Australian Government
Department of Industry, Innovation and Science

National Measurement Institute

Development of standards and services for LPG

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LPG Australia

Australians have been using LPG since the 1950s as a fuel for ovens, stoves, hot water systems and space heating.

Today, around one million Australian households use LPG for these purposes.

Another seven million households use LPG for barbeques and outdoor heating.

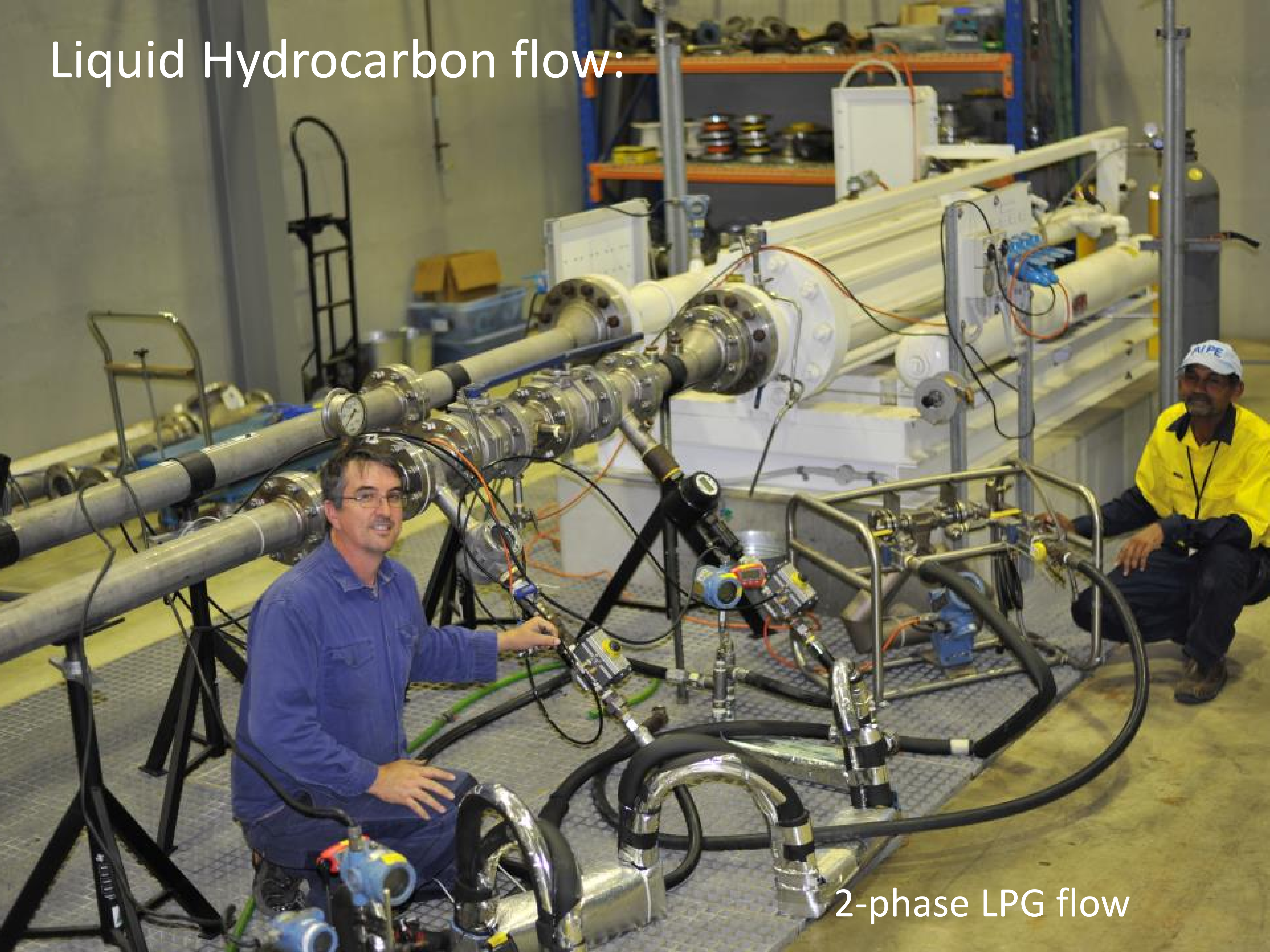
Around 100,000 Australian businesses use LPG for a range of industrial uses, including heating and power generation

