

What Do We Mean by C₆₊?

Chris Cowper, EffecTech Ltd

1 INTRODUCTION

Transmission quality natural gases contain inert components (helium, nitrogen, carbon dioxide) and hydrocarbons up to C₉ or C₁₀, occasionally C₁₂ at trace levels. Calculation of properties from composition would, in an ideal world, require fully detailed analysis so that the contributions of components or component groups can be properly assessed. This approach, however, is not compatible with the on-line or process application of gas chromatographs (GCs) because of the constraints of expected cycle time and the diversity and complexity of the equipment required for full analysis.

Process GCs can be easily configured to give analysis of nitrogen, carbon dioxide and hydrocarbons from methane to pentane as individual components. This means that these components can be quantified by direct one-to-one calibration, which minimises uncertainty and bias in the results. Hydrocarbons in the range hexanes and above consist of a number of isomers which increase rapidly with carbon number, and diminish exponentially in concentration. Even if they were all identified, which they are not, it is impractical to attempt one-to-one calibration for all these components.

As a result, a compromise is made in the measurement of these hydrocarbons, either by restricting the range of components measured and the limits of detection applied to them, or by recombining them into a single chromatographic peak which sums all their contributions. Such a peak is referred to as C₆₊, since it contains all the hydrocarbons from hexanes upwards. This paper is concerned with the practicality of C₆₊ measurement.

2 BACKGROUND

Properties such as calorific value (CV), relative density (RD) and Wobbe Index (WI) can be derived with acceptable uncertainty from a C₆₊ analysis, according to ISO 6974 [1]. Compression factor can be calculated according to AGA8 [2] with some reservations as described in ISO 12213 [3].

While the CVs and RDs of individual higher hydrocarbons are high relative to methane, the major component, their low concentrations mean that their contributions to the overall properties are low. For this reason, C₆₊, which, since the compositional breakdown is not known, is an approximation to the total of hexanes and higher hydrocarbons, is accepted as a sufficiently good measurement. It is instructive to compare figure 1, which is a typical C₆₊ chromatogram, with figure 2, which is a detailed analysis up to C₁₂. Figure 2 is derived under laboratory conditions, using a complex system which is not amenable to process application, and shows 100 or so peaks, many of which will contain more than one component. These are all summed in the C₆₊ peak of figure 1. This comparison gives rise to another question; how does the uncertainty of measuring 100 peaks compare with the uncertainty of measuring one?

The correct use of a C₆₊ analyser requires answers to three questions:

- how well can a composite C₆₊ peak be measured, given that its composition will vary between different gases
- how can the raw data be converted into a quantity (mol fraction or mol %) without knowledge of the detailed breakdown
- how should a property (CV etc.) be allocated to the derived quantity?

Each of these answers influences the quality of data generated by the C₆₊ component.

