



What do we mean by C_6+ ?

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What are we going to do about C₆+?

Three sequential questions arise:

1. Can we measure it?

- it may be a single recombined pseudo-component
- it may be a compilation of a large number of individual components

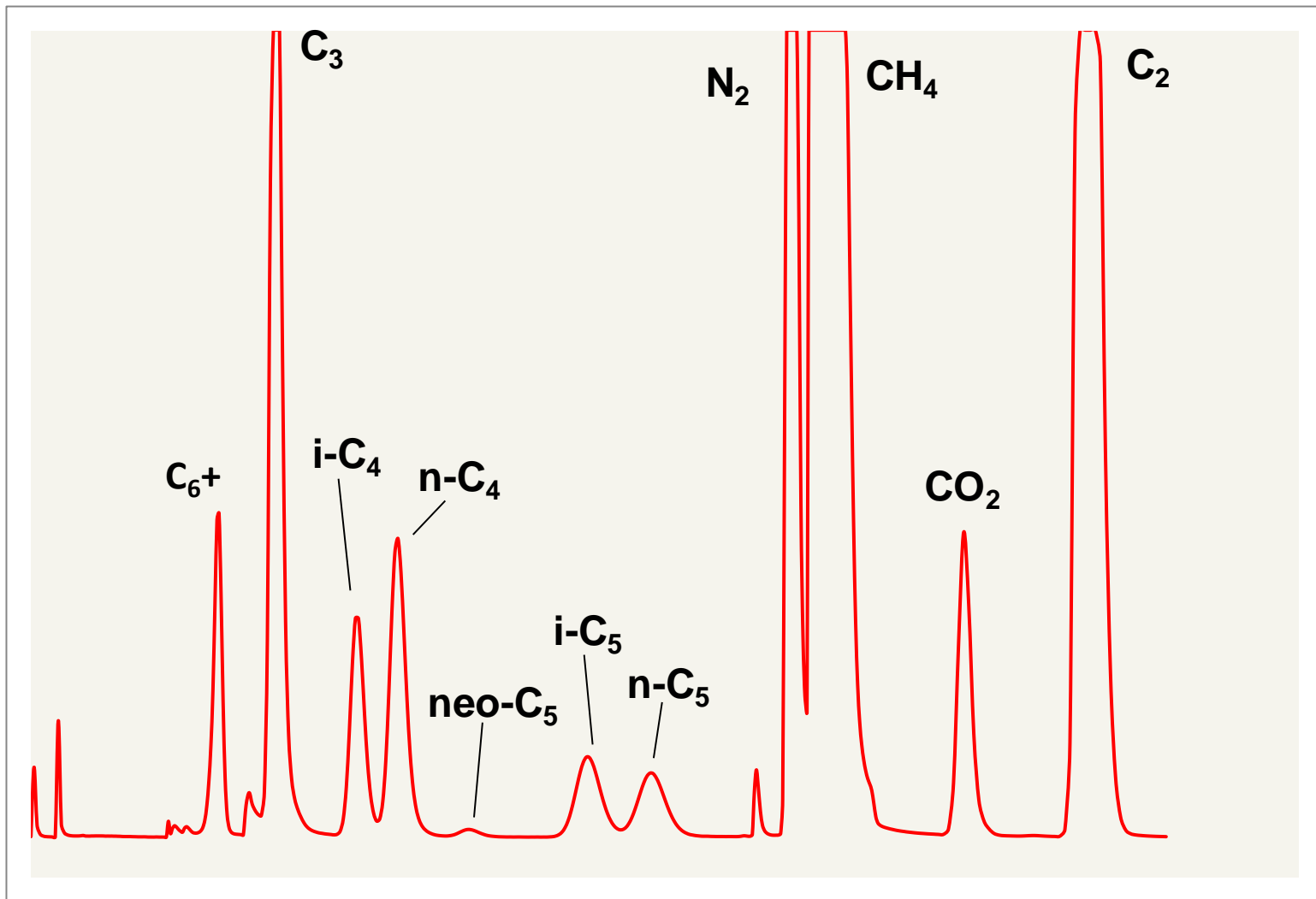
2. Can we quantify it?

- is a recombined peak sufficiently well resolved from baseline disturbances?
- what calibration gas or response factor should we use?

3. Can we allocate a property to it?

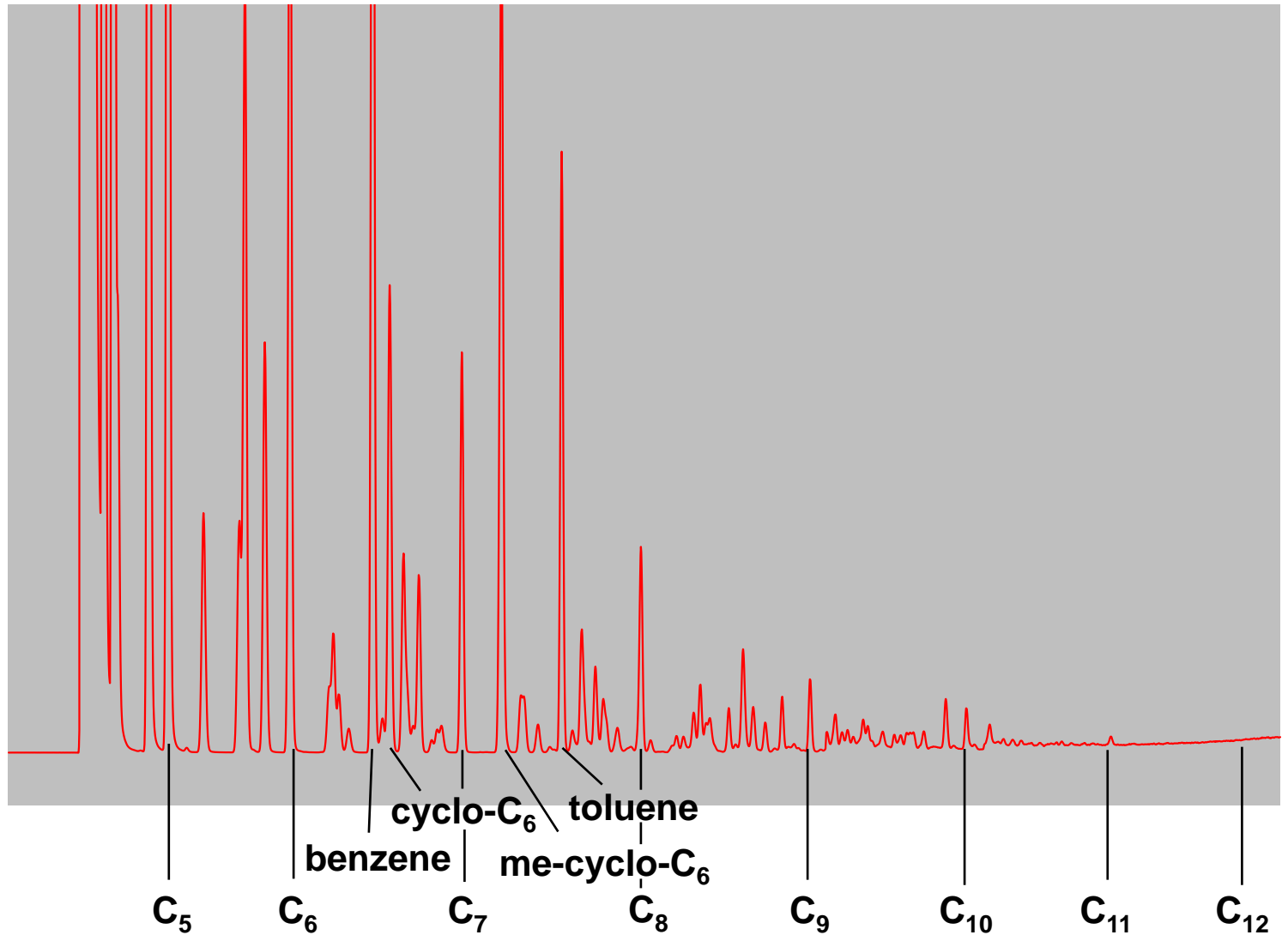
- without a quantitative or qualitative description, what is its calorific value?

