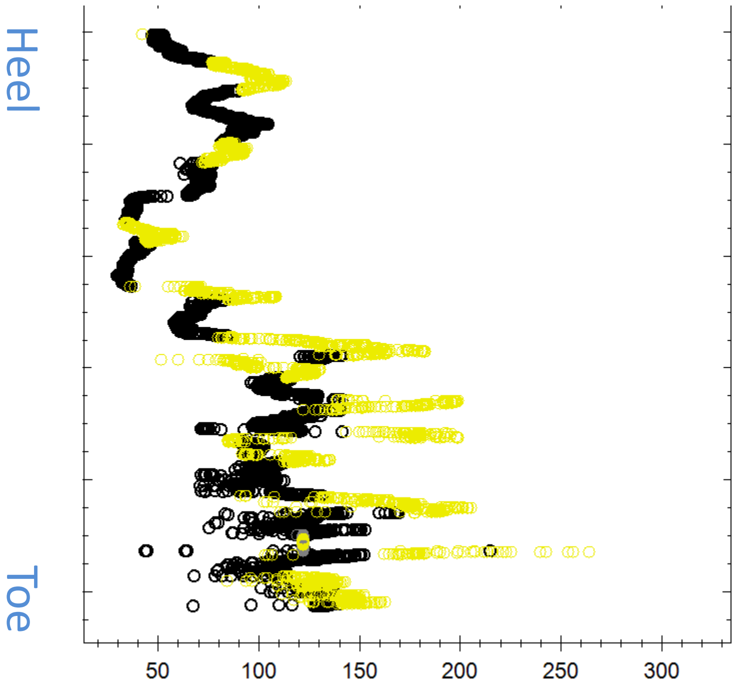




Example on the left has the trailer too close to the pits. The Helium on the left is simply showing Helium at it’s several minute average, except when the methane is so high it acts as a “cut” and Helium actually shows less, for instance TG, DTG, and CG events.

We call an index of C5 through C10 the Oil Index

The whole reason for Pixler and Ch-Wh-Bal ratios was an attempt to predict oil from light HCs.



The sum of each: C5 through C10

When the temperature goes up the heavies are made more volatile and read higher. The yellow data are the values that occur between 10 AM and 5 PM when it's hot. The longer we make that little greenhouse we call our sample tube the worse this gets.

FID does not detect at all for the wetter hydrocarbons, so this wasn't a factor in the past.

Go as ‘old school’ as they will let you.

The best results are achieved with the lab placed as close to the pits as can be managed.

Remember: every foot of sample line length is your enemy.

In closing;

Direct Quadrupole Mass Spectrometry offers an extremely wide of array of analytical inputs. With care and some simple QC controls you will be able to offer your clients a valuable tool at a cost / benefit ratio they will appreciate.

FGT

FUTURE GEOLOGICAL TECHNOLOGIES

Crown Geochemistry, Inc..

Our two companies are very eager to be the service provider you choose.
We are both here to help. If you don’t succeed we won’t either, and we know that.