More than 490,000 light vehicles run on LPG in Australia

LPG is a popular fuel in rural and regional Australia, in areas not connected to a natural gas network

Liquid Hydrocarbon flow:

calibration of flowmeters


Liquid Hydrocarbon flow:
2-phase LPG flow

LPG Australia

- LPG and condensate are significant by-products of the numerous LNG trains that now operate in Australia.
- These by-products are important for the feasibility of the LNG plants.

- In the past we have received a number of requests for LPG composition standards and PT studies for LPG. Typically these requests came from natural gas producers who were obtaining their standards from DCG Partnerships in the USA.
- Until recently we did not have the capability to service these requests.

LPG

- Australia's laboratory accreditation body (NATA) identified that there were no readily available PT services for LPG composition.

Chemical Testing – PT Program Needed: Liquefied Petroleum Gas (LPG)

The participant facilities should be provided with sample/s of LPG, which must be transported according to the current regulations of the state concerned and the Australian Dangerous Goods Code (ADG). The following tests are suggested:

METHOD	TEST INVOLVED
ASTM 2163	Determination of Hydrocarbons in Liquefied Petroleum (LP) Gases and Propane/Propene Mixtures by Gas Chromatography
ASTM 2784	Standard Test Method for Sulfur in Liquefied Petroleum Gases (Oxy-Hydrogen Burner or Lamp)

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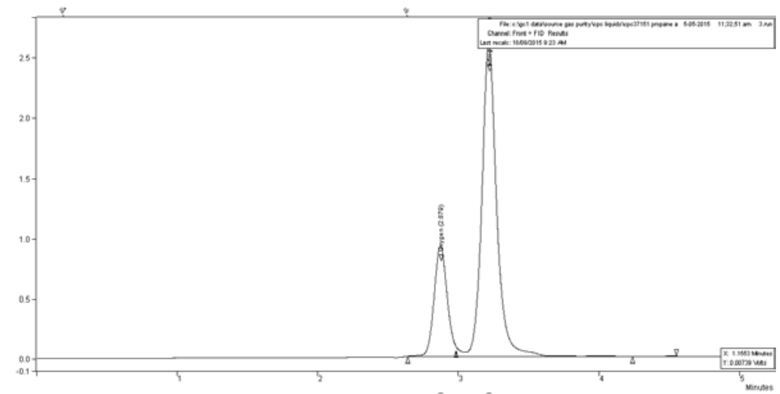
PT Programs Needed - Requirements Identified by NATA

Development of LPG standards
Stages

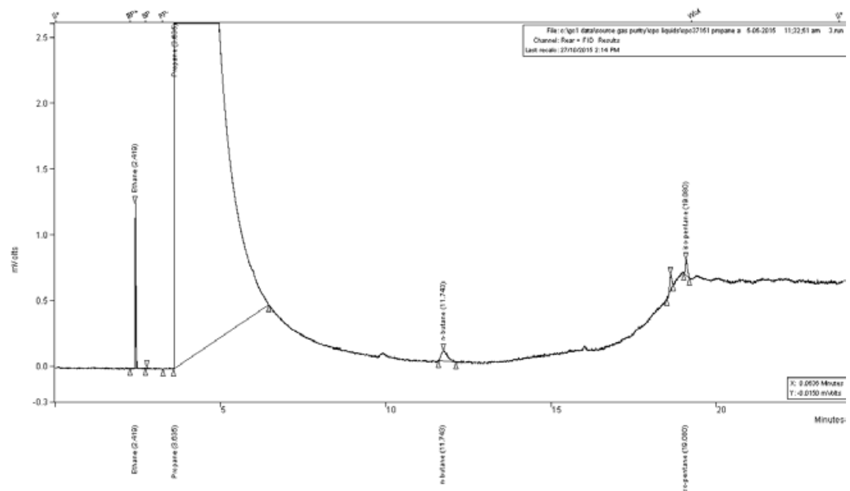
- Planning and purchase of GCs for LPG analysis
- Purchase of CPCs
- Purchase of liquid hydrocarbons
- Purchase of mass comparator for weighing CPCs
- Manufacture of CPC stand for weighing
- Manufacture of loops
- Development of LPG filling methods
- Development of analysis and verification methods