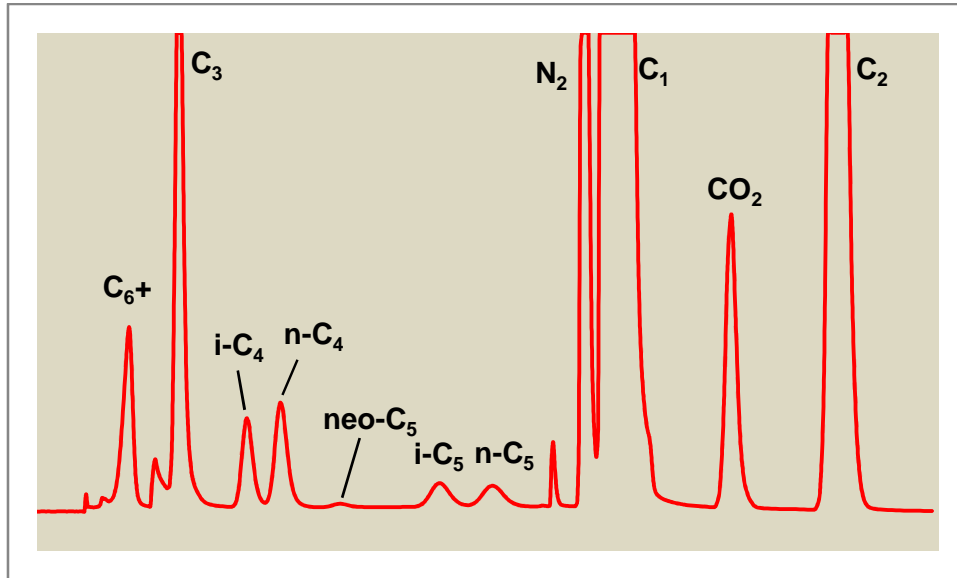


Figure 1 - Chromatogram showing C₆₊ peak

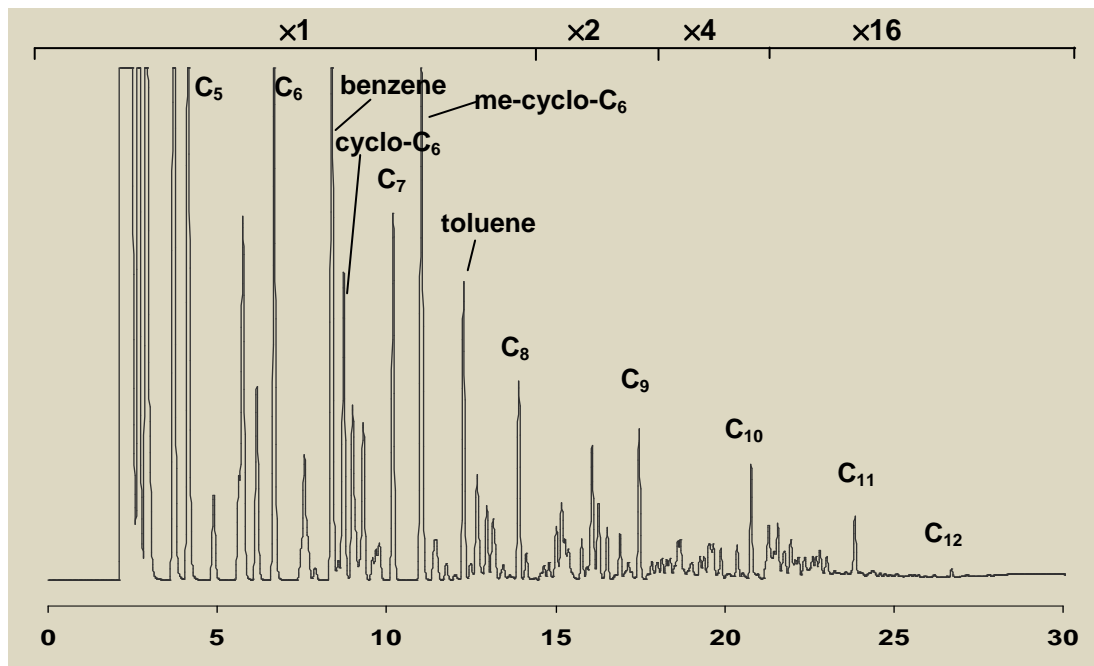


Figure 2 - Chromatogram showing detail of C₆₊ components

3 MEASUREMENT OF C₆₊ PEAK

3.1 Timing of backflush.

As seen in figure 1, the C₆₊ backflushed peak appears at the beginning of the analysis. This accelerated backflush is achieved by using a short pre-column. At the start of the cycle, this column (column 1) is placed in series with a longer column (column 2) designed to measure C₃ to C₅ hydrocarbons. After a defined time, when all the n-C₅ is deemed to have passed onto column 2, and before any C₆ component has done so, column 1 is switched to immediately before the detector, and at the same time the carrier flow through it is reversed. This change in the direction of flow recombines the components which are still in column 1.

The lighter C₆ isomers, which have travelled the greater distance within column 1, now travel faster in reverse flow and catch up with the heavier components to emerge as a single peak. Figure 3 shows the forward flow configuration and figure 4 shows that for the backflush operation.

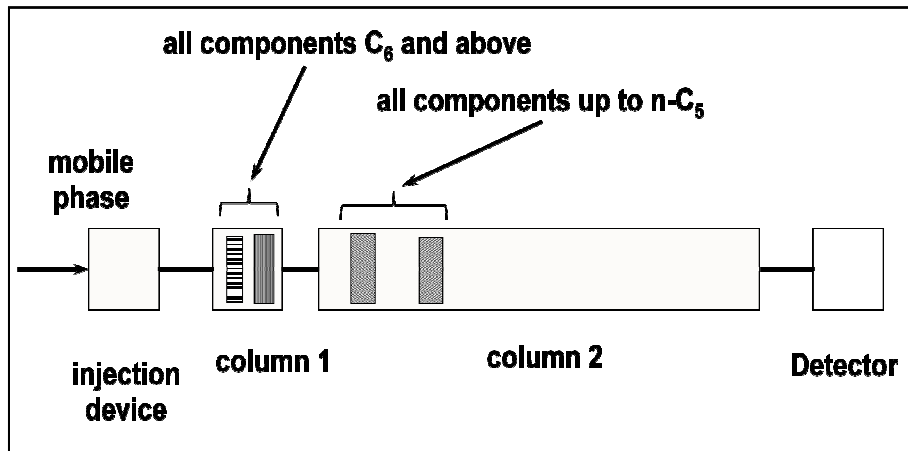


Figure 3 - Forward flow

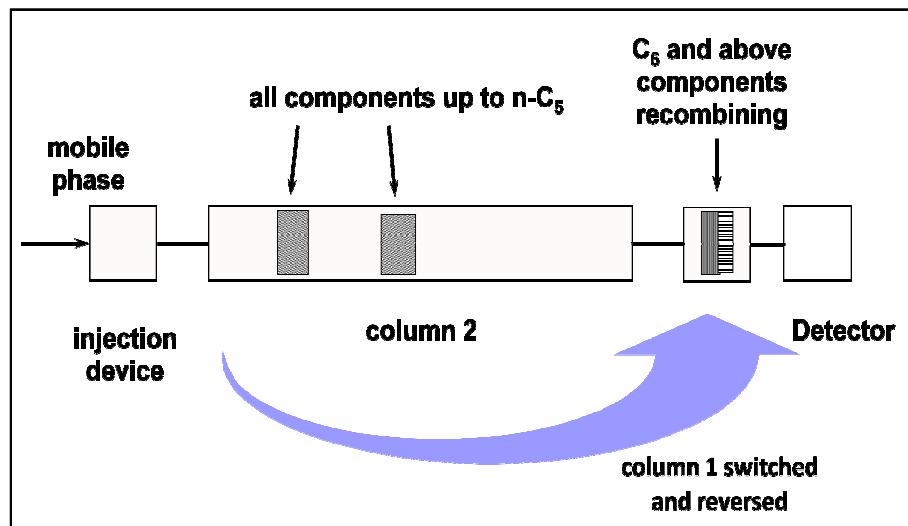


Figure 4 - Backflush of C₆+

The timing of the backflush, which is found by trial and error, is required to ensure that all the n-C₅ has passed the junction to column 2, while none of the lightest C₆ isomer (2,2-di-methyl butane) has yet reached it. If the timing is not correct, then either some n-C₅ will be included in the backflushed peak, or C₆ components will pass onto the longer column, where, since they are not expected, they will not be measured.

