Quality control procedure for the gas chromatographic determination of light hydrocarbons in petroleum liquid

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ABSTRACT

The accurate determination of light hydrocarbons by gas chromatography is crucial to the petroleum industry. In production operations, it helps determine engineering applications at the wellsite and the refinery and assists in formulating production negotiations with business partners. This paper describes the steps taken to control the quality of gas chromatographic determination of C_2–C_{12} hydrocarbons in samples of petroleum liquid.

INTRODUCTION

Analysis and design of petroleum production facilities and schemes require thorough knowledge of the thermodynamic and physical properties of hydrocarbon fluids. It would, naturally, be best if knowledge of the physical properties was available from experimental observations. Those are, however, impossible to measure for all hydrocarbon fluids in all relevant conditions. Thermodynamic equations of state are therefore used to simulate and predict the phase and physical behaviour of fluids.

For oil and gas mixtures, the phase behaviour and physical properties, such as density and viscosity, are uniquely defined by the state of the system, *i.e.* the temperature (T), pressure (p) and the composition of the fluid. In simulating phase behaviour and physical properties of complex hydrocarbon mixtures accurately, it is a prerequisite to have detailed and accurate compositional information for each mixture.

The compositional description of production fluids at specific reservoir conditions of high p and T is usually achieved by analysis of separate gas and liquid phases after it has been flashed to ambient p and T (Fig. 1). When these analyses are combined in the correct gas-to-liquid ratio, the result is the total composition of the original pressurised fluid.

The analysis of the petroleum liquid can be performed in two steps: a simulated distillation (packed column) technique is used to determine integral C_1 to C_9 components and individual C_{10} to C_{39} pseudo-components*. The individual C_1 to C_9 hydrocarbons are determined by a capillary column technique, and the distribution is scaled to the C_1 to C_9 integral from the simulated distillation analysis. The methods employed to quality control the front end analysis of petroleum liquids is the subject of this paper.

EXPERIMENTAL

The gas chromatography system is conventional and comprises a nominal 100 m × 0.25 mm I.D. fuscd-silica wall-coated open tubular (WCOT) analytical column internally coated with OV-1 cross-linked stationary phase. Upstream of the analytical column is a short pre-column (150 × 6.35 mm)

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* A pseudo-component is the sum of all individual components that elute from the chromatographic column after one *n*-alkane up to and including the next *n*-alkane. For example, the C_{12} pseudo-component is the sum of all components that elute after *n*-C_{11} up to and including *n*-C_{12}.
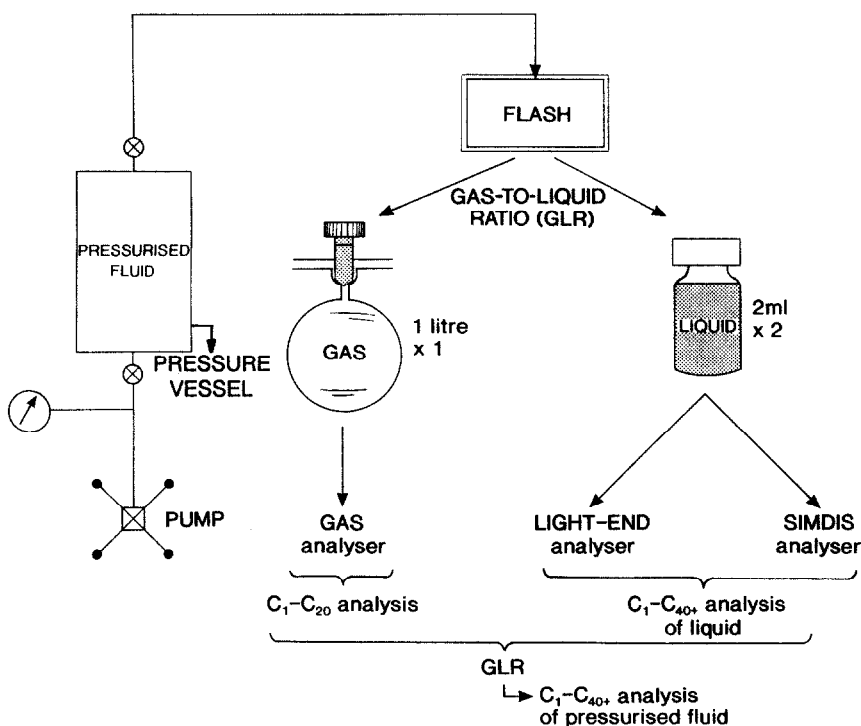
Fig. 1. Single flash separation and analysis (schematic).