Development of LPG standards
Assessment of liquid purity

- Liquid hydrocarbon purity was assessed by GC with FID and PDHID detectors
- Liquid hydrocarbons were transferred to CPCs for testing
- A Gasifier was used to turn the liquid into gas for analysis
- Had to be compared with gaseous impurity standards - so issues with identification and the amount of impurities



Impurities in propane – MS and PDHID



Impurities in propane – Alumina and FID

Development of LPG mixtures

Initial attempts to manufacture LPG mixtures used ‘loops’ and liquid injection.

Challenges:

- Difficult to fill loops
- Difficult to transfer liquid out of loops
- No indication of how much liquid was transferred into or out of the loops
- Slow
- Control of the composition was limited
- Little confidence in the mixtures that were made this way

Development of LPG mixtures

Moved to the manufacture of LPG mixtures using CPCs to force the liquid transfer.

- ‘Receiving CPC’ was weighed during the liquid transfer
- Individual CPCs were used for each liquid hydrocarbon

Development of LPG mixtures

Advantages:

- Fast
- Compositions were consistent and close to the target mixture

Disadvantages:

- Expensive: need multiple CPCs

Unknowns:

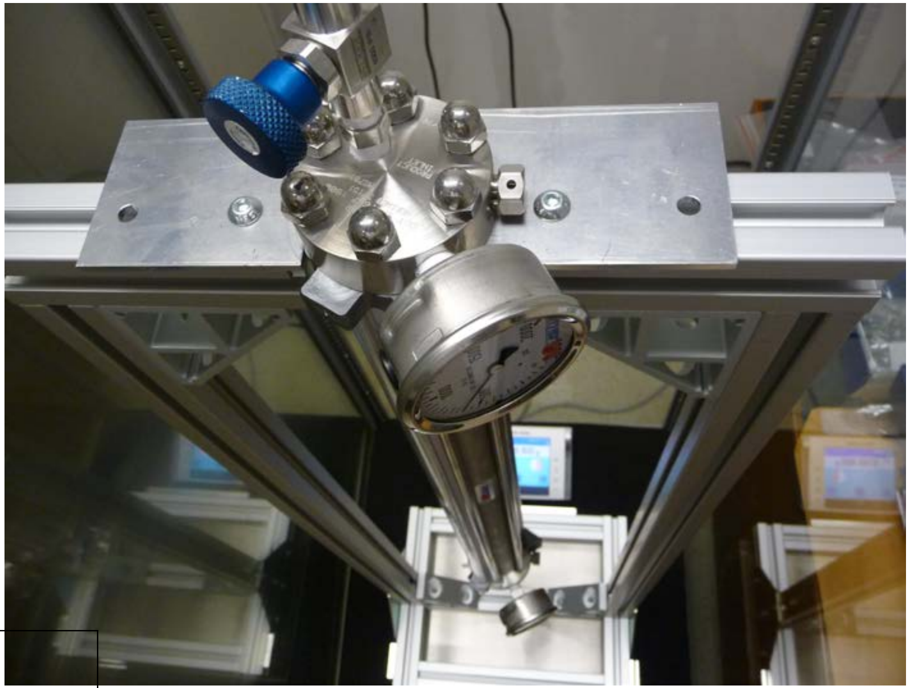
- How much of the pressurizing gas ends up in the hydrocarbon being transferred?