Figure 5 shows the effect of different backflush times on the measured amounts of n-C₅ and C₆+, using a calibration mixture in which n-C₆ represents the C₆+ components. The use of n-C₆ in this way is common in such calibration gases. As the backflush time is increased, the amount of n-C₅ stabilises from about 16.5 seconds, and the C₆+ remains at a steady value until about 18.5 seconds. This seems a reasonable time window, and a backflush time of 17.5 seconds would be a good choice. When the same test was repeated with a natural gas sample, the results are shown in figure 6. The behaviour of n-C₅ is unchanged, but the C₆+ measurement starts to diminish from 17 seconds. This is due to the presence of lighter C₆ isomers which travel through column 1 more rapidly than n-C₆.

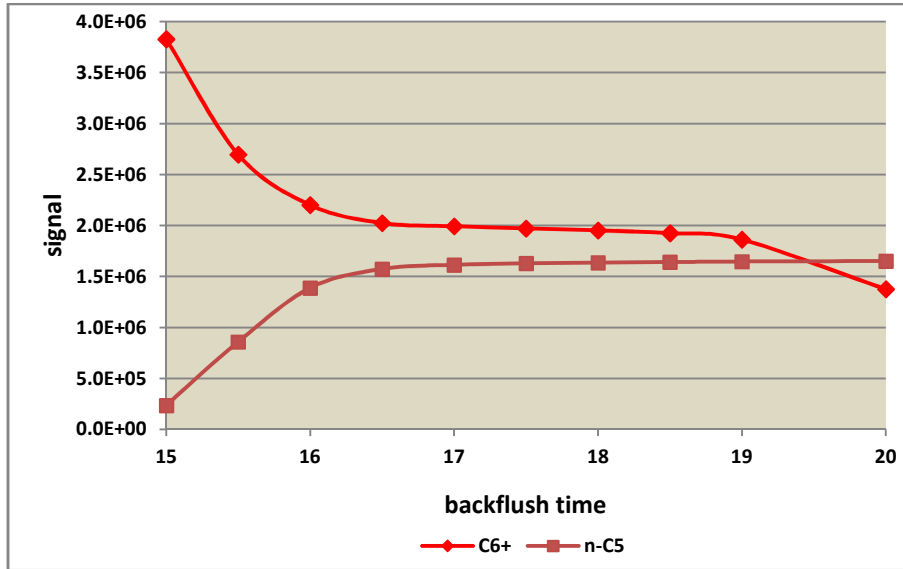


Figure 5 - Backflush timing with calibration gas

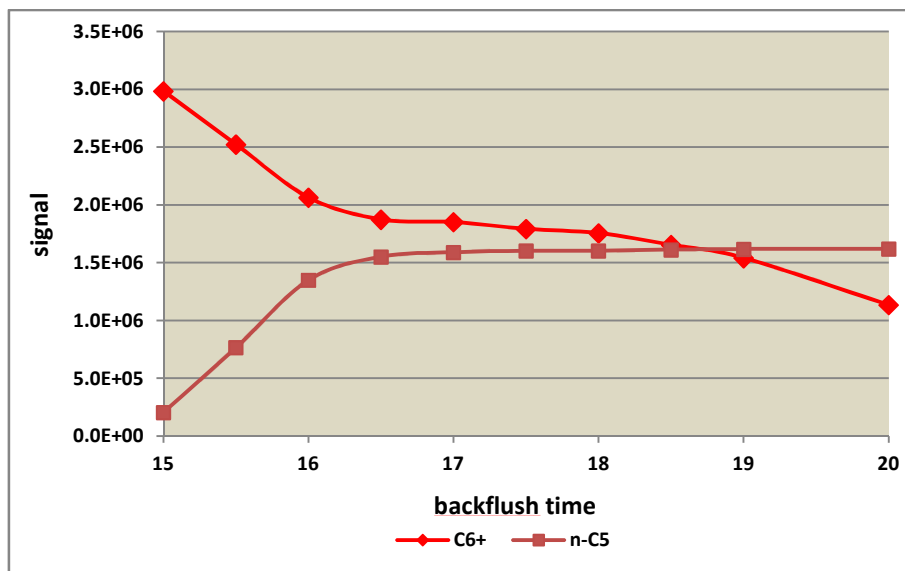


Figure 6 - Backflush timing with natural gas

Generally, if a small part of a component peak is lost due to column switching, it does not matter because the same will apply to both calibration gas and sample. If 97% (say) of a component in the sample is compared with 97% of the same component in the calibration gas, the quantitative measurement is unaffected. In this case, however, the C₆+ component in a sample is more likely to lose a fraction of the total than n-C₆ in the calibration gas. It is recommended that setting of the backflush time should be undertaken with a natural gas sample rather than with a calibration gas.

3.2 C₆+ peak position.

Another aspect of C₆+ measurement concerns the position of the peak relative to baseline disturbances. All valve switching operations, such as sample injection and backflushing, cause temporary flow upsets. The thermal conductivity detector (TCD) is sensitive to flow changes as well as to composition changes and we want to take advantage of the latter while

minimising the former. Figure 7 shows a C_6+ peak immediately following a baseline disturbance caused by the backflush operation. Among the important criteria for correct peak measurement are identification of the baseline signal at the start and finish of the peak, and projection of the baseline between these points. In figure 7 the exact location of the baseline before the peak start is difficult to define, and this necessarily adversely influences the peak measurement.