packed with Chromosorb W coated with 5% OV-101. Backflush of the pre-column after a pre-determined time (*ca.* 1 min) after sample injection, prevents heavy hydrocarbons reaching and degrading the analytical column. The pre-column is kept isothermal at 200°C, whilst the analytical column is programmed from 25°C (hold for 20 min) to 180°C (hold for 10 min) at 3°C min^{-1}. A schematic of the gas chromatography system is shown in Fig. 2.

Samples

Petroleum samples at ambient pressure and temperature are generated from flash separation of pressurised fluids at temperatures and pressures that are commonly encountered during production operations. The samples are presented for analysis in 2-cm^3 septum-capped glass vials with a small ullage space. They are analysed by gas chromatography as soon as possible after generation.

Quality control

It is vital to verify that compositional analyses by a chromatography system meet precision and accuracy criteria required by the end-user of the data. It is therefore imperative to have quality control procedures in place to be assured of the relevance and value of analytical data being produced.

Daily maintenance includes leak tests, "blank" runs and analyses of natural and synthetic standards of known and accepted composition. Failure to reach a desired performance results in remedial action being taken and satisfactory re-verification of the chromatographic system before samples are analysed.

The traditional method for verifying the performance of gas chromatographs for determining light hydrocarbons in liquid samples was by the analysis of a synthetically prepared blend of C_5–C_{20} *n*-alkanes and benzene, toluene, ethylbenzene and *o*-xylene diluted in CS_2. The drawbacks of using a C_5–C_{20} hydrocarbon blend to quality control a
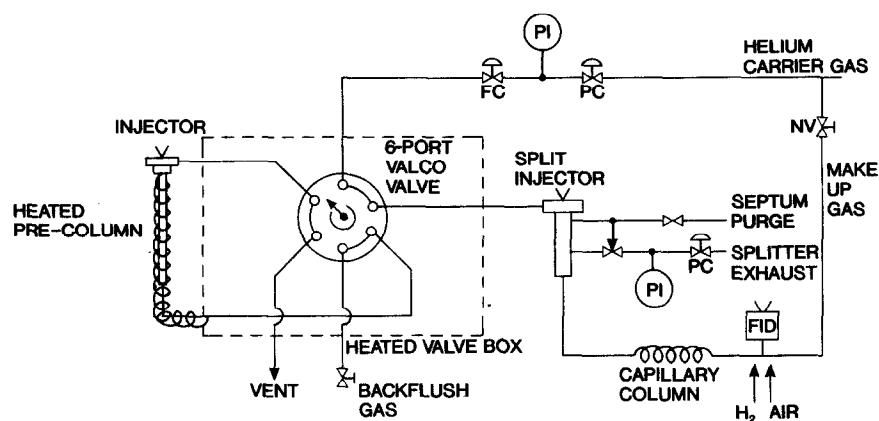
Fig. 2. Flow diagram of gas chromatography system. FC = Flow controller; FID = flame ionization detector; PC = pressure controller; PI = pressure indicator; NV = needle valve.

C_1–C_9 analysis method are obvious: (i) this blend can only quality control the analysis down to C_5; (ii) sample light-ends may be rapidly lost; and (iii) the verification procedure can only be rigorously applied when a fresh batch of standard is prepared.