Chromatogram including C₆+

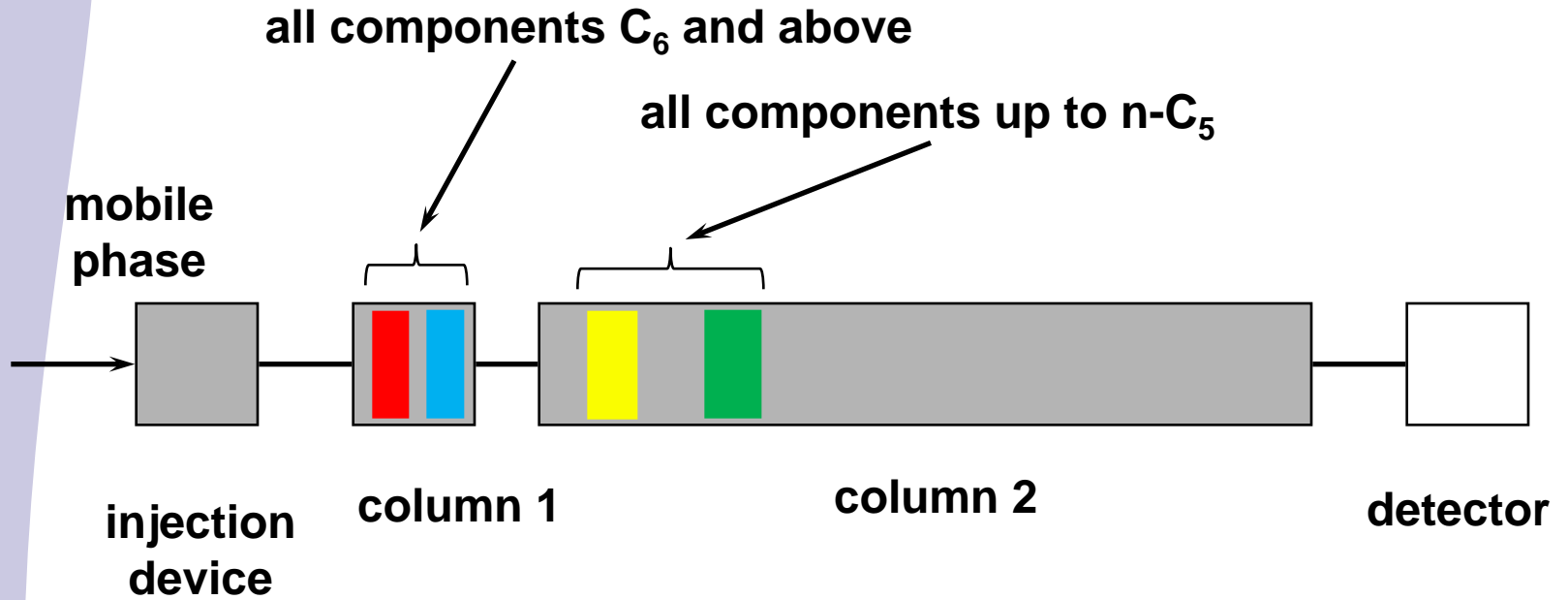




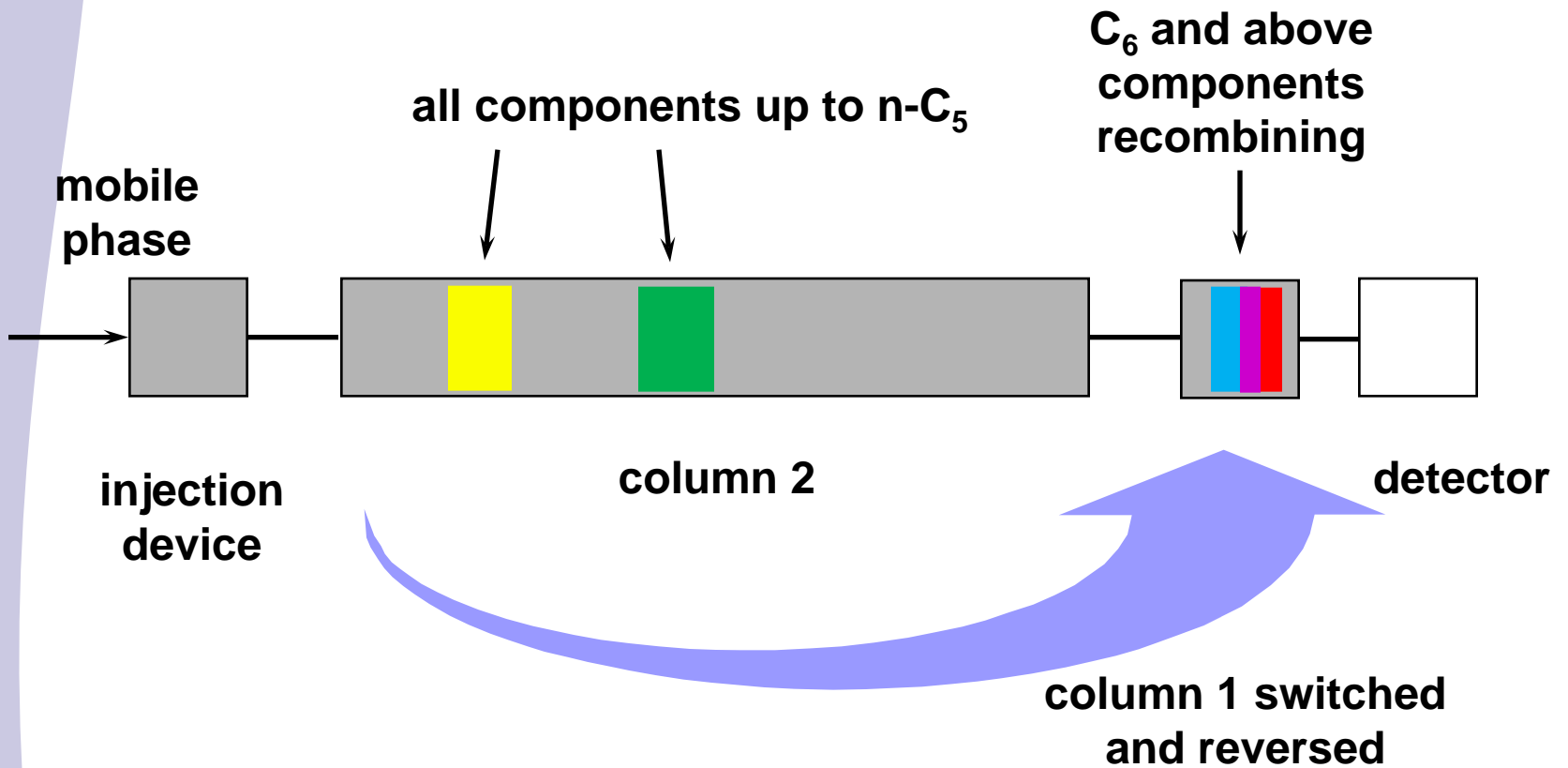
Detailed analysis of higher hydrocarbons



