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Comparison of methods for direct and indirect measurement of hydrocarbon dewpoint

Andrew Brown, Martin Milton & Gergely Vargha
National Physical Laboratory, Teddington, UK

Richard Mounce & Chris Cowper, EffecTech Ltd, Uttoxeter, UK

Andrew Stokes, Mike Bannister & Andy Benton, Michell Instruments, Cambridge, UK

Dave Lander & Nick Bates, National Grid, Warwick, UK

Andy Ridge, Orbital, Swynnerton, UK

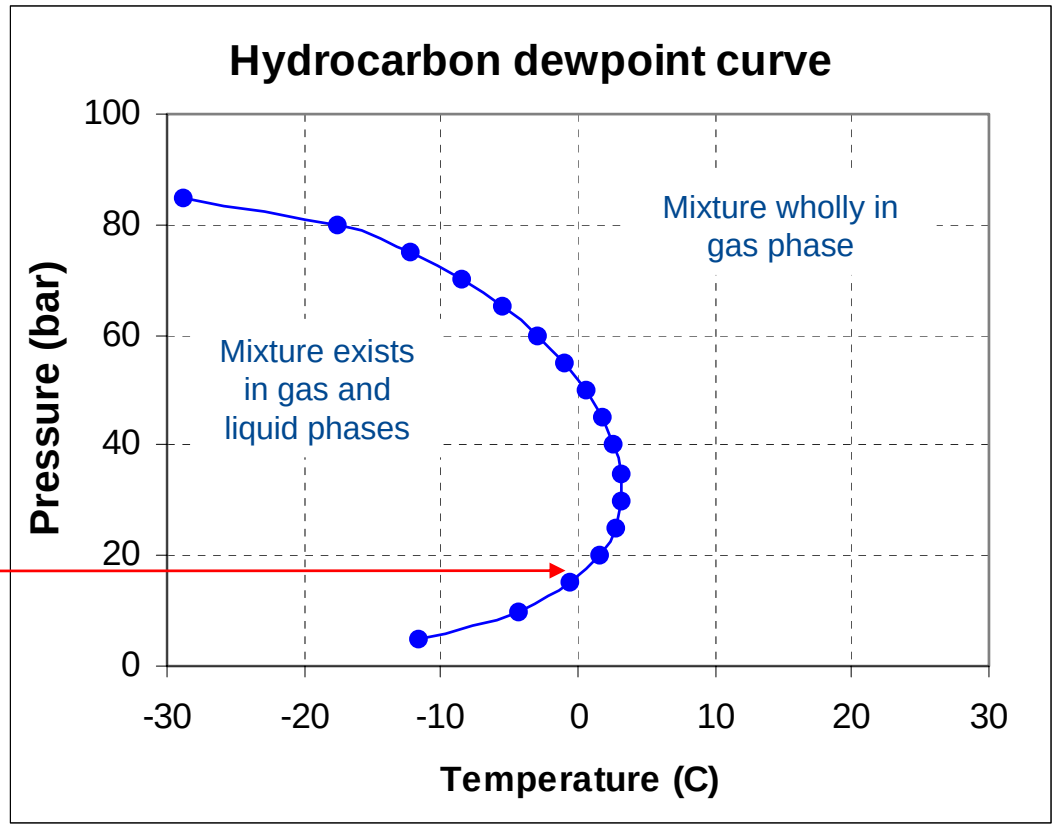
Hydrocarbon dewpoint

ISO 14532:2005 (Natural gas – Vocabulary) definition:

"*The temperature above which no condensation of hydrocarbons occurs at a specified pressure*."

'cricondentherm'

maximum temperature at which condensation can occur (at any pressure)



Hydrocarbon dewpoint curves may be:

- Calculated from gas composition using an equation of state
- Measured directly using a chilled mirror method

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Hydrocarbon Joint Industry Project
Aims and outline

Aims

- To compare the performance of
  - GC methods: process v laboratory
  - Dewpoint instruments: manual v automatic
  - Process methods: process GC v automatic chilled mirror
- To produce a definitive dataset for use in future studies and to support ISO standardisation activities

Outline

- Five synthetic natural gas mixtures
- Seven ‘real’ natural gases

Collaborative project, but all analyses carried out with no prior knowledge of other results

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Measurement techniques: Gas chromatography

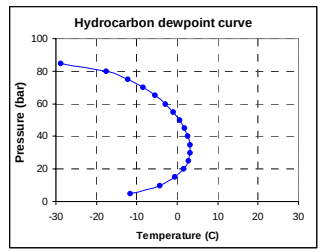
Gas samples

GC analysis

Component	% mol/mol	Component	% mol/mol
Helium	0.032	2,3-di-me-C4	0.0121
Hydrogen	0.008	2-me-C5	0.0546
Oxygen	0.027	3-me-C5	0.0309
Nitrogen	6.112	n-C6	0.0327
Carbon dioxide	0.057	Benzene	0.0002
Methane	83.507	cyc-C6	0.0171
Ethane	5.760	C7 fraction	0.0339
Propane	2.399	Toluene	0.0000
i-Butane	0.486	Me-cyC6	0.0056
n-Butane	0.891	C8 fraction	0.0022
neo-Pentane	0.009	C9 fraction	0.00026
i-Pentane	0.282	C10 fraction	2.6E-06
n-Pentane	0.231	C11 fraction	ND
2,2-di-me-C4	0.0085	C12 fraction	ND

Calculated gas composition

Equation of state



Calculated dewcurve

GC systems used:

- Lab GC 1 — Danalyser model 500 (up to C_5) with HP 4890 GC (C_{5+})
- Lab GC 2 — Danalyser model 500 (up to C_5) with Varian 3400 GC (C_{5+})
- Process GC 3 — Danalyser model 700 (all species)
- Process GC 4 — Orbital ‘all in one’ system – based on Siemens Maxum GC

- Calibrated using the same traceable, multi-component, reference gas standards
- Calibration gas also used to define GC retention times *etc*.