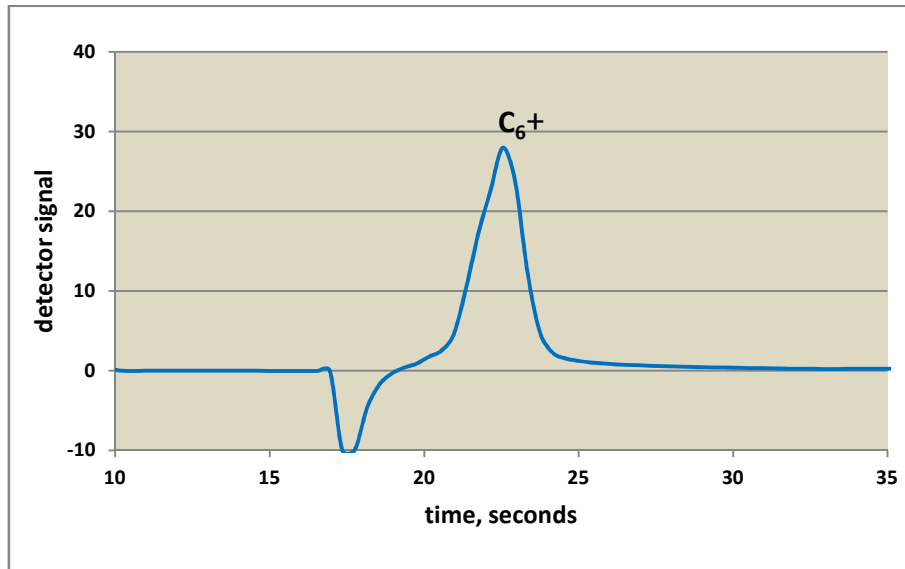


Figure 7 - C_6+ peak following baseline disturbance

A relatively simple plumbing modification allows baseline disturbances to be reduced. A C_6+ peak from an analyser which has been modified is shown in figure 8. This peak can be measured with much less uncertainty, since the baseline both before and after the peak is easily defined.

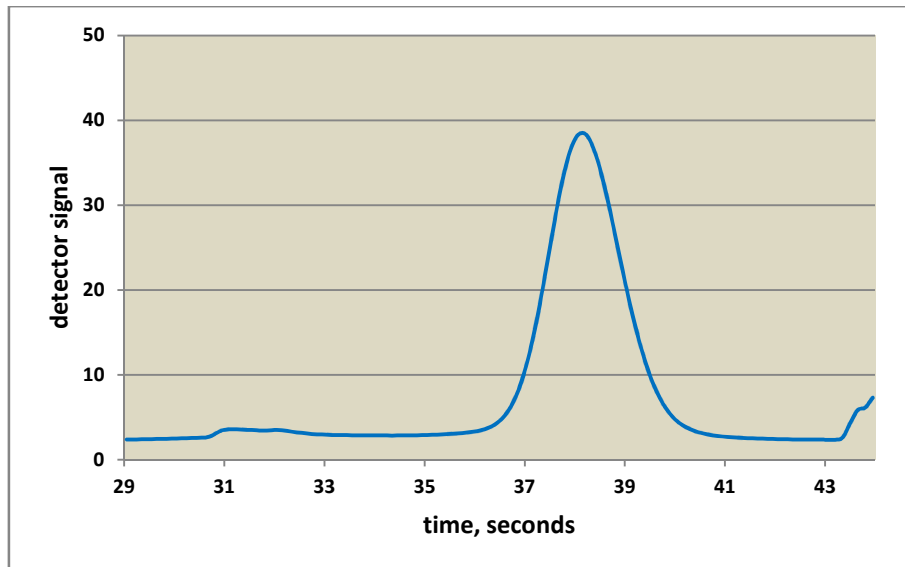


Figure 8 - C_6+ peak with improved baseline

3.3 C₆+ peak shape.

Figure 8 shows a peak from a calibration gas, containing n-C₆ only. The peak is symmetrical about its centre, and integration (peak measurement) can be allowed between 35 and 41 seconds.

C₆+ peaks from the calibration gas in figure 8 and from four different natural gases are superimposed in figure 9. The two larger peaks (gases 3 and 4) show leading edge asymmetry such that the start point for measurement should be earlier than 35 seconds. Gases 1 and 2, which have smaller overall peaks than the calibration gas, show even more marked asymmetry. All of the peaks show similar behaviour at the tailing edge, and the baseline in all cases is re-established by 41 seconds.