Backflushing – stage 1

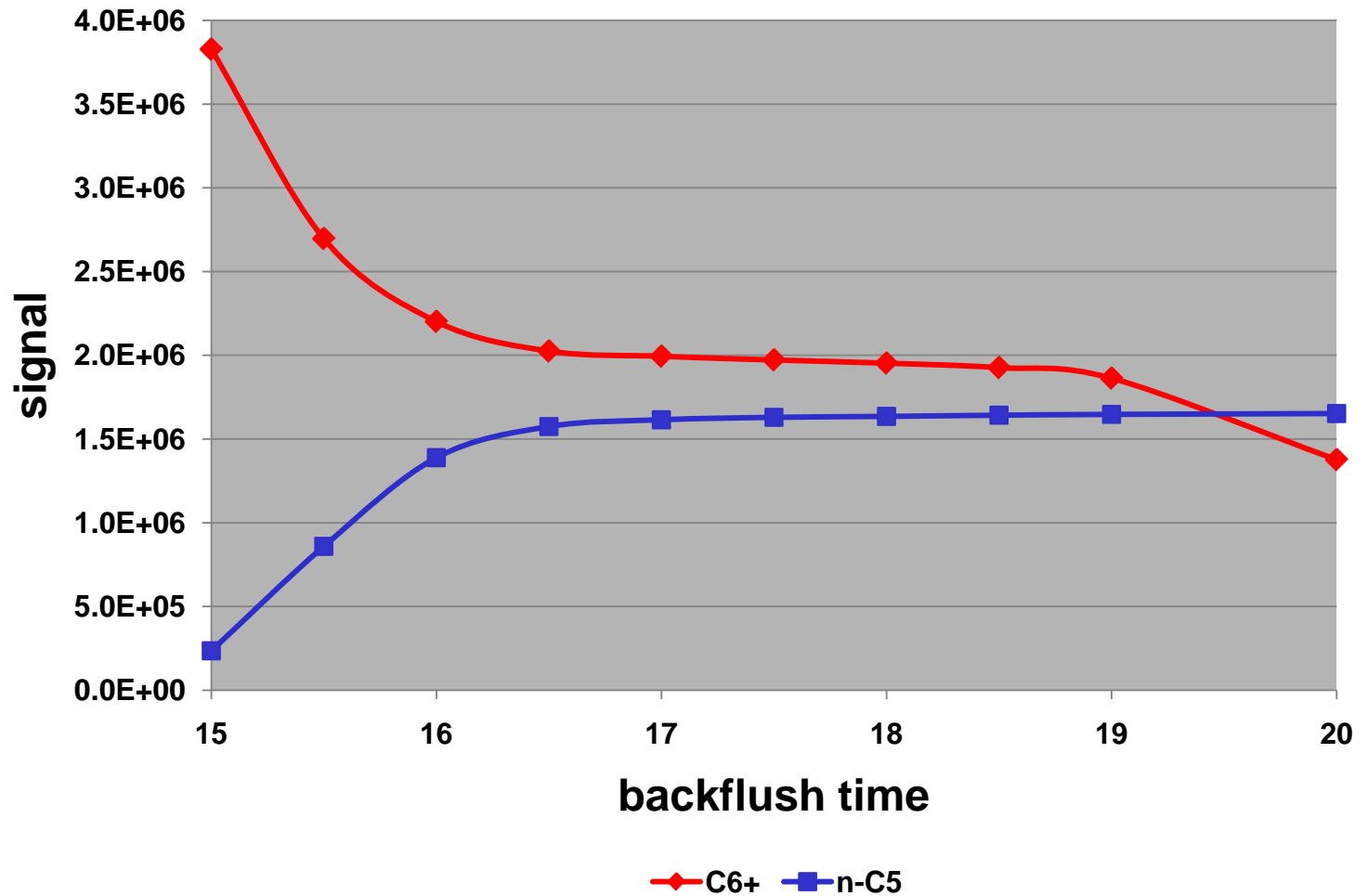


Backflushing – stage 2



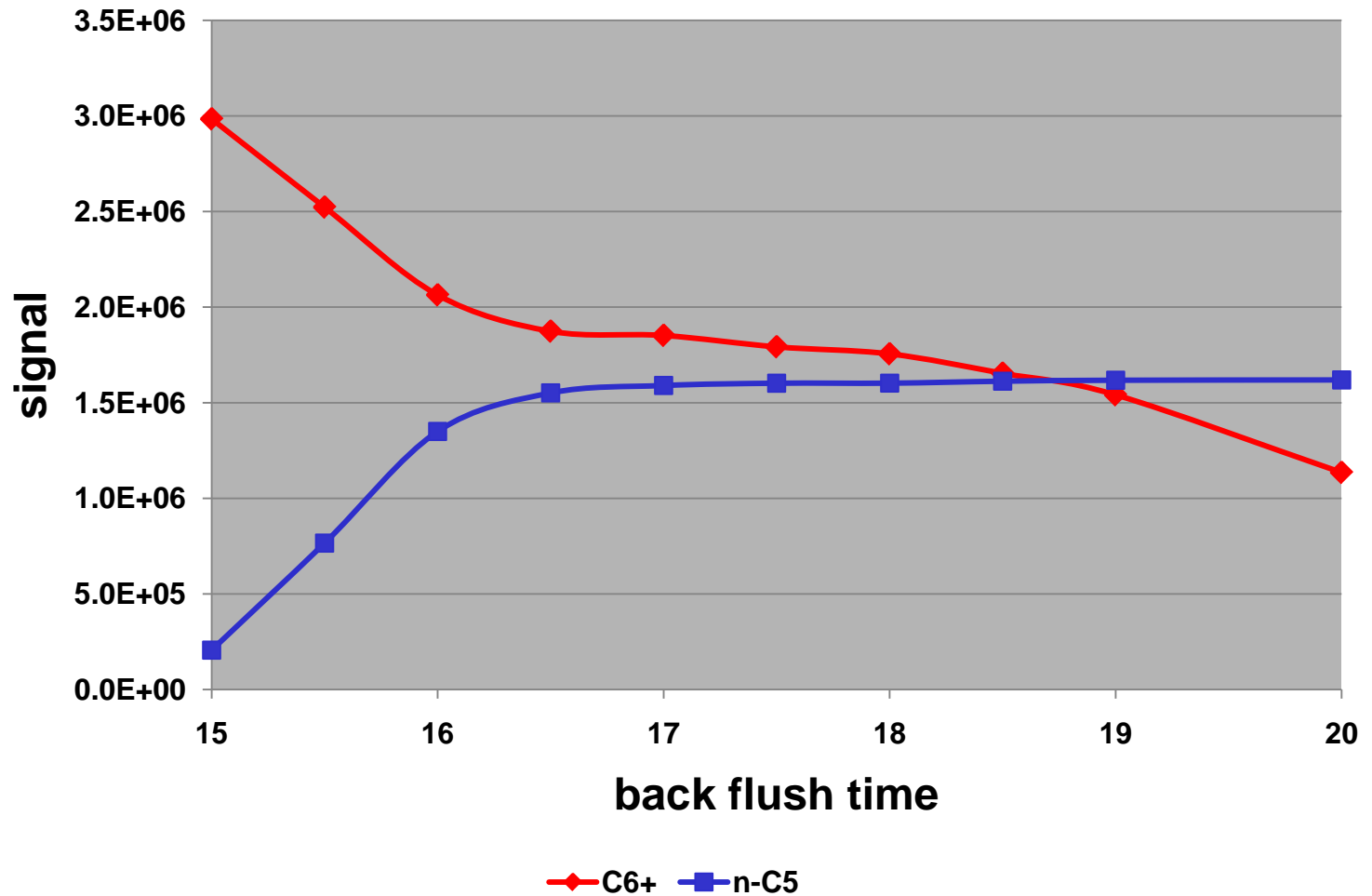


Timing of backflush with calibration gas