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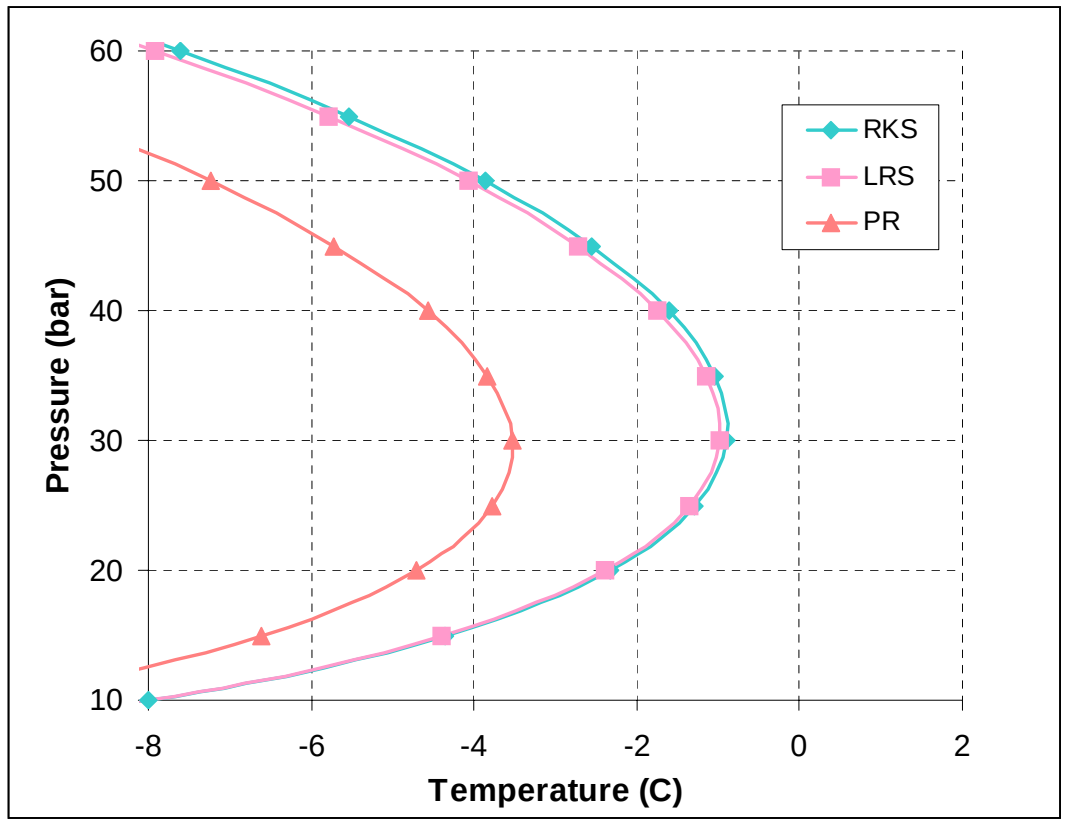
Use of equations of state

- Hydrocarbon dewcurves were calculated using:
  - RKS (Redlich-Kwong-Soave)
  - LRS (London Research Station; variant of RKS with different functional forms for some constants)
  - PR (Peng Robinson)
- All three EoS are cubic



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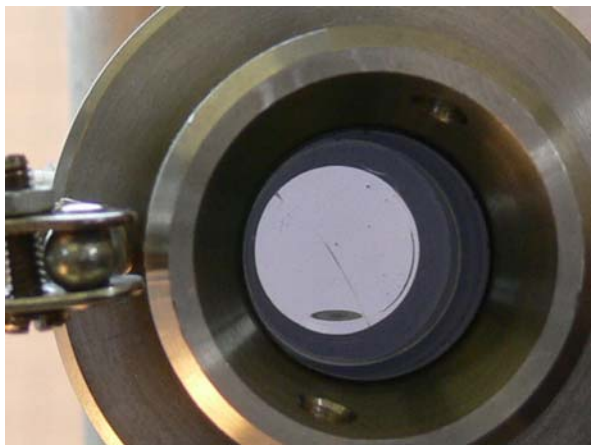
Measurement techniques: Chilled mirror (manual and automatic)

- Chandler model A-2 **manual** chilled mirror



(diameter of visible mirror approx 1 cm)