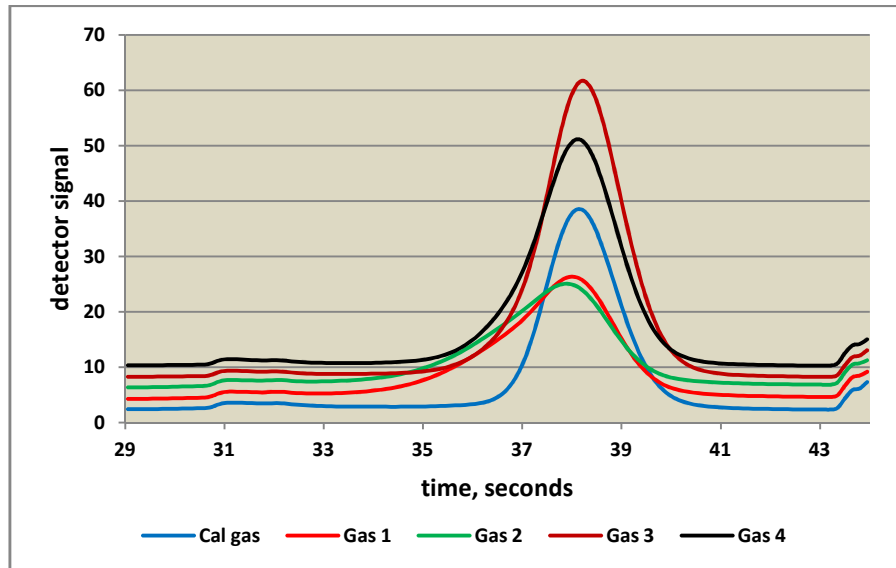


Figure 9 - C₆+ peaks from different gases

This behaviour results from the compressibility of the carrier gas. As the pressure falls from the beginning to the end of the column, the carrier gas velocity increases. Since velocity controls the rate at which components pass through the column, the effect is that components accelerate as they travel. When the column is backflushed, the pressure regime and hence the acceleration is reversed. This means that heavier components, which have travelled only a short distance in forward flow, are more rapidly eluted in backflush than lighter components, causing the leading edge asymmetry. The greater the proportion of heavier to lighter hydrocarbons, the greater is the asymmetry.

Figure 10 repeats the calibration gas peak from figure 8 and one of the more asymmetric peaks from figure 9. If the integration is enabled at 35 seconds, which would be appropriate for the calibration gas, then a considerable error would be found for the sample. The broken lines show how the baseline for each peak would be allocated. For the sample gas, integration relative to this line would ignore the triangular area beneath it and the area before 35 seconds. An integration start time of 32 seconds is much more appropriate when measuring real gases.

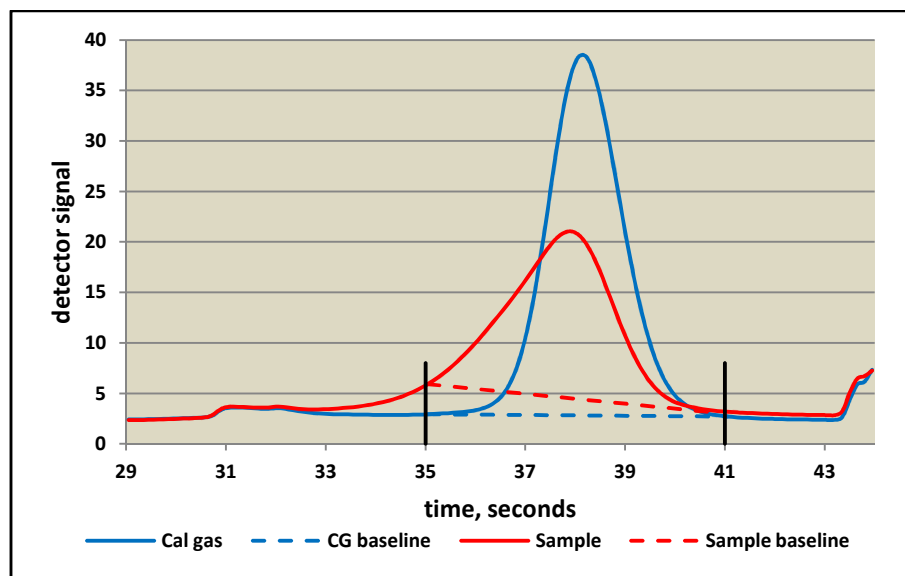


Figure 10 - Comparison of calibration gas and natural gas peaks

4 CONVERSION OF RAW PEAK DATA TO MOLAR QUANTITY

The TCD, which is used without exception in natural gas process GCs, responds to the difference between the thermal conductivity of the continuously flowing carrier gas (usually helium) and that of the individual components which reach the detector at different times during the analytical cycle. The response factor (RF) for any component is a function of the difference between the value for helium and that for the component, and is determined by calibration with a gas mixture of known composition. RFs for hydrocarbons are not uniform, and generally increase with carbon number, which means that the factor for a C₆₊ peak will vary according to its composition. It is not practicable to tailor the calibration mixture to each possible variation in the C₆₊ composition, and such mixtures generally contain a single component (n-hexane or an isomer). This will introduce a bias in the measured quantity of C₆₊ since the composite peak from the sample gas is unlikely to have the same RF as the single component peak in the calibration mixture.

Data are available for TCD RFs [4], [5], [6], but these are all old and were mainly obtained using liquid mixtures, and are regarded as having relatively high uncertainties. We preferred to use gas mixtures, which would enable values to be established from propane upwards, giving a clearer picture of the overall trend, rather than only using C₆ and higher components. Also, experience suggests that data obtained from liquid mixtures may not apply unequivocally to gas samples. Reference materials containing hydrocarbons up to C₁₀ are now available through the U.K. National Physical Laboratory (NPL) and these were used to certify our own mixtures for evaluation of RFs.

These measurements were made using a new process GC. This uses micro-GC modules packaged for process application. Two modules were used for the analysis, one covering light gases (nitrogen, carbon dioxide, methane and ethane) and the other dealing with hydrocarbons. Neither module uses column switching or backflushing, and so is appropriate for our needs. Conditions for the second module were adjusted to allow measurement to C₉. RFs were measured as the ratio of response to molar percentage of each component, and expressed relative to the RF for propane. These relative response factors (RRFs) are shown in figure 11 and table 1.