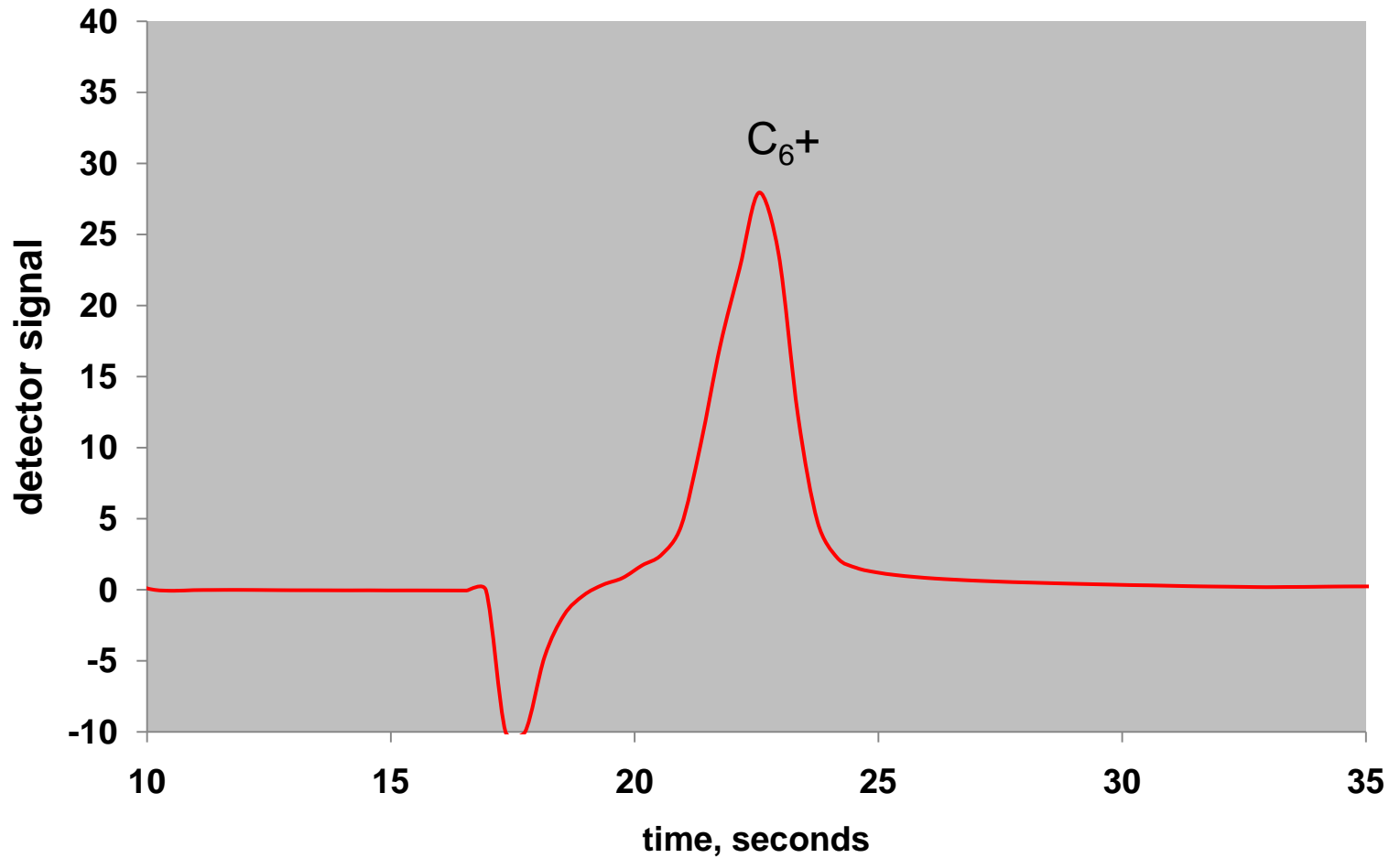


Timing of backflush with natural gas sample



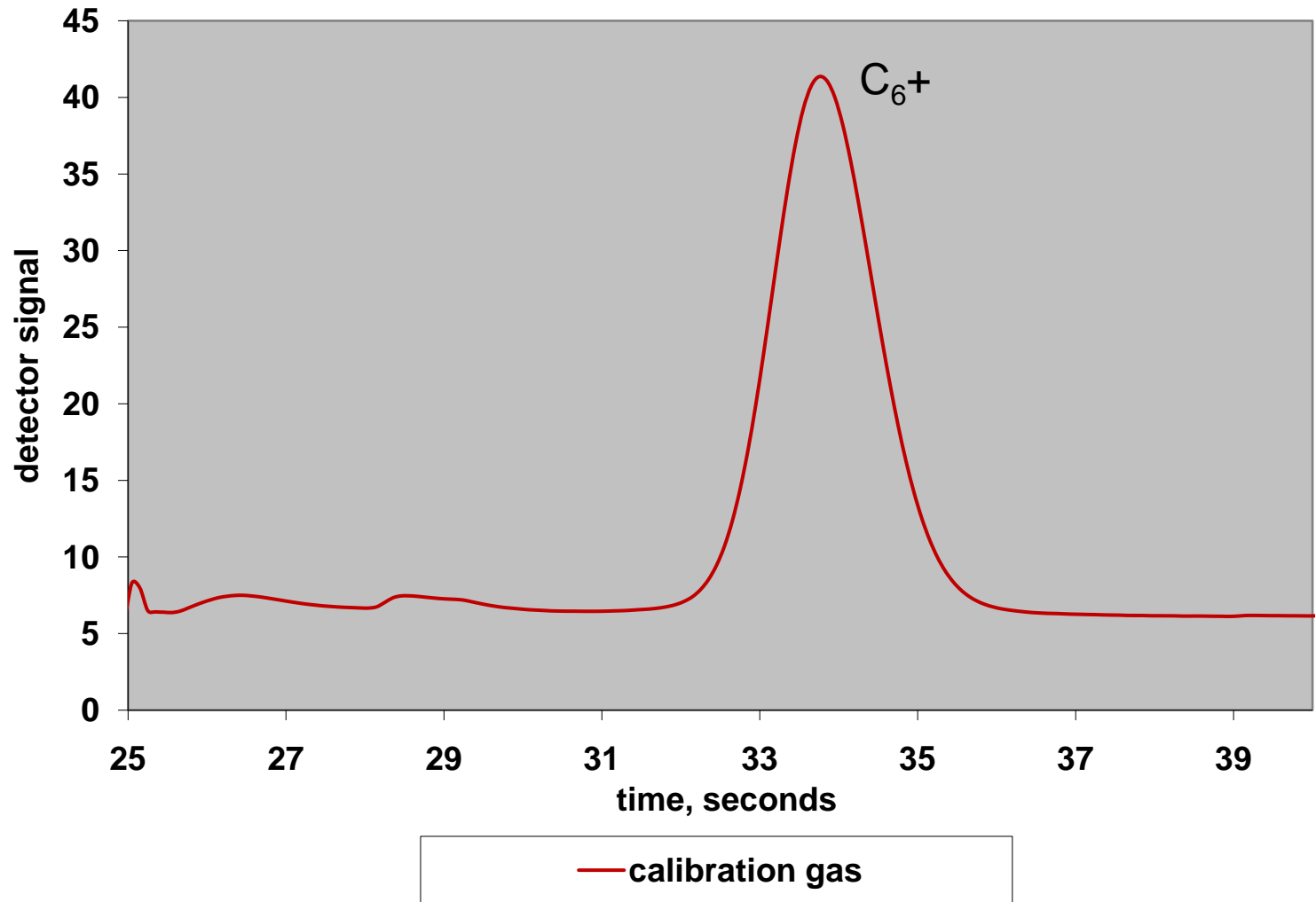


Backflushed peak immediately after baseline disturbance

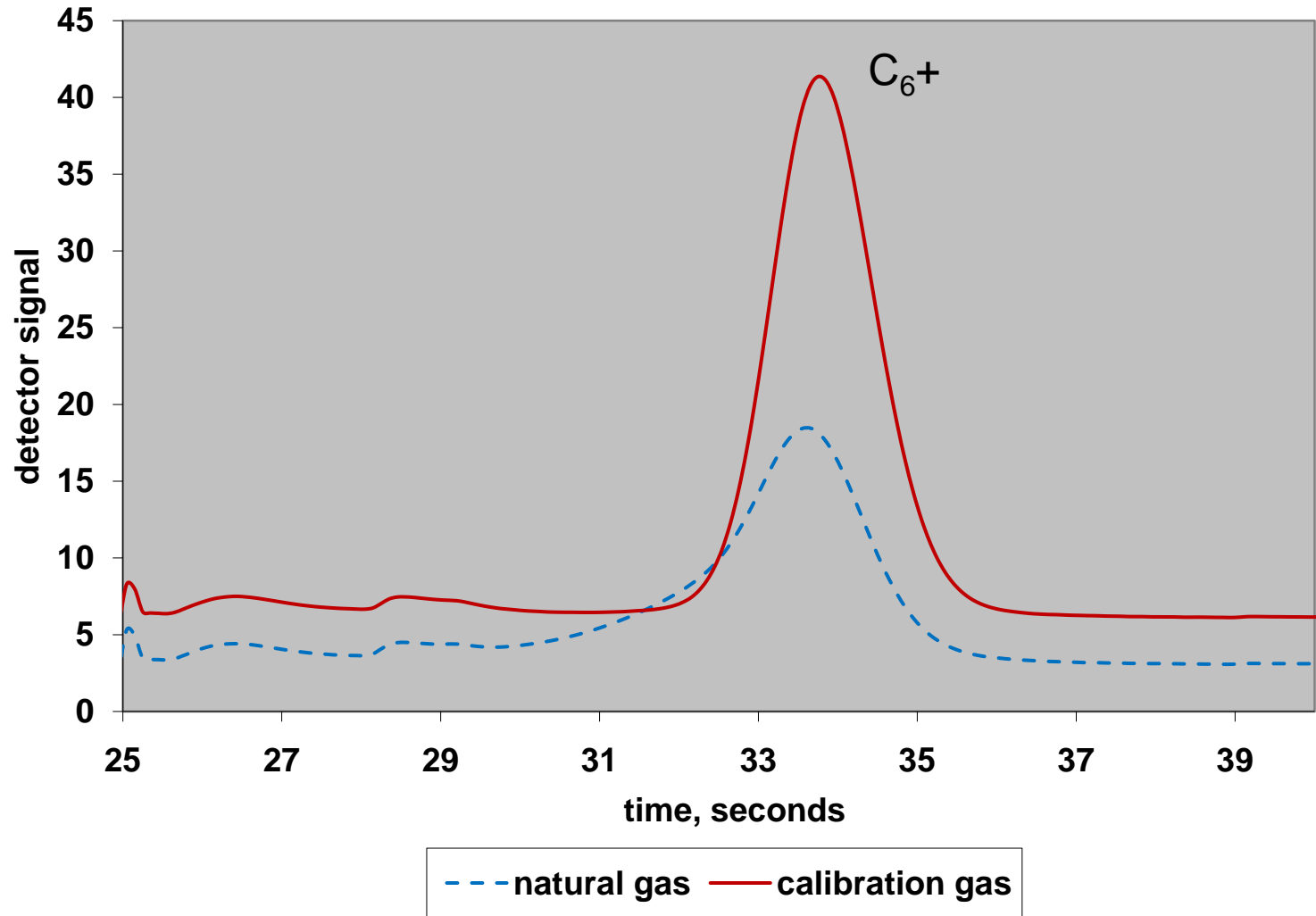