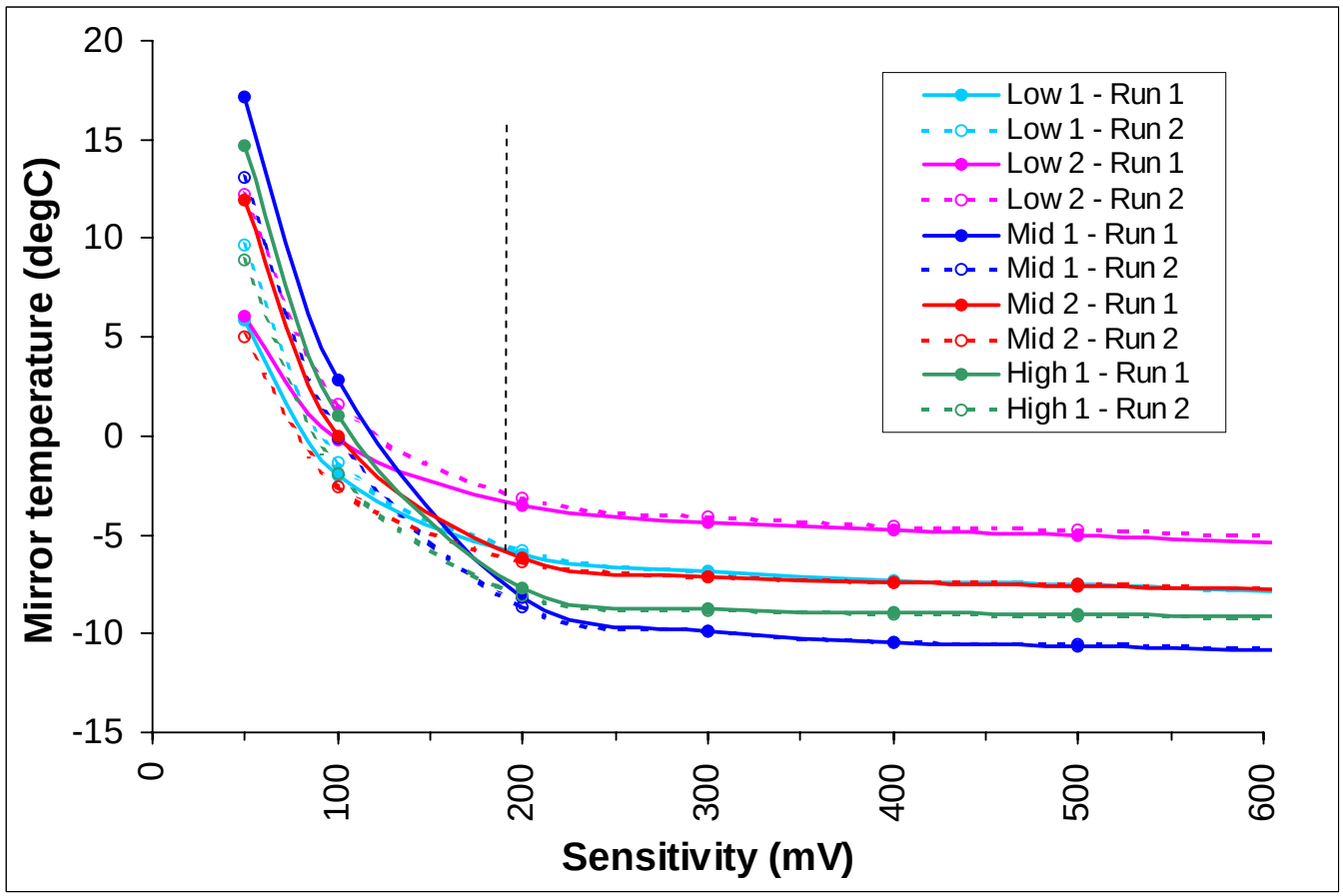
2.0 ºC

visible

- Michell Instruments' Condumax II **automatic** chilled mirror

- 'Dark spot' optical principle
  - Collimated red light focussed on conical depression in optical surface - condensate reduces light intensity in dark spot

Manual chilled mirror: Sensitivity

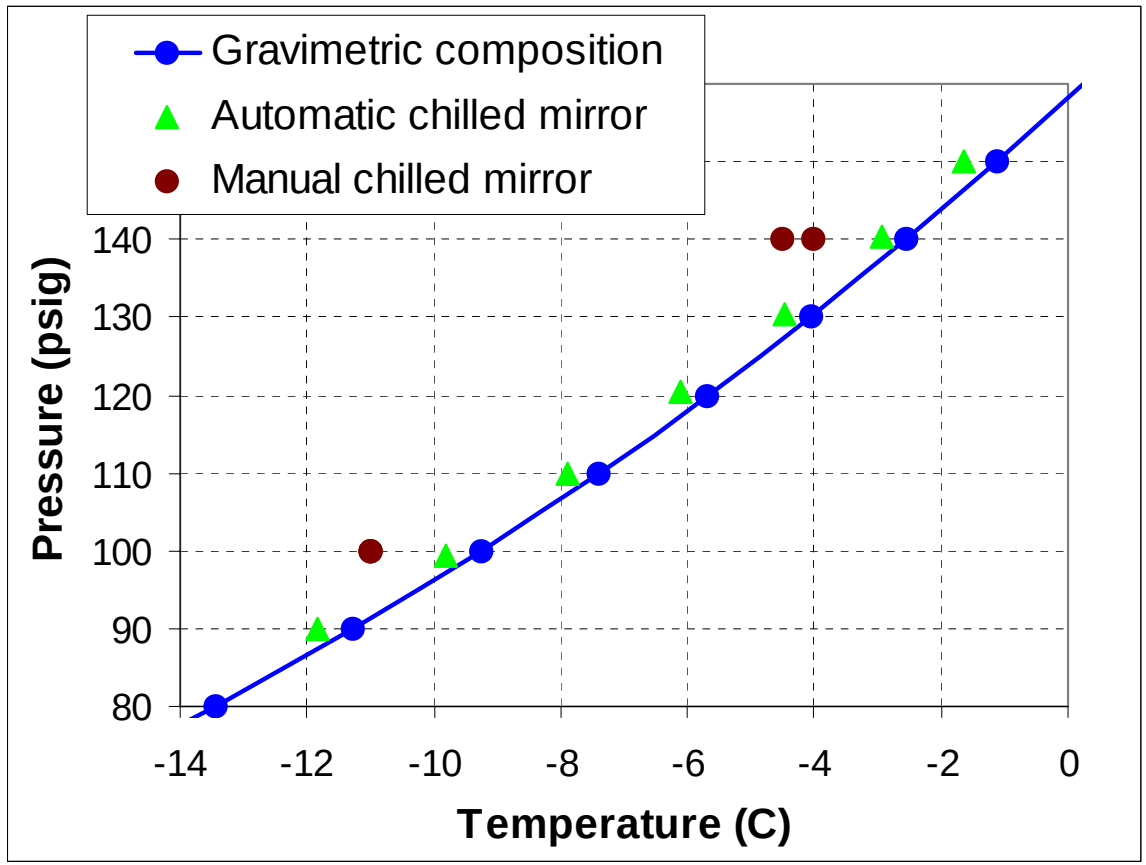


- Sensitivity - setting of 275 mV equivalent to manual chilled mirror
- 'Adaptive trigger point' correction under development.

Instrument calibration

Chilled mirror instruments

- Calibrated thermometers / temperature sensors
- Instruments validated by measurement of a gravimetric mixture of 10% *n*-butane in nitrogen



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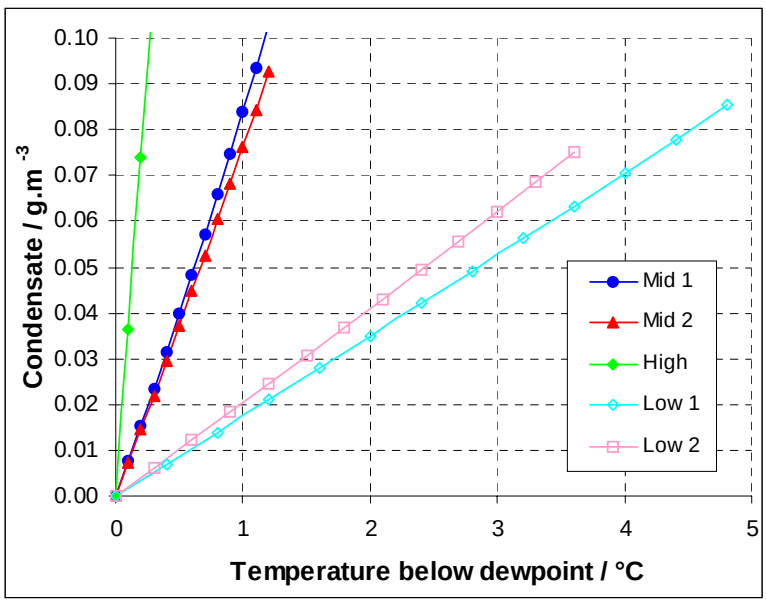
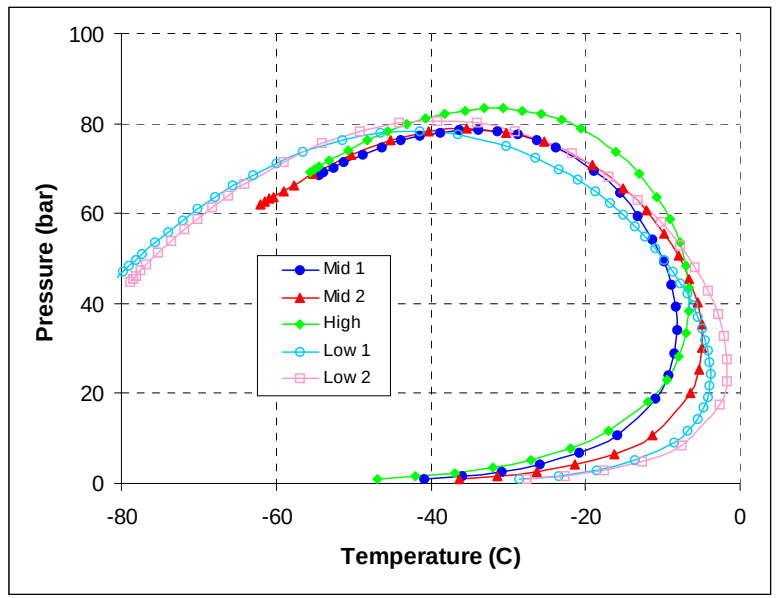
Synthetic mixtures