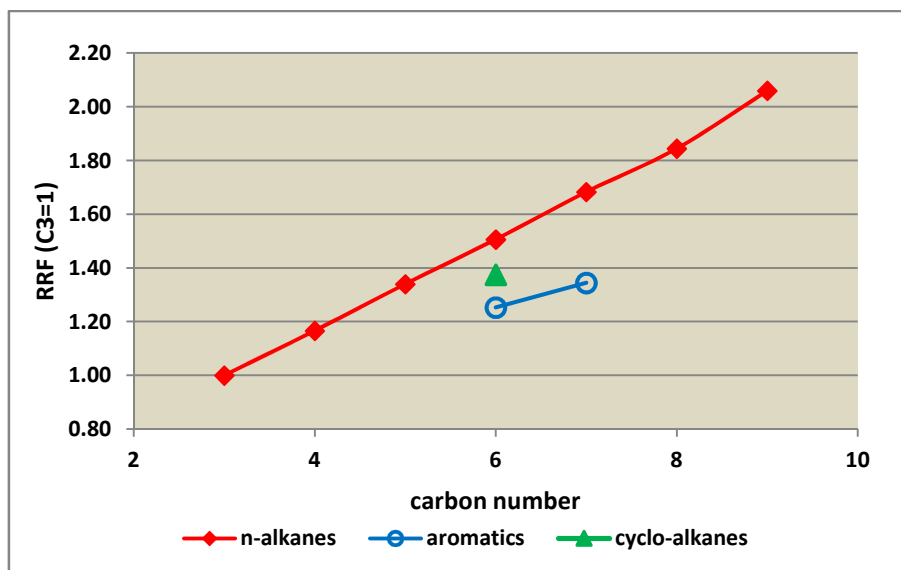


Figure 11 - RRF data for hydrocarbons to C₉

The alkane RRFs show good linearity, with some deviation around C₈ and C₉. This is not surprising since these components, measured individually, are near the TCD limit of detection. Aromatics (benzene and toluene) have substantially lower RRFs with respect to their carbon number, and cyclohexane has a value which is intermediate. In fact, these RRFs for carbon number 6 and above show reasonable agreement with the compilation of Dietz [6].

Table 1 - Response factors relative to propane

component	relative response factor
propane	1.000
n-butane	1.166
n-pentane	1.340
n-hexane	1.506
benzene	1.253
cyclohexane	1.375
n-heptane	1.683
toluene	1.345
n-octane	1.845
n-nonane	2.060

These variations in RFs show that the RF of a C₆+ peak depends entirely on its composition, and the only way to ensure correct quantitative interpretation is to simulate the expected C₆+ composition in the calibration gas. This is impractical, as this particular calibration gas would be useful for only one type of sample gas and would no longer be suitable if the sample composition changed.

From table 1 it is clear that the presence of C₇ and higher alkanes will increase the RRF of C₆+ and cause the calculated quantity to be overestimated. However, the presence of aromatics and, to a smaller extent, cycloparaffins will reduce the RF and lead to an underestimate of quantity. Several UK natural gases have relatively high aromatics content, and this can neutralise the effect of higher alkanes. Table 2 shows the effective molar carbon number for a number of gases, calculated from detailed composition. The relative errors shown in table 2 arise from calculation of the C₆+ response using a calibration gas containing only n-C₆.

Table 2 - Effective molar carbon number of C₆₊

natural gas #	molar C number	relative error %
1	6.12	2.05
2	5.81	-3.14
3	6.07	1.21
4	6.22	3.68
5	5.98	-0.37
6	5.99	-0.13
7	6.34	5.60

Table 2 shows that the actual carbon numbers of C₆₊ are distributed around 6, and so the errors involved in using the RF for n-C₆ are relatively small. The only one greater than 5% is gas 7, where the C₆₊ content is 0.0027% or 27 parts per million. The actual error in this case is insignificantly small.

5 APPLICATION OF APPROPRIATE PHYSICAL PROPERTIES

CV is the property most frequently calculated from composition. The same problem arises as with mol % calculations of C₆₊. Without knowledge of the detailed composition of this fraction, an exact CV contribution cannot be derived. Component CVs increase with carbon number, and we know that values for aromatics are significantly lower than their carbon number would suggest, and values for cycloalkanes are slightly lower. Figure 12 shows the plot of component CV against carbon number.

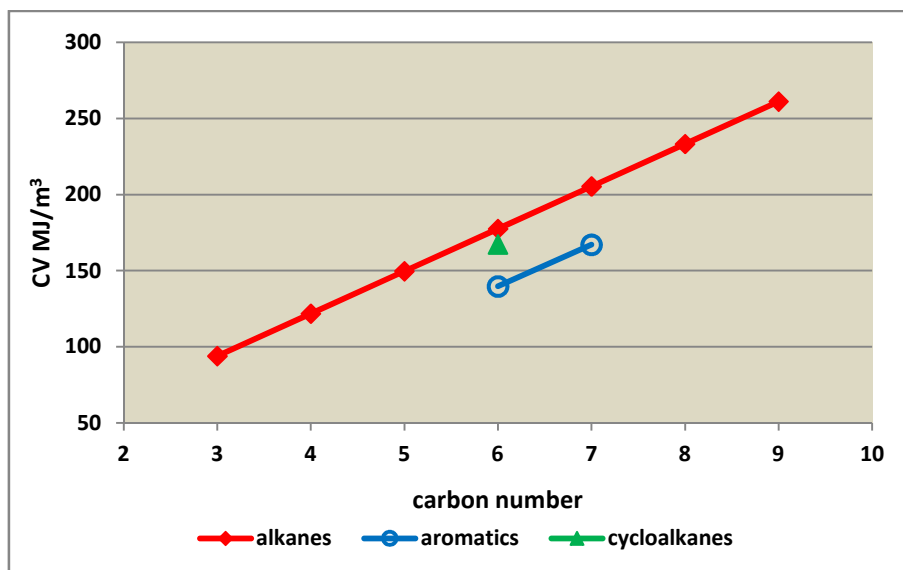


Figure 12 - CVs of hydrocarbons

The plot in figure 12 is comparable to that in figure 11, which suggests a correlation between relative response and CV. This is further illustrated by plotting these parameters against each other, as shown in figure 13.