Steadier baseline due to instrument modification



Asymmetry of real natural gas peak





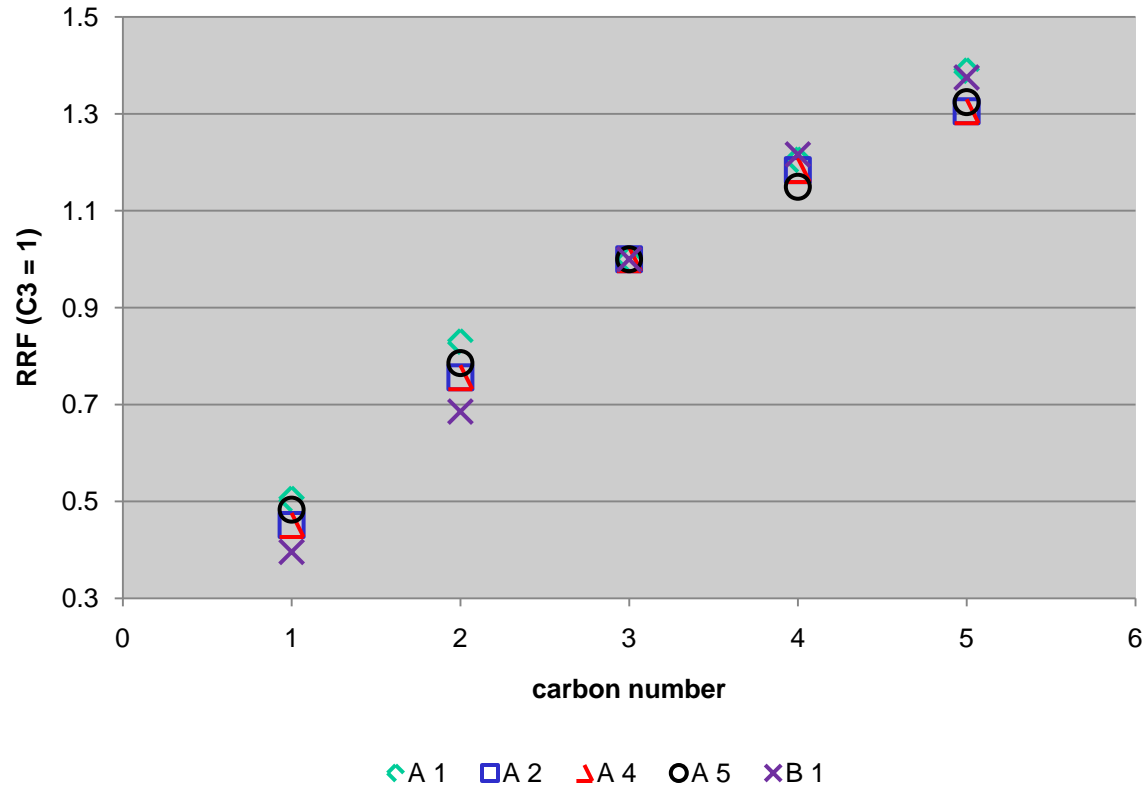
Can we measure C_6+ as backflushed peak?