- Five synthetic Primary Reference Gas Mixtures prepared gravimetrically and verified by NPL
  - Mixtures contained *n*-isomers up to C_{10}, benzene, toluene and cyclohexane
  - Compositions chosen to encompass the range of hydrocarbon condensation rates found in gas fields around the British Isles

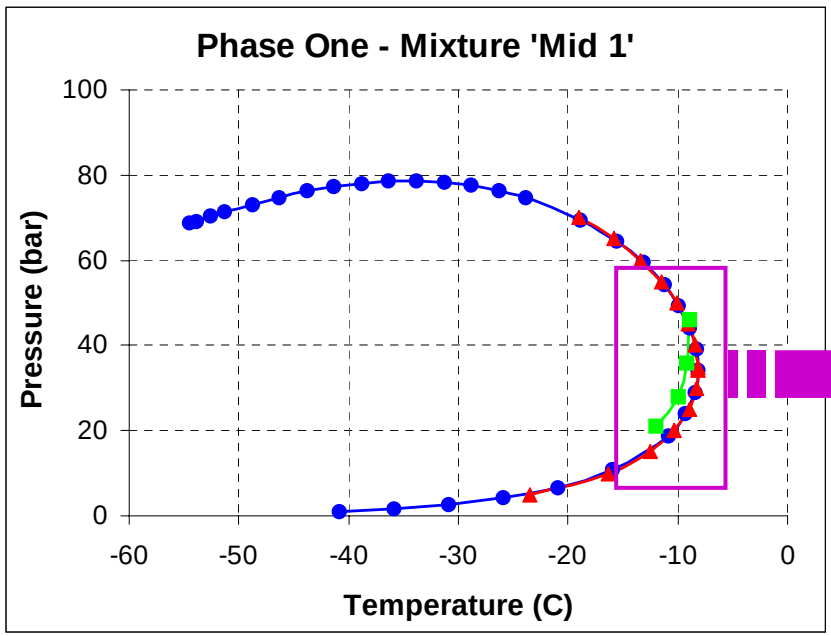


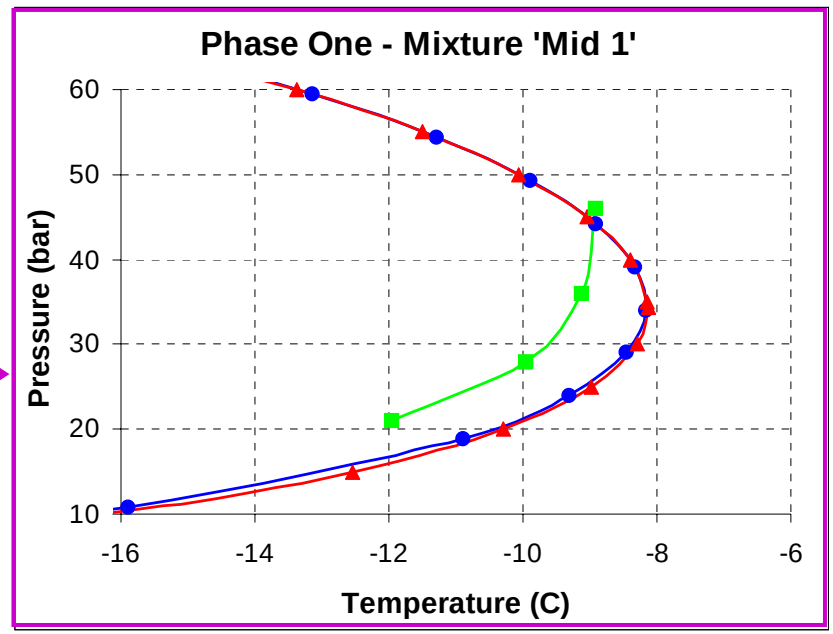
Calculated condensation rates



Calculated hydrocarbon dewcurves

Synthetic mixtures: Results (1)