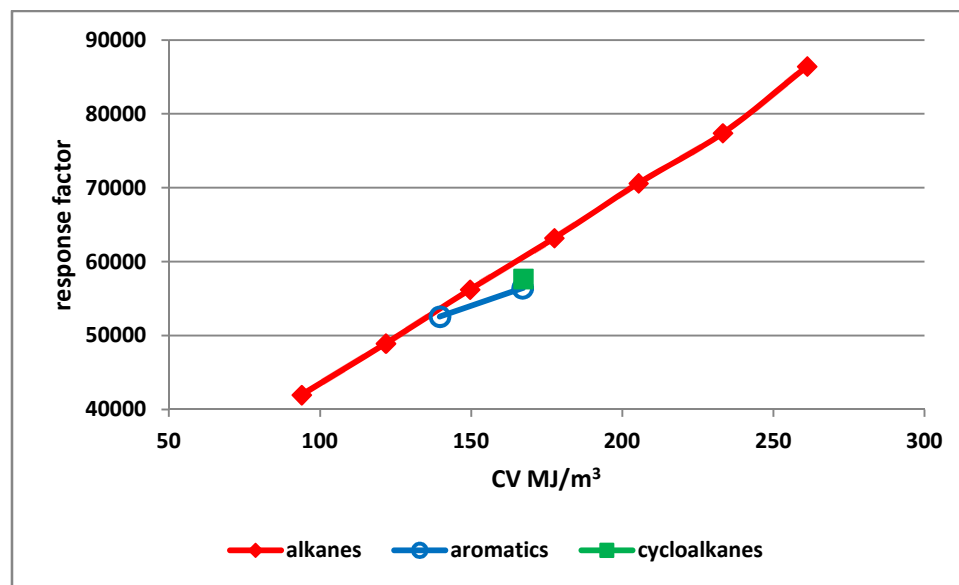


Figure 13 - Response factor against CV

The ratio of response factor to CV is calculated for each of five reference gases and shown in table 3, where the reference component is n-hexane, which is the most likely component of choice in a calibration gas. Regression analysis of the average responses against CV gives the first-order equation

$$\text{Response} = 15598 + 265.3 * \text{CV}.$$

The intercept term means that the ratios are not completely uniform, as the values for propane and butane are high and those for octane and nonane are low. (This may in part reflect the difficulty of measuring nonane at levels around 10 parts per million.) Overall, however, the values are sufficiently close, particularly for hexanes and higher, to show that TCD responses and CVs are correlated.

Table 3 - Ratio of response factor to CV.

component	RF/CV relative to C ₆	
	average	standard deviation
propane	1.25	0.026
n-butane	1.13	0.023
n-pentane	1.06	0.016
n-hexane	1.00	
benzene	1.06	0.067
cyclohexane	0.97	0.009
n-heptane	0.97	0.014
toluene	0.95	0.048
n-octane	0.93	0.044
n-nonane	0.93	0.064

To test this hypothesis, test gases containing both n-hexane and n-heptane, designed for C₇₊ analysers, were measured on a C₆₊ analyser, which had been calibrated with a mixture containing only n-hexane. The results are summarised in table 4. The C₆₊ peaks from the test gases comprised varying known concentrations of the two components. This meant that the reported mol % of C₆₊ was higher in each case than the true value, the extent depending on the proportions of the two components. The CV contributions of C₆₊ were also higher than

that of n-hexane. If, therefore, the CV of n-hexane is applied to the measured C₆₊ component, this will produce a smaller than expected CV contribution. With a correlation between response factor and CV, these two effects should largely cancel each other. The overestimated quantity will be balanced by an underestimate of the CV to be applied.

Table 4 - Errors on C₆/C₇ test gases

Test gas	composition mol %		equivalent C ₆ + C No.	relative error %	
	n-C ₆	n-C ₇		mol %	CV
1	0.0505	0.0816	6.62	8.52	-0.92
2	0.3431	0.0058	6.02	1.25	0.41
3	0.2792	0.0205	6.07	1.91	0.50
4	0.1470	0.0486	6.25	2.80	-1.07
5	0.0053	0.0972	6.95	12.22	-1.93
6	0.2086	0.0350	6.14	3.56	1.21
7	0.0991	0.0629	6.39	9.63	1.69

Table 4 describes this simple test of the hypothesis. In the table, the C₆₊ carbon number represents the mean carbon number calculated from the relative amounts of C₆ and C₇. As expected, both types of error increase as the C₆₊ carbon number approaches 7, but in all cases the CV error is significantly smaller than the mol % error.