Difficulties in measurement arise from:

- selection of back flush time depending upon the type of gas used (calibration gas or real sample)
- proximity of baseline disturbances to the measured peak
- asymmetry of back flushed peak which varies with the distribution of components in the C_6+ range

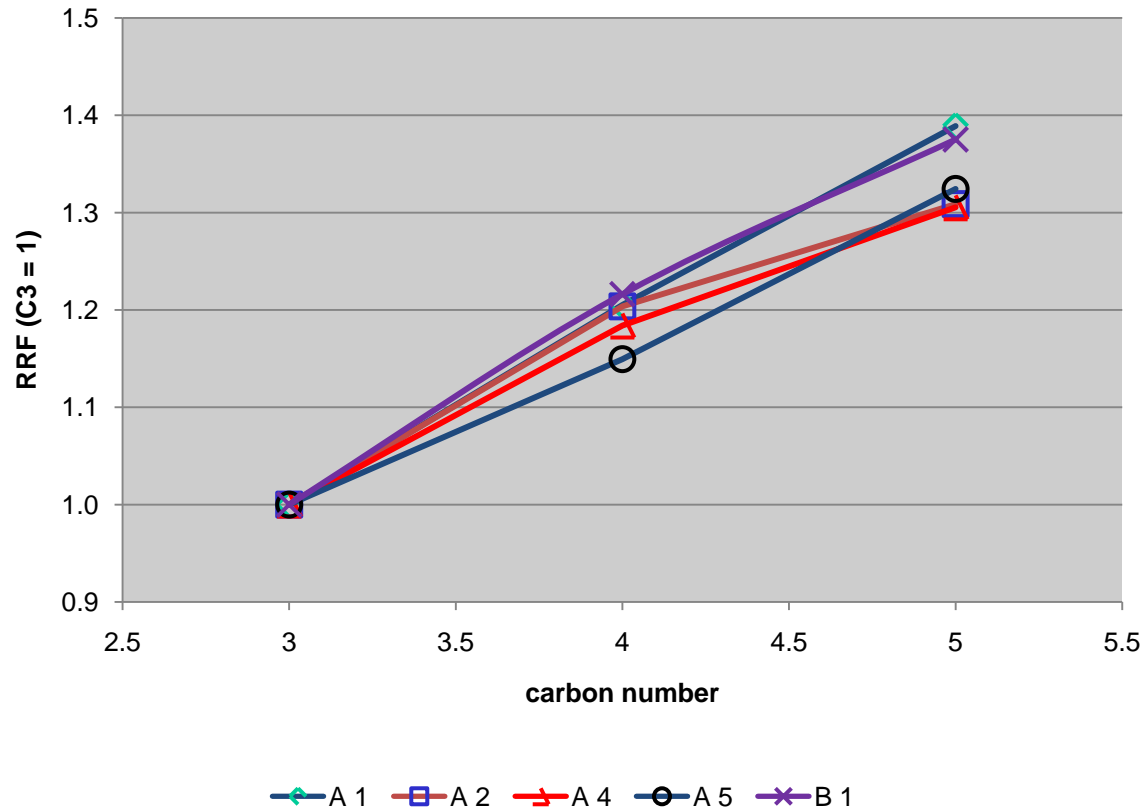


Molar relative response factors (RRFs) from 5 process GCs



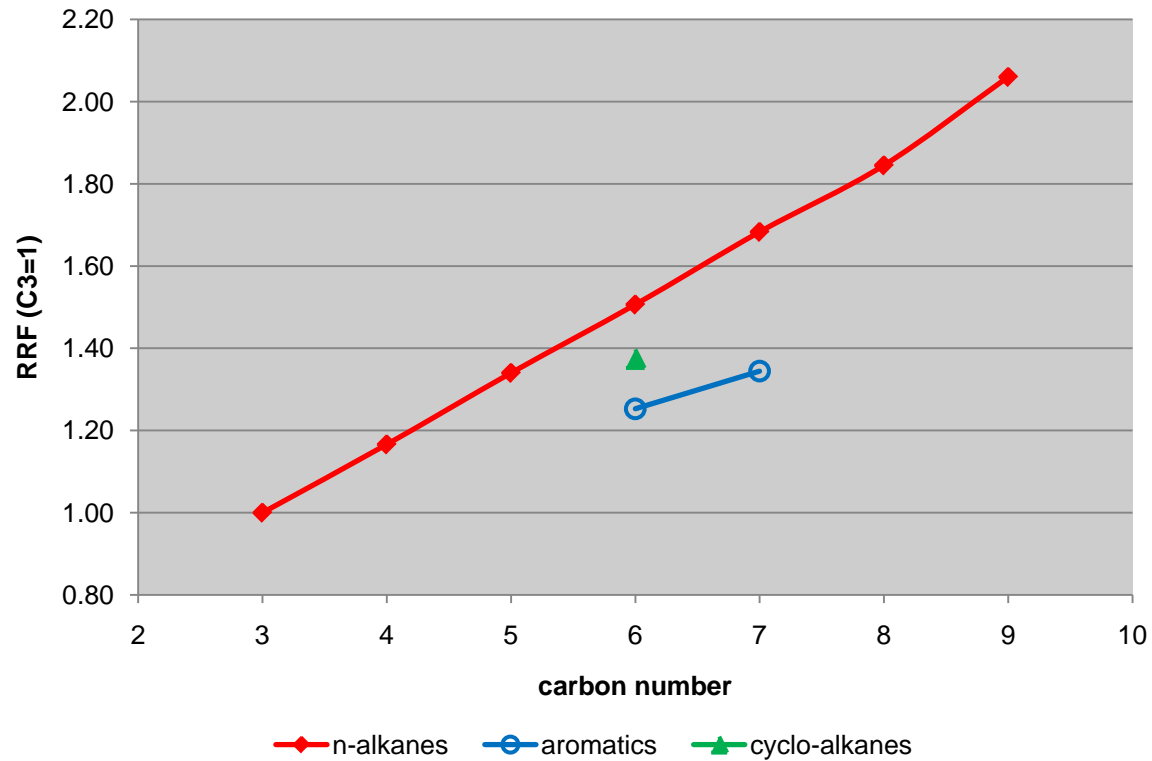


RRF variations in the C₃ to C₅ range



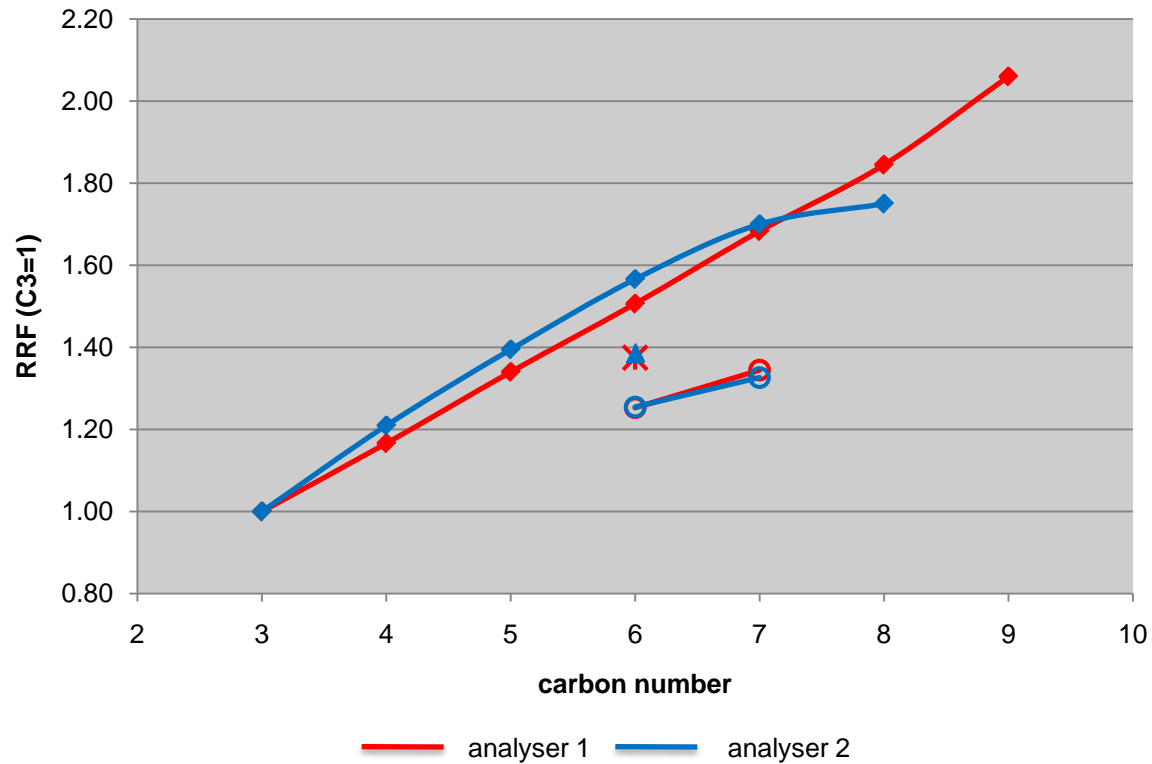


RRFs as a function of carbon number



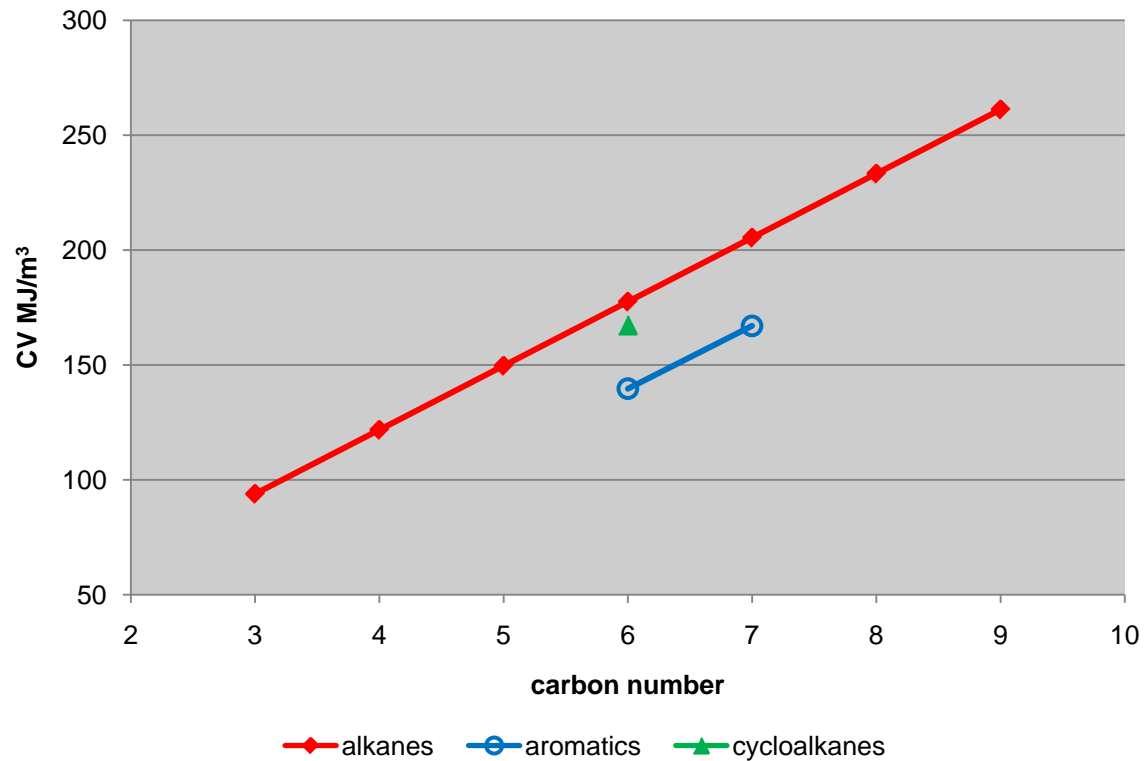


RRFs from different analysers

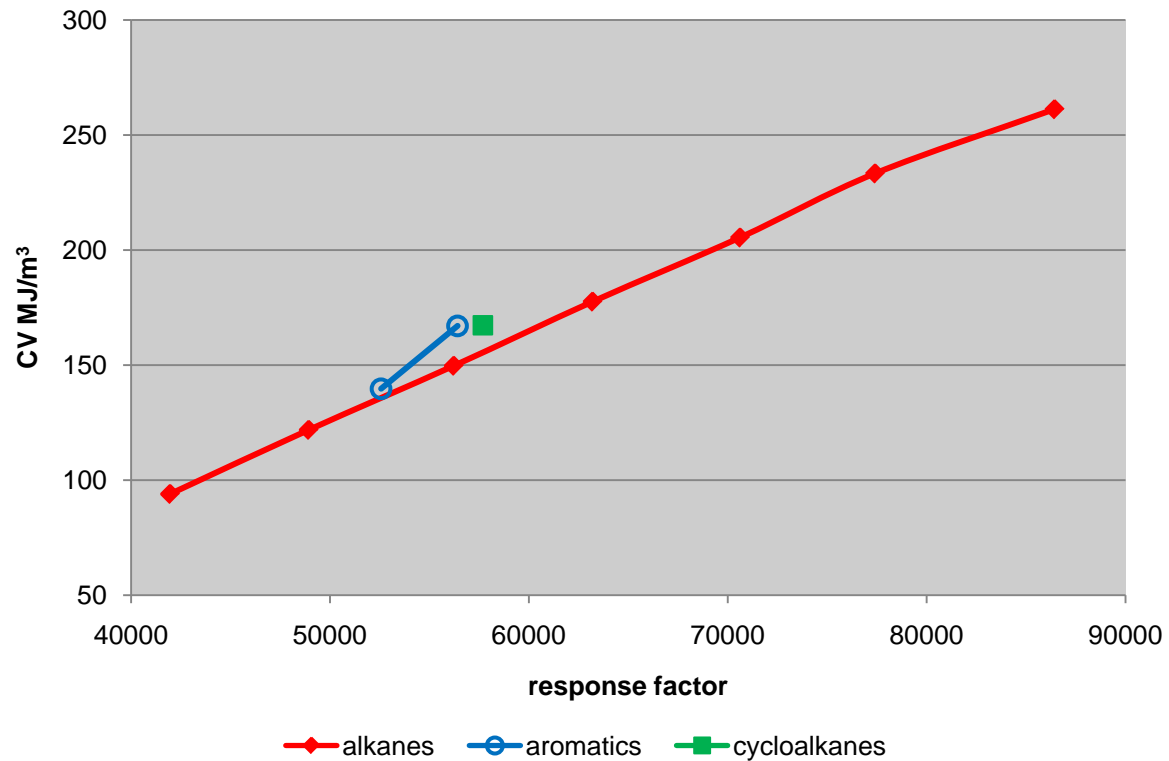




Calorific value (CV) as a function of carbon number



CV as a function of response factor





Variation in RF/CV ratio

- The RF/CV ratio, while not constant, varies over a small range from C₆ upwards.

	RF	CV	RF/CV	rel. to C ₆
propane	41960.7	93.94	446.7	1.25
n-butane	48930.8	121.79	401.8	1.13
n-pentane	56226.4	149.66	375.7	1.06
n-hexane	63205.3	177.55	356.0	1.00
n-heptane	70621.0	205.42	343.8	0.97
n-octane	77410.6	233.28	331.8	0.93
n-nonane	86435.8	261.19	330.9	0.93
benzene	52569.8	139.69	376.3	1.06
toluene	56417.3	167.05	337.7	0.95
cyclohexane	57686.4	167.31	344.8	0.97



Use of the RF/CV relationship

- A correlation can be seen between response factor (RF) and CV for C_6 and heavier hydrocarbons.
- Variations in the RF of C_6+ (due to composition differences) should be matched by equivalent variations in the C_6+ CV.
- Hence the use of a calibration gas containing hexane will over-estimate the molar quantity of C_6+ if it has a higher RF than that of hexane.
- Application of the CV of hexane to the over-estimated quantity of C_6+ will produce a more nearly correct CV contribution from the fraction.



Test on simple mixtures

- This is demonstrated by measurement of test gases containing both n-C₆ and n-C₇ in different ratios. The amount of C₆+ is calculated using a calibration gas containing n-C₆ only, and its CV contribution calculated by assigning the CV of n-C₆ to the calculated amount.