● Gravimetric data
▲ Lab GC 1
■ Automatic chilled mirror

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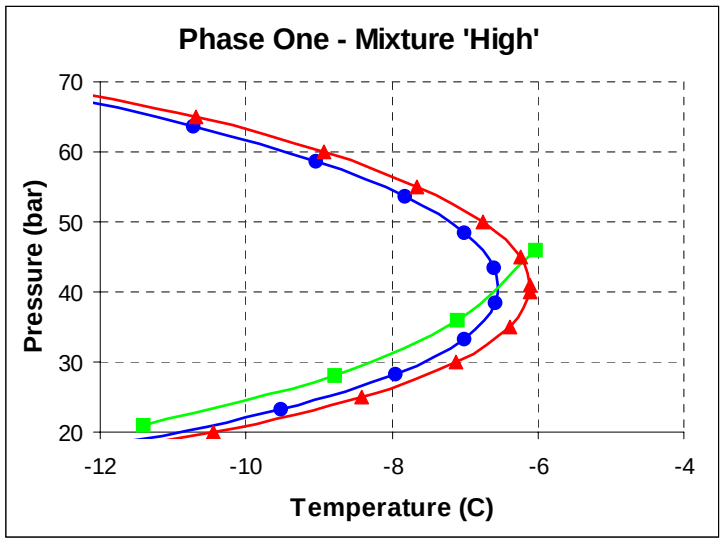
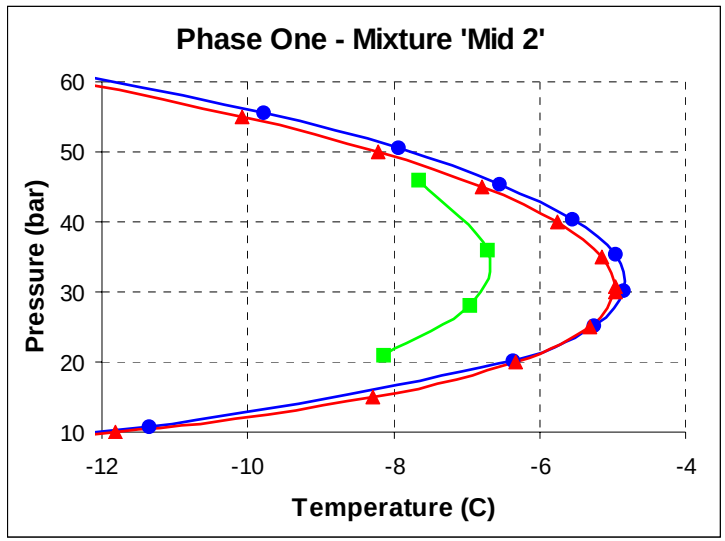
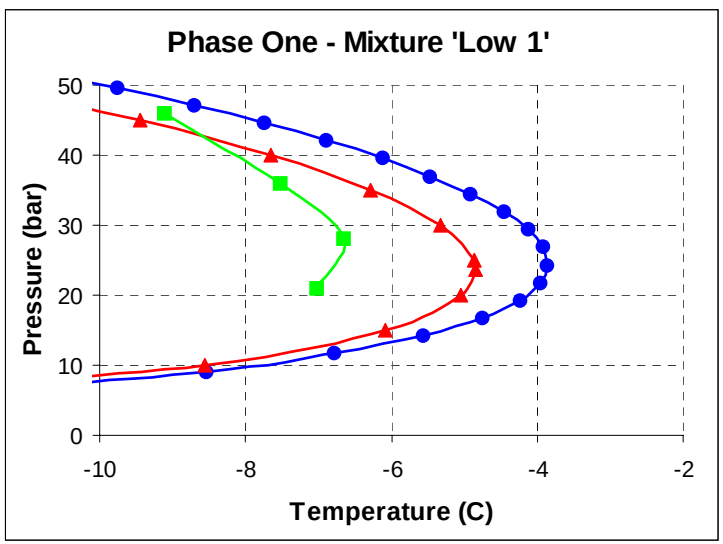
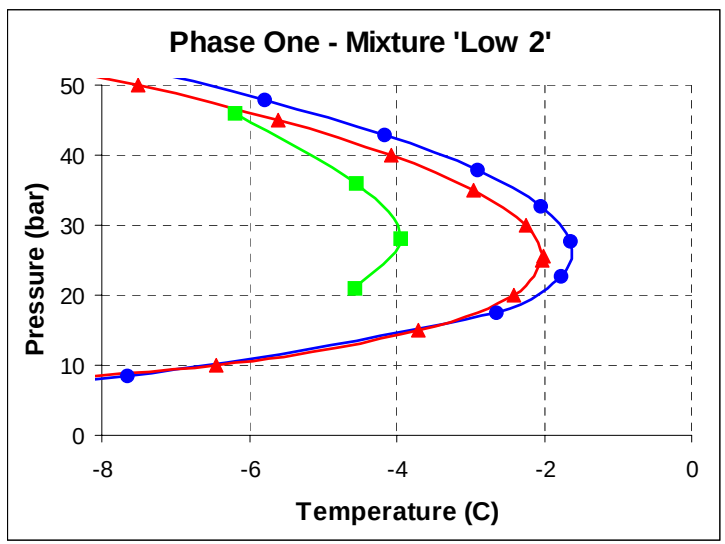
Synthetic mixtures: Results (2)

● Gravimetric data
▲ Lab GC 1
■ Automatic chilled mirror









Synthetic mixtures: Results summary

- Strong agreement between GC and gravimetric data
  - Average difference at cricondentherm of 0.3°C
- Good agreement between automatic chilled mirror and gravimetric data
  - Average difference at cricondentherm of 1.9°C
  - These differences are within the uncertainty of the measurement
    - The use of a different equation of state can lead to a difference in calculated dewpoint of more than 2°C
  - Automatic chilled mirror results are always lower than the gravimetric data
  - Closer agreement is observed when comparing the automatic chilled mirror data to an calculated dewpoint for 70 $mg.m^{-3}$ of condensate…

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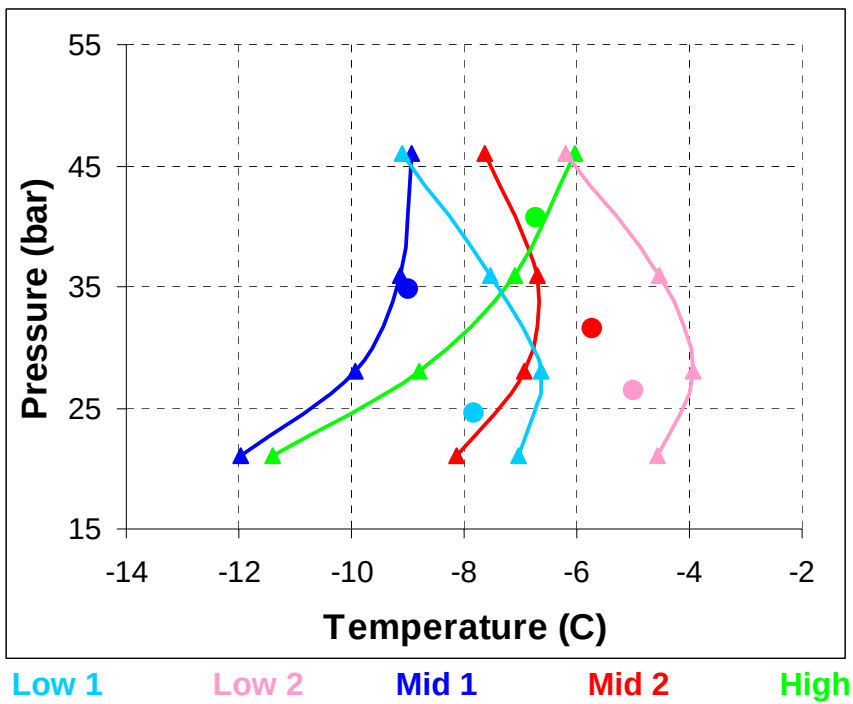
Synthetic mixtures: Dewpoint at 70 mg.m^{-3} of condensate