A standard for the quality control of gas chromatographic determinations of C_1–C_9 hydrocarbons in liquid samples need to fulfil several stringent criteria. A standard needs to be: (i) a representative example of the majority of sample compositions encountered; (ii) homogeneous; (iii) available in sufficient quantities to last a significant period of time (preferably > 1 year); (iv) stable in long-term storage; and (v) stored as a single phase.

A representative stabilised condensate sample from a producing field gave a C_1–C_{12} composition given in Table I. With the exception of the ethane content, this analysis provides a useful target composition for a synthetic gravimetrically blended standard. In order to make the standard easier and more accurate to prepare, a higher concentration of ethane was used in the preparation of the standard.

Predicted phase behaviour

A most important consideration for the preparation of a standard is for it to be stored and sampled as a single homogeneous phase. The phase behaviour of the target composition was determined as a function of temperature and pressure using a cubic equation of state based on that of Peng and Robinson [1].

The resultant phase envelope that describes the predicted phase behaviour of the standard composition is given in Fig. 3. The area inside the curve describes the temperature and pressure conditions in which the standard would exist as two discrete phases. Outside of this region the blend occurs as a single phase; to the left of the critical point as a single

TABLE I

PETROLEUM LIGHT HYDROCARBON ANALYSIS

| Component/ pseudo-component	Representative analysis (%, w/w)	Composition of standard (%, w/w)
Methane	0.000	0.000
Ethane	0.011	0.204
Propane	1.363	1.331
2-Methylpropane	1.774	1.861
Butane	6.766	6.927
2-Methylbutane	3.824	3.786
Pentane	6.051	7.081
Hexanes	10.260	10.248
Heptanes	15.167	15.278
Octanes	15.313	15.026
Nonanes	8.500	8.508
Decanes	9.733	8.141
Undecanes	7.032	7.025
Dodecanes	5.413	5.421
Benzene	1.600	1.588
Toluene	3.168	3.256
Ethylbenzene	0.850	1.031
o-Xylene	3.175	3.286
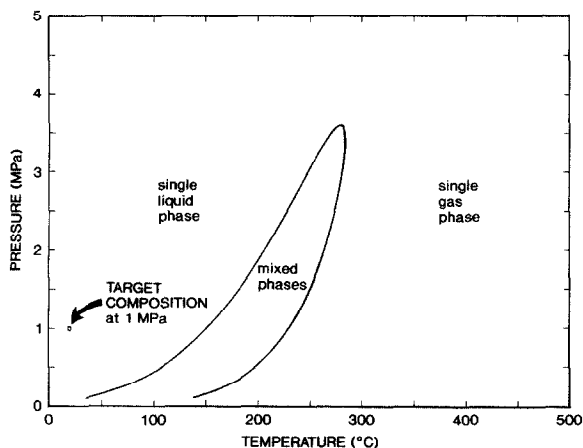
Fig. 3. Predicted phase diagram for C_2-C_{12} gravimetric blend.

liquid phase and to the right as a single gas phase. At *ca.* 1 MPa (10 bar) and ambient temperature, the blend is expected to be well within the desired single liquid phase region.

Preparation of the standard

The most common type of pressure vessel used for petroleum phase studies employs metallic mercury as the pressuring medium. The requirement of a gas ullage space in a mercury-containing vessel also prevent these type of vessel being used. As a consequence, hydrocarbons were blended within mercury-containing pressure vessels and then transferred to a mercury-free piston vessel for storage and dispensation.

The light hydrocarbon standard was prepared in two parts: a gas fraction (ethane to pentane) and a liquid fraction (hexane to dodecane). This allowed the minor components to be weighed in acceptable masses to help minimise any weighing errors.

The mercury pressure vessel which was used to prepare the gas fraction had no seals exposed to the fluid. The vessel was evacuated and then weighed on a double pan swing balance before ethane, the component destined to have the lowest concentration in the blend, was introduced. The vessel was reweighed to give the mass of ethane.