6 APPLICATION TO REAL NATURAL GASES

The complexity of the C₆₊ composition of real natural gases (see figure 2) makes the measurement more difficult for a number of reasons:

- The C₆₊ content of real gases varies by up to a factor of 50.
- The distribution of higher hydrocarbons varies substantially between gases from different sources.
- The shape of the C₆₊ peak and hence the ease of quantitative measurement depends on the (unknown) hydrocarbon distribution.
- Depending on the configuration of the analyser, baseline disturbances can interfere with peak measurement.
- The presence of aromatic, and to a lesser extent, of cycloalkane components means that the CV of the C₆₊ can be lower than that of hexane, due to the relatively low individual CVs of these components.

Three natural gases from different sources were sampled from the UK National Transmission System. They were analysed in detail using laboratory analysers against certified reference gases, and also on a process GC where the C₆₊ response is calibrated with a reference gas containing n-C₆. Table 5 gives the results. In the section headed 'detailed analysis' the values for mol % and CV of C₆₊ are the "true" values for the gases, summing the contributions of all components. The CV C No. is the equivalent "pseudo-alkane" which has the same CV as found from the detailed analysis. The section headed 'C₆₊ analysis' contains the values measured with a C₆₊ process GC, calibrated with n-C₆. Differences in both mol % and CV contribution are small by comparison with some of the values in table 3. This is the likely effect of the equivalent carbon numbers being close to 6.

Table 5 - Errors for real natural gases

Detailed analysis			
	Gas 1	Gas 2	Gas 3
C ₆₊ total mol %	0.0966	0.1048	0.1422
C ₆₊ CV contribution	0.1693	0.1918	0.2628
CV of C ₆₊ fraction	175.20	182.95	184.86
equivalent C No.	5.92	6.19	6.26
C ₆₊ analysis			
	Gas 1	Gas 2	Gas 3
C ₆₊ mol %	0.0963	0.1063	0.1458
difference	-0.35%	1.40%	2.56%
C ₆₊ CV contribution	0.1710	0.1887	0.2589
difference	0.99%	-1.60%	-1.50%

Some process GCs offer alternative factors for C₆₊, to allow different CVs to be applied, in cases where composition differences are significant. These are based on different ratios of C₆, C₇ and C₈, and the results are shown in table 6.

Table 6 - Errors for different C₆₊ compositions

C ₆₊ analysis			
C ₆ /C ₇ /C ₈ ratio	Gas 1	Gas 2	Gas 3
100/0/0 (n-C ₆)			
C ₆₊ CV contribution	0.1710	0.1887	0.2589
difference	0.99%	-1.60%	-1.50%
50/50/0			
C ₆₊ CV contribution	0.1844	0.2025	0.2792
difference	8.91%	6.13%	6.23%
58/28/14			
C ₆₊ CV contribution	0.1860	0.2053	0.2816
difference	9.86%	7.05%	7.16%
48/35/17			
C ₆₊ CV contribution	0.1895	0.2092	0.2869
difference	11.92%	9.06%	9.17%
50/25/25			
C ₆₊ CV contribution	0.1911	0.2110	0.2893
difference	12.87%	9.99%	10.10%

Table 6 shows that the use of alternative CV factors for C₆₊ is inappropriate, and the CV contribution of C₆₊ should be calculated using n-C₆ for calculation of the molar quantity and the CV of n-C₆ applied to the calculated amount. If, for any reason, the calibration gas contains more than one component to represent C₆₊, such as a mixture of C₆ and C₇, then the molar sum of these components should be used to calculate the quantity and the CV of the mixture applied to calculate the CV contribution.

7 CONCLUSIONS

- 7.1 TCD response factors for C₆ and heavier alkanes increase with carbon number and are correlated with component CVs. Aromatics and to a lesser extent cycloalkanes have smaller response factors for the same carbon number, but this is also correlated with CV. The use of hexane alone in calibration gases will cause errors in calculated C₆₊ mol %, but if the CV of hexane is applied to these measured C₆₊ components, the error in CV contribution will be smaller.

30th International North Sea Flow Measurement Workshop
23 – 26 October 2012

- 7.2 The use of any other composition in the calibration gas will also cause errors in the calculated mol %, except where the compositions in calibration gas and sample match exactly. If the CV of the calibration gas C₆₊ composition is applied to the measured sample peaks, the error CV contribution will be minimised.
- 7.3 If the C₆₊ CV contribution is calculated in a flow computer, based on detailed analysis, the error will be greater than if the CV of the calibration gas C₆₊, whether that is a single component (n-C₆) or a mixture, is used.
- 7.4 Any difficulty in C₆₊ measurements for real gases may not be recognised when an instrument is tested with gases containing only hexane.
- 7.5 Measurement (integration) parameters for a C₆₊ peak should be optimised with care, particularly if there are adjacent baseline disturbances.
- 7.6 The use of calibration gases containing a range of heavier hydrocarbons to simulate C₆₊ is likely to create problems with stability and dew point. A single C₆ component (hexane) is recommended.

8 REFERENCES

- [1] ISO 6974:2012, Natural gas – Determination of composition and associated uncertainty by gas chromatography.
- [2] Starling, K.E., Savidge, J.L., “Compressibility Factors for Natural Gas and Other Related Hydrocarbon Gases”, American Gas Association (AGA) Transmission Measurement Committee Report No. 8 (1985).
- [3] ISO 12213:1997, Natural gas – Calculation of compression factor.
- [4] Rosie, D. M., Grob, R. L., Anal. Chem., **29**, 1263, (1957).
- [5] Messner, A. E., Rosie, D. M., Argabright, P. A., Anal. Chem., **31**, 230, (1959).
- [6] Dietz, W. A., J. Gas Chromatography, 68, (February 1967).