- 70 mg.m^{-3} is an empirical estimate of the amount of condensate required for detection by the automatic chilled mirror
  - Corresponds approximately to an automatic chilled mirror sensitivity of 275mV
  - 70 mg.m^{-3} of condensate equivalent to approx 11ppm *n*-decane



- Average difference between the automatic chilled mirror and 70 mg.m^{-3} of condensate (calculated from gravimetric data) now **0.7°C**

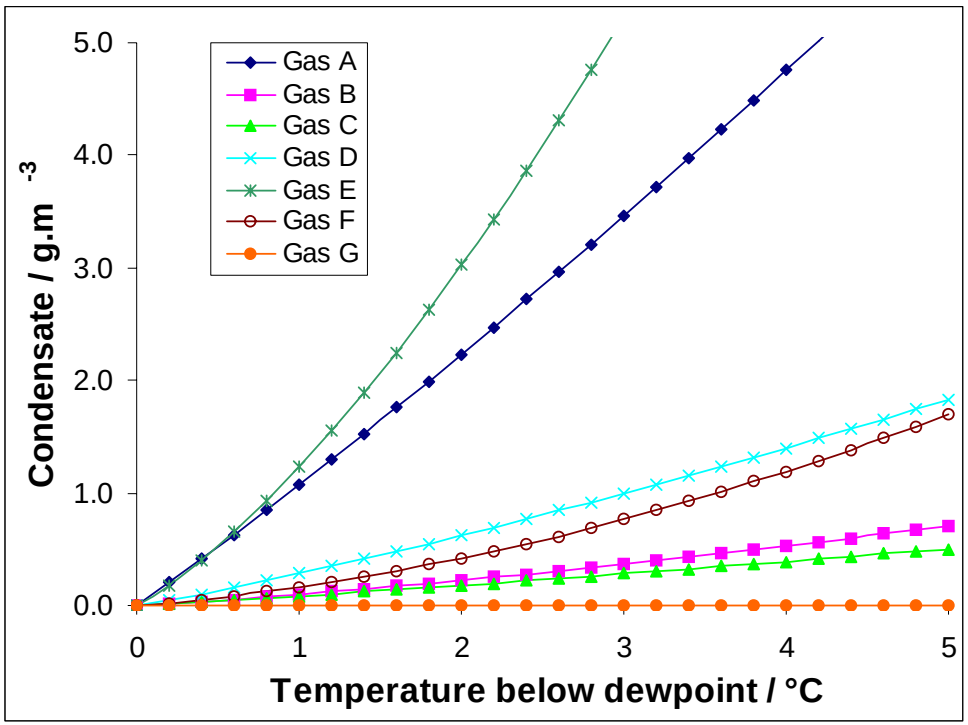
  (was **1.9°C** for theoretical dewpoint)

Lines = automatic chilled mirror measurement

Circles = calculated *T* for the formation of 70 mg.m^{-3} of condensate

Real natural gases: Outline

- Seven samples of real natural gas
  - Sampled (following ISO 10715:2001) into evacuated 50 litre cylinders



Calculated hydrocarbon condensation rates:

(from GC analysis data)

Analysis much more challenging than for synthetic mixtures due to the highly complex nature of the gases

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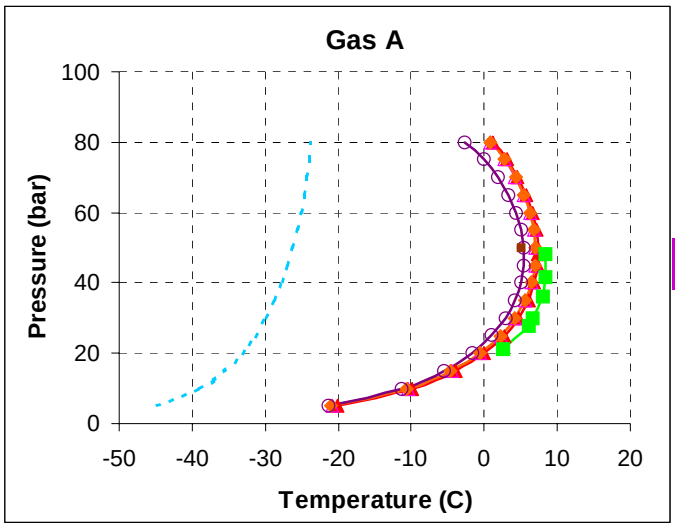
Real natural gases: Analysis methods

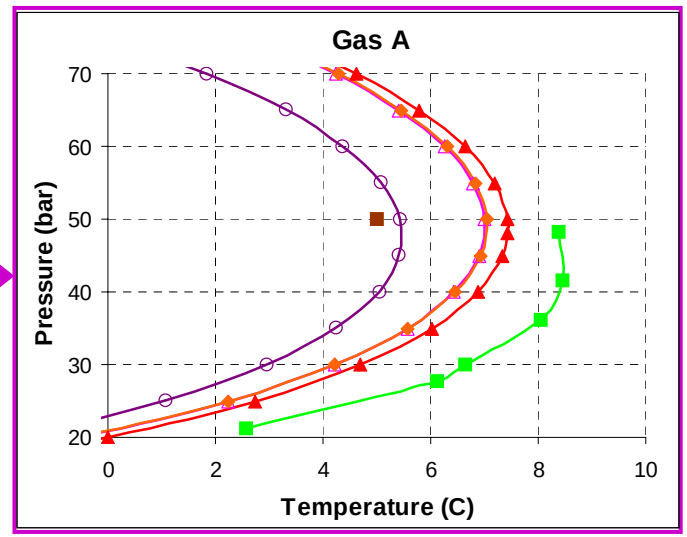
- GC
  - Lab GC 1 [Danalyser 500 + HP 4890 GC]
  - Lab GC 2 [Danalyser 500 + Varian 3400 GC]
  - Process GC 3 [Danalyser 700]
  - Process GC 4 [Orbital ‘all in one’ system:- Siemens Maxum GC]
- Automatic chilled mirror
  - ‘Standard’ sensitivity setting (275mV)
- Manual chilled mirror
- Calculations
  - All hydrocarbon dewcurves calculated using RKS equation of state
  - Water dewlines calculated using RKS equation of state with interaction parameters, $R_{ij} = 0.5$.