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



Data from simple mixtures

- The table shows that calibration with n-C₆ produces an error in composition which increases with the C₇/C₆ ratio in the C₆+ peak.
- In each case, calculation of the CV contribution by applying the CV of n-C₆ to the calculated amount of C₆+ gives relative errors in the property which are substantially smaller than those in the composition.
- This is obviously the simplest case. Measurements on real natural gases are complicated by a number of factors.



Application to real gases

- Among the complicating factors are:
 - the C_6+ 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 C_6+ 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
 - if a gas has a significant content of aromatics (and to a lesser extent cyclo-alkanes), their influence can lower the C_6+ CV to a greater extent than higher alkanes increase it, & the CV carbon number may be less than that of hexane



Errors on real gases

- Note that the CV carbon number (the alkane with the equivalent CV) is less than 6 for these 3 gases

		B 1		A 1		A 2		A 4		A 5	
Gas 1	detailed analysis	error % rel.	error absolute	error % rel.	error absolute	error % rel.	error absolute	error % rel.	error absolute	error % rel.	error absolute
C ₆ + mol %	0.0273	1.5	0.0004	-3.5	-0.0009	-1.0	-0.0003	31.3	0.0085	1.9	0.0005
C ₆ + CV MJ	0.0479	2.6	0.0012	-2.4	-0.0011	0.1	0.0000	32.7	0.0157	3.0	0.0015
CV C. No.	5.93										
Gas 2											
C ₆ + mol %	0.0919	-0.2	-0.0002	20.9	0.0192	1.1	0.0010	16.9	0.0155	6.8	0.0062
C ₆ + CV MJ	0.1572	3.6	0.0056	25.5	0.0401	4.9	0.0077	21.3	0.0335	10.8	0.0179
CV C. No.	5.77										
Gas 3											
C ₆ + mol %	0.0037	56.7	0.0021	-40.8	-0.0015	13.6	0.0005	150.1	0.0056	-11.2	-0.0004
C ₆ + CV MJ	0.0065	59.2	0.0038	-39.9	-0.0026	15.4	0.0010	154.2	0.0100	-9.8	-0.0006