A second vessel was filled with propane and pressurised to *ca.* 7 MPa (70 bar) with mercury. This second vessel was then connected to the first vessel

using 3.175 mm O.D. stainless-steel tubing. All the pipework and valves were purged with propane. With a knowledge of the density of propane at these conditions, the volume required to give the desired mass was calculated and introduced into the first vessel. This vessel was then reweighed to determine the exact mass of propane transferred. This procedure was repeated for all the hydrocarbons up to pentane.

For each weighing the barometric pressure, humidity and laboratory temperature were recorded so that buoyancy corrections for the weighed masses could be determined. All weights used were traceable to national standards.

The liquid fraction (C_6-C_{12} and aromatics) was prepared in a 250-cm^3 volumetric flask. The highest molecular mass (*i.e.*, lowest vapour pressure) hydrocarbons were weighed in first, using a single pan electronic balance. This blend was then transferred to an evacuated and preweighed pressure vessel.

The two fractions were combined by first pressuring the gas fraction to *ca.* 7 MPa with mercury, and then inverting the vessel several times to ensure homogeneity of the fluid. After ensuring that the valves were free of residual mercury the required mass of gas was then added to the liquid fraction. The resultant blend was finally pressured to 7 MPa and inverted several times to ensure homogeneity.

The blend was transferred to a mercury-free piston vessel (500 cm^3 capacity) for long-term storage. Aliquots of the blend were sampled into a smaller (30 cm^3 capacity) piston vessel and diluted to *ca.* 10% in hexadecane. Both piston vessels were pressurised with nitrogen, the diluted blend is used as the quality control standard as the neat blend is too concentrated to use directly.

Analysis technique

The sampling pipework on the piston vessel between the valve and septum is removed and cleaned with acetone and vacuum dried before each sample is taken. The hydrocarbon blend is thoroughly mixed with an internal mixing rod prior to a sample being taken.

The phase envelope of the gravimetric mixture shows that the bubble pressure is *ca.* 0.1 MPa absolute (1 bar a) at room temperature (Fig. 3). In order to keep the blend single phase when sampling, it was expected that gas- and liquid-tight syringes

needed to be used. However, it was found that the conventional 5- or 10-μl syringes were suitable. The sampling technique withdraws 5 μl of liquid (the pressure of the blend pushes sample into the syringe) of which 4 μl is ejected immediately prior to manual injection.

RESULTS

The light-hydrocarbon blend was analysed on two different instruments at different laboratories and with different operators. The instruments were given designations GC1 and GC2. Analytical results from GC1 (8 analyses) were taken over a two-week period, whilst those for GC2 (7 analyses) were taken over a 4-week period subsequent to the former. All component recoveries are taken relative to n-octane = 100% (Table II). Detector response factors for all alkanes was taken to be unity; those for the aromatic components are specified in Table II.

The recovery of normal and branched alkane

Fig. 4. Results summary.

TABLE II

LIGHT-HYDROCARBON ANALYSIS OF GRAVIMETRIC STANDARD

Relative response factor $(RRF)_{benzene}$ = 0.89; $RRF_{toluene}$ = 0.94; $RRF_{EB/X}$ = 0.97. EB = ethylbenzene, X = xylenes.

Component	Mean recovery (%)		S.D.	
	GC1		GC2	
Ethane	95.7	1.84	100.6	0.96
Propane	96.5	1.38	99.2	1.95
2-Methylpropane	97.1	0.98	100.2	1.50
n-Butane	97.9	1.15	100.2	1.26
2-Methylbutane	101.6	1.10	101.0	1.07
n-Pentane	98.3	1.07	100.0	1.17
n-Hexane	99.5	0.81	100.8	0.94
Benzene	99.5	0.80	103.4	0.88
n-Heptane	99.5	0.45	100.3	0.50
Toluene	103.2	0.31	104.7	0.38
n-Octane	100.0	0.00	100.0	0.00
Ethylbenzene	99.5	1.63	99.7	0.64
o-Xylene	105.2	0.41	105.5	0.46
n-Nonane	98.0	0.43	97.1	0.64
n-Decane	100.5	1.88	98.7	1.07
n-Undecane	100.2	0.33	^{a}	
n-Dodecane	98.4	0.64	^{a}	