Real natural gases: Gas A results

Lab GC 1 ▲
Lab GC 2 △
Process GC 3 ●
Process GC 4 ○
Manual chilled mirror ■
Automatic chilled mirror ■
Water dewline – – – –

Highest dewpoint; second highest condensation rate



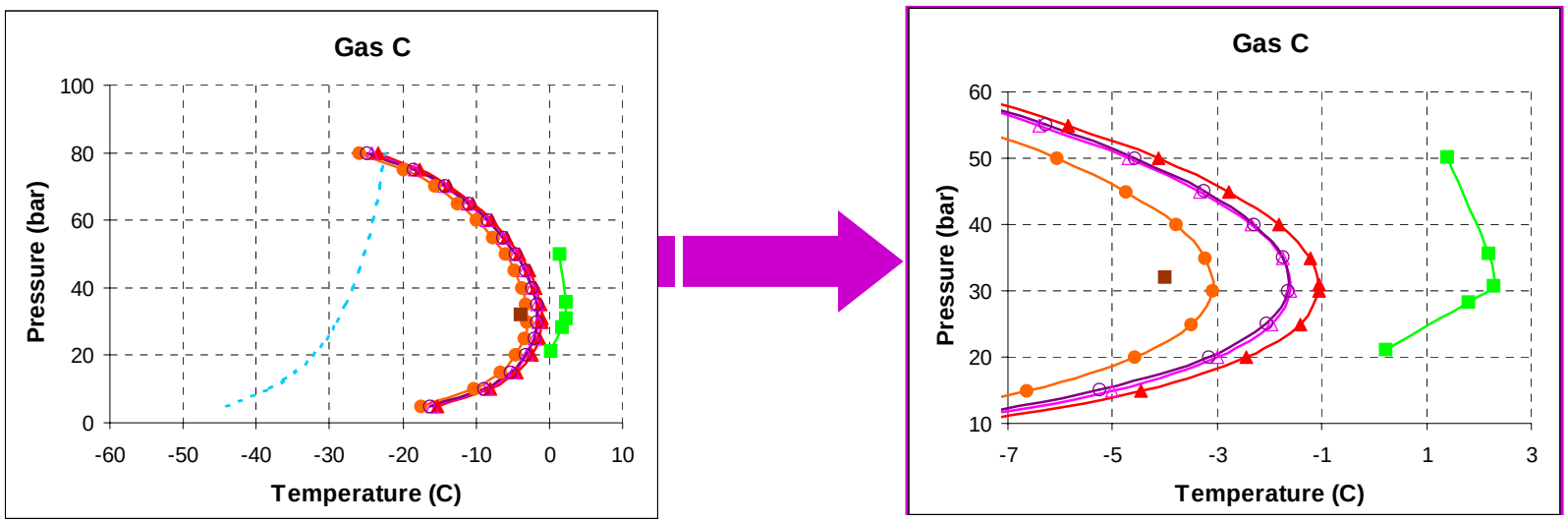


- Very good agreement between GC methods 1, 2 & 3
  - Gas A has the highest dewpoint, a high C_6 to C_7 content and a low C_{8+} content – 'easy to analyse'
- Process GC 4 results are lower than lab GCs (but close to manual chilled mirror)
  - May be due to the automatic allocation of boiling points by the process GC or choice of equation of state (*under investigation*)

Real natural gases: Gas C results

Lab GC 1 ▲
Lab GC 2 △
Process GC 3 ●
Process GC 4 ○
Manual chilled mirror ■
Automatic chilled mirror ■
Water dewline – – – –

Second lowest condensation rate; high aromatic content; highest C_8 to C_{12} content



- Relatively large difference between manual and automatic chilled mirrors
  - Gas has the longest hydrocarbon tail
  - Difference may be due to sampling issues, or other factors related to the operation of the instrument (cooling rate, sensitivity, etc.)
- Close agreement between manual chilled mirror and process GC data

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Real natural gases: Discussion (1)

- **GC methods:**

  process GC v laboratory GC

  - For six out of seven real gases the measured dewpoints are in the order:

    Lab GC 1 > Lab GC 2 > Process GCs
    - Order demonstrates sensitivity of instruments to detect higher hydrocarbons
    - The outstanding has a low hydrocarbon dewpoint – measurements in this temperature region are not crucial to legislators

  - Results for Process GCs show more variability. Due to:
    - Automated assignment of boiling points by process GC instrument?
    - Sampling issues?
    - Sensitivity to equation of state?
    - **Under investigation**

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Real natural gases: Discussion (2)

- **Dewpoint instruments:**
  manual chilled mirror v automatic chilled mirror

  - For all real gases, the measured dewpoints are in the order
    Automatic chilled mirror > Manual chilled mirror

  - Difference in measured dewpoint ranges from 1.7°C (Gas E) to 9°C (Gas F)
    - Differences larger than expected

  - For some gases, closer agreement obtained when using the ‘adaptive trigger method’
    - Replicates retrograde behaviour of calculated dewcurves
    - Method still under development