CV C. No.	5.90										

Errors on real gases



		B 1		A 1		A 2		A 4		A 5	
Gas 4	detailed analysis	error % rel.	error absolute	error % rel.	error absolute	error % rel.	error absolute	error % rel.	error absolute	error % rel.	error absolute
C ₆ + mol %	0.1209	-5.6	-0.0068	-6.6	-0.0080	-4.8	-0.0058	-2.3	-0.0028	-4.9	-0.0059
C ₆ + CV MJ	0.2204	-8.1	-0.0178	-9.1	-0.0200	-7.3	-0.0161	-4.9	-0.0107	-7.4	-0.0162
CV C. No.	6.17										
Gas 5											
C ₆ + mol %	0.1376	3.6	0.0050	6.3	0.0087	5.0	0.0069	7.2	0.0099	7.1	0.0098
C ₆ + CV MJ	0.2510	0.9	0.0021	3.5	0.0087	2.2	0.0056	4.4	0.0109	4.3	0.0107
CV C. No.	6.17										
Gas 6											
C ₆ + mol %	0.0487	-9.2	-0.0045			-11.5	-0.0056	2.7	0.0013	-12.0	-0.0058
C ₆ + CV MJ	0.0873	-10.1	-0.0088			-12.3	-0.0107	1.8	0.0015	-12.8	-0.0111
CV C. No.	6.06										
Gas 7											
C ₆ + mol %	0.0962					4.2	0.0040	17.7	0.0171	9.0	0.0087
C ₆ + CV MJ	0.1683					5.7	0.0096	19.5	0.0328	10.6	0.0179
CV C. No.	5.91										



Comment on real gas tests

- The analysers used in this test were used “as found” rather than having been optimised for C₆+ analysis.
- There are clear differences in performance between analysers. This should be capable of being resolved.
- Some of the relative errors are dauntingly high. This tends to apply to the gases with lower C₆+ content.
- Despite these high relative errors, none of the errors in CV exceed 0.05 MJ/m³.

Conclusions

- C_6+ measurement requires more thought than just identifying the peak.
- A simple instrument modification can reduce baseline disturbances and make peak measurement more secure.
- The use of calibration and CV data from detailed analysis may be preferred where a single unvarying composition is being analysed. Any variations in composition make this a less good option.
- The use of n-hexane as the calibration component and the application of the CV of n-hexane to the measured C_6+ minimises errors in CV calculation.





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