^{a} Data collection stopped after n-decane.
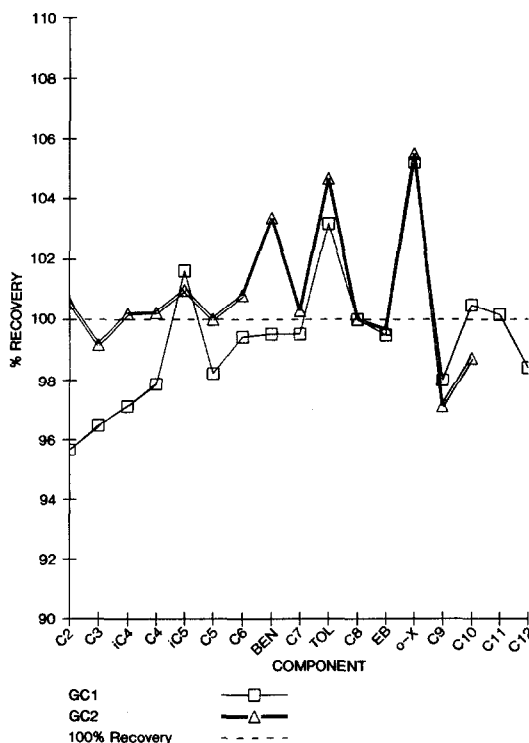
components fall within a narrow 98–102% range, with the exception of the lighter ($< C_4$) components recovered from GC1 (Fig. 4). The loss of these components was attributed to the use of an unchilled syringe in this laboratory. When the syringe was chilled in a refrigerator at 4°C for at least 5 min before sampling (as with GC2), the C_2–C_4 component recoveries are greatly improved.

The other outliers from the 98–102% recovery interval are the aromatic components, where the component recoveries are generally greater than expected. Both instruments tested show this behaviour for toluene and o-xylene (103–105% recovery), although for benzene there is a difference between the two instruments (100% and 103%). Ethylbenzene has a recovery of $ca.$ 100% in both instruments.

It is difficult to reconcile these apparent discrepancies from "expected" behaviour in a consistent way. Aromatic species exhibit a different flame ionisation detector response than aliphatic species. The response factors applied for this study were originally derived experimentally [2]. However,

these response factors may depend on such factors as detector design or gas flow into it.

The aromatic hydrocarbons are also present in much lower concentrations compared to most components in the blend: this makes the examination of aromatic hydrocarbon recoveries a very stringent test of the system.

The analytical performance of the gas chromatographs are considered excellent for the analysis of C_2–C_9 hydrocarbons in liquid petroleum samples. The apparent loss of some of the lightest alkanes in GC1 is practically insignificant in view of the small amounts of these components in most liquid samples, which is further reduced when the analytical results from both gas and liquid samples are combined to yield compositional analyses of total petroleums.

Response factors

Dietz's classical work on the experimental determination of weight relative response factors [2] suggests that response factors of between 0.92 and 1.00 should be applied to aliphatic species between C_2 and n-C_9, and that the response factors between these end members vary in an unsystematic way. Our findings, however, demonstrate that it is satisfactory for response factors of 1.00 to be applied to all alkanes between C_2 and C_{12}, which is widespread practice with flame ionisation detectors.

SUMMARY

In summary, the synthesis and routine analysis of a pressurised blend of hydrocarbons between ethane and dodecane verifies our standard operation procedures for the determination of light hydrocarbons in liquid samples. The determinations validate precision ($<2\%$ relative standard deviation) and accuracy (generally 98–102% component recovery). With contentious production issues providing the most stringent analytical quality requirements, it is believed that only with such a quality control procedure are such analyses fit for purpose.

REFERENCES

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