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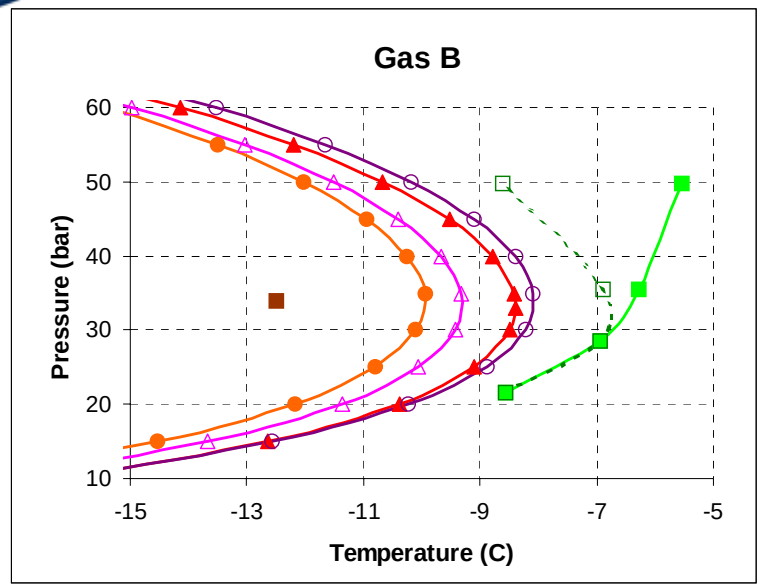
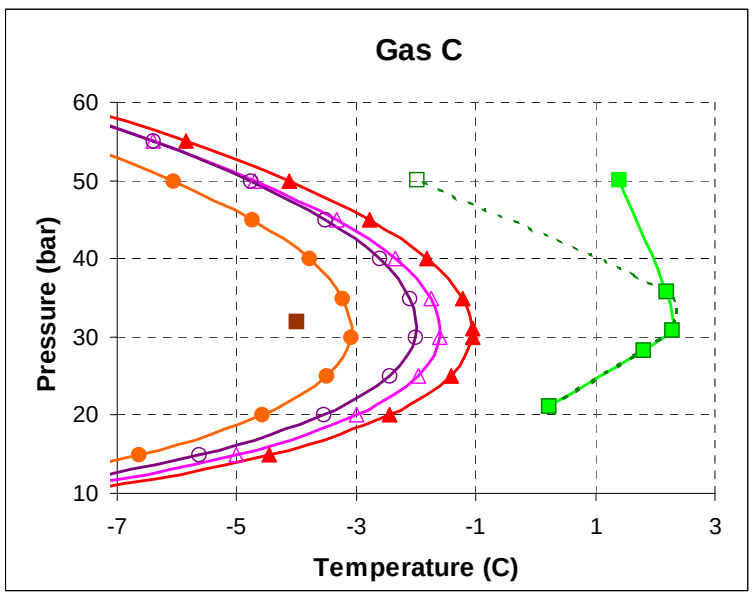
Automatic chilled mirror ‘adaptive trigger method’

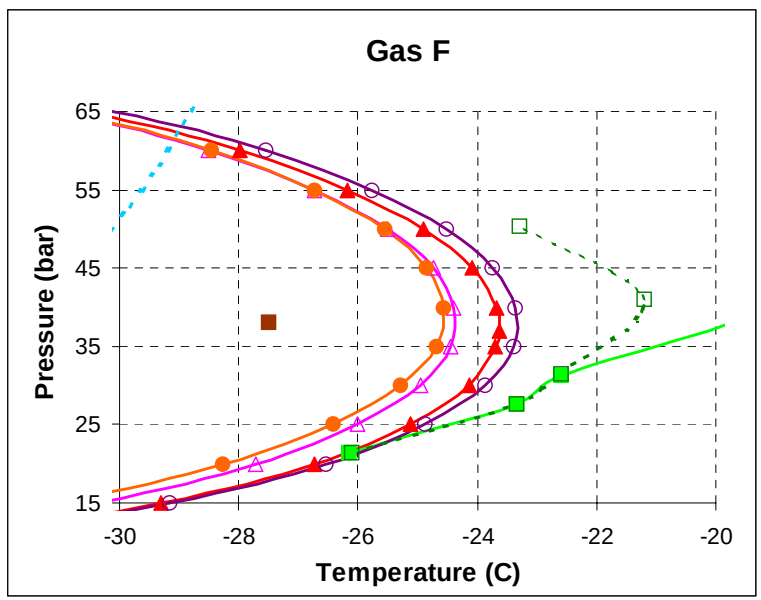
- An ‘adaptive trigger point’ correction can be applied to account for variations in the amount of gas in the cell with changing pressure

Standard (275 mV) sensitivity

Adaptive trigger method







Real natural gases: Discussion (3)

- **Process methods:**

  process GC v automatic chilled mirror

  - Real gases: Automatic chilled mirror > Process GCs
    - Difference would be more pronounced if the GC data was used to calculate the dewpoint at 70 $mg.m^{-3}$ of condensate
    - In complex gas mixtures, GCs may undermeasure, not detect or misidentify higher hydrocarbons and unexpected components
    - But…the manual chilled mirror measures dewpoints that are lower than those measured by the GCs.

  - Synthetic mixtures: Process GCs > Automatic chilled mirror
    - Simple gas mixtures. Measurement by GC relatively is straightforward – GC results agree very well with the gravimetric data

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Real natural gases: Discussion (4)

- **Role of synthetic gas mixtures**
  - Essential for the calibration of laboratory and process GCs
  - Role in the calibration of chilled mirror instruments may be limited
  - Calibration using an *n*-butane in nitrogen standard is straightforward and inexpensive, but the mixture does not form a typical hydrocarbon film

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What is the ‘true’ value of hydrocarbon dewpoint?

- **What is the ‘true’ value of hydrocarbon dewpoint?**
  - Methods agree to within a reasonable estimate of their uncertainties
  - None of the methods can be said to definitively measure the ‘true hydrocarbon dewpoint
    - GCs may not measure trace quantities of higher hydrocarbons, or ‘unexpected’ components (e.g. heavy oils, glycols, etc.)
    - Chilled mirror instruments are dependent on detection of a liquid film, and other operational and instrumental factors
  - Reported hydrocarbon dewpoint should be appended with the method used and any assumptions made

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Conclusions

- Comprehensive study of hydrocarbon dewpoint measurement of synthetic and real natural gases
- Close agreement for measurement of synthetic natural gases
- Measurement of real natural gases more difficult. Methods agree to within a reasonable estimate of their uncertainties
- ‘True’ value of hydrocarbon dewpoint difficult to define
- Data from the project available at:
  www.npl.co.uk/environment/hydrocarbondewpoint.html

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Contributions of project partners

EffecTech
Specialists in Gas Measurement

- Laboratory gas chromatography
- Process gas chromatography

MICHELL Instruments
The Dew Point Specialists

- Automatic chilled mirror

ORBITAL

- Manual chilled mirror
- Process gas chromatography

nationalgrid

- Facilitated collection of real gas samples
- Owner and operator of Great Britain's national gas transmission system

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- Preparation and certification of high-accuracy natural gas standards

dti
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What is hydrocarbon dewpoint?

- ISO 14532:2005 (Natural gas – Vocabulary) definition:
  - "*The temperature above which no condensation of hydrocarbons occurs at a specified pressure*."
- Theoretical dewpoint cannot be measured in practice – requires the detection of the first molecule of liquid condensate
  - Discussions on-going within ISO/TC193/SC1 to redefine as a 'technical' or 'measurable' dewpoint e.g. define the amount of hydrocarbon liquid formed for a given gas at a given temperature and pressure
  - Alternative approach would be to define a technique-specific 'correction factor' and include suspected error in the uncertainty budget
- 'Hydrocarbon dewpoint' often not well defined in legislation
  - Term should be appended with, e.g. the method of determination or a maximum permissible error

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