Development of LPG mixtures

Gravimetry:

- Mettler Toledo XPE32003LC

Model	XPE32003LC
Max. Load (g)	32100
Weighing Range (g)	32100
Resolution (mg)	5
Repeatability (mg)	5
Linearity (mg)	40



- Typical gravimetric uncertainties:

	CPC 39961		
	(cmol/mol)	u (cmol/mol)	Rel. u (%)
Ethane	1.8436	0.011	***0.62***
Propylene	8.9804	0.009	0.10
Propane	71.085	0.015	0.02
n-Butane	10.089	0.006	0.06
iso-Butane	4.038	0.007	0.16
iso-Pentane	0.8827	0.007	***0.75***
But-1-ene	3.0814	0.007	0.21

Development of LPG mixtures

Gravimetry:

- Next steps:

1. LPG premixes
2. Higher resolution balance

Model	MCM10K3
Max. Load (g)	11000
Weighing Range (g)	11000
Resolution (mg)	1
Repeatability (mg)	0.8
Linearity (mg)	6

- The new balance will help reduce the uncertainties on the minor components (ethane, pentanes) where the uncertainty due to preparation was significant

Verification and Certification
GC with alumina PLOT column to an FID

Three different GC set-ups were developed during the establishment of this capability.

This system:

GC with alumina PLOT column to an FID (hydrocarbons)

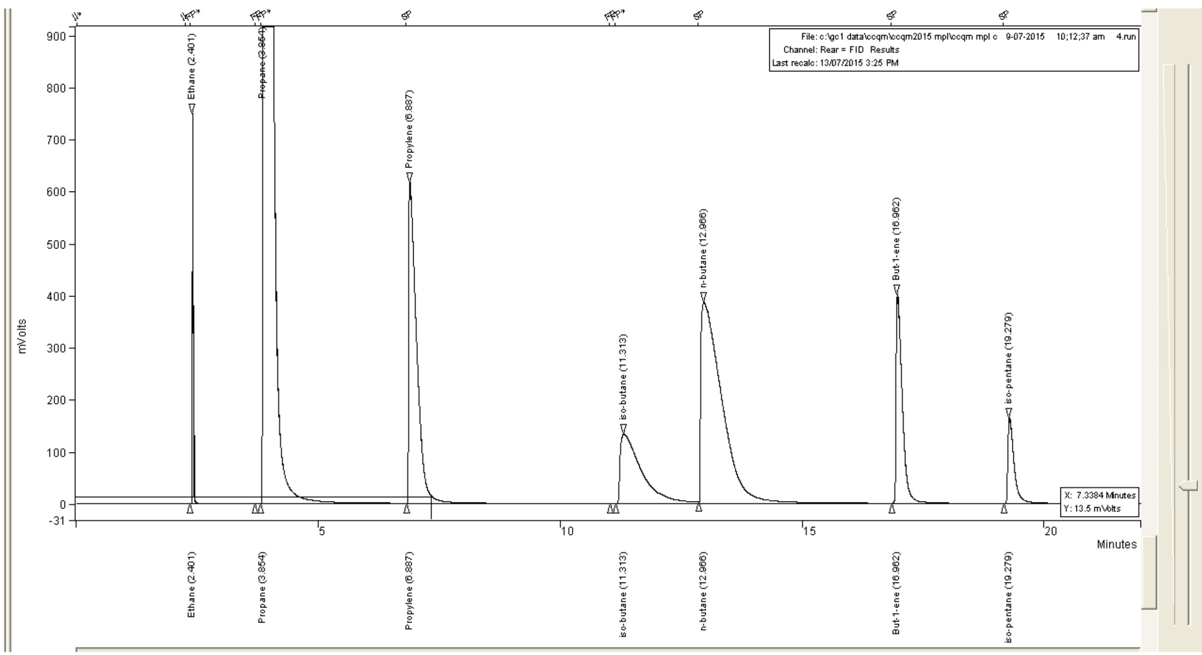
Alumina PLOT columns with KCl or Na_2SO_4 were trialed.

Second channel: Packed MS column to PDHID. (only for nitrogen, argon, methane)

LPG injection was performed using a gasifier

Verification and Certification
GC with alumina PLOT column to an FID

- GC could only be used for the measurement of impurities in source hydrocarbons.
- Retention times were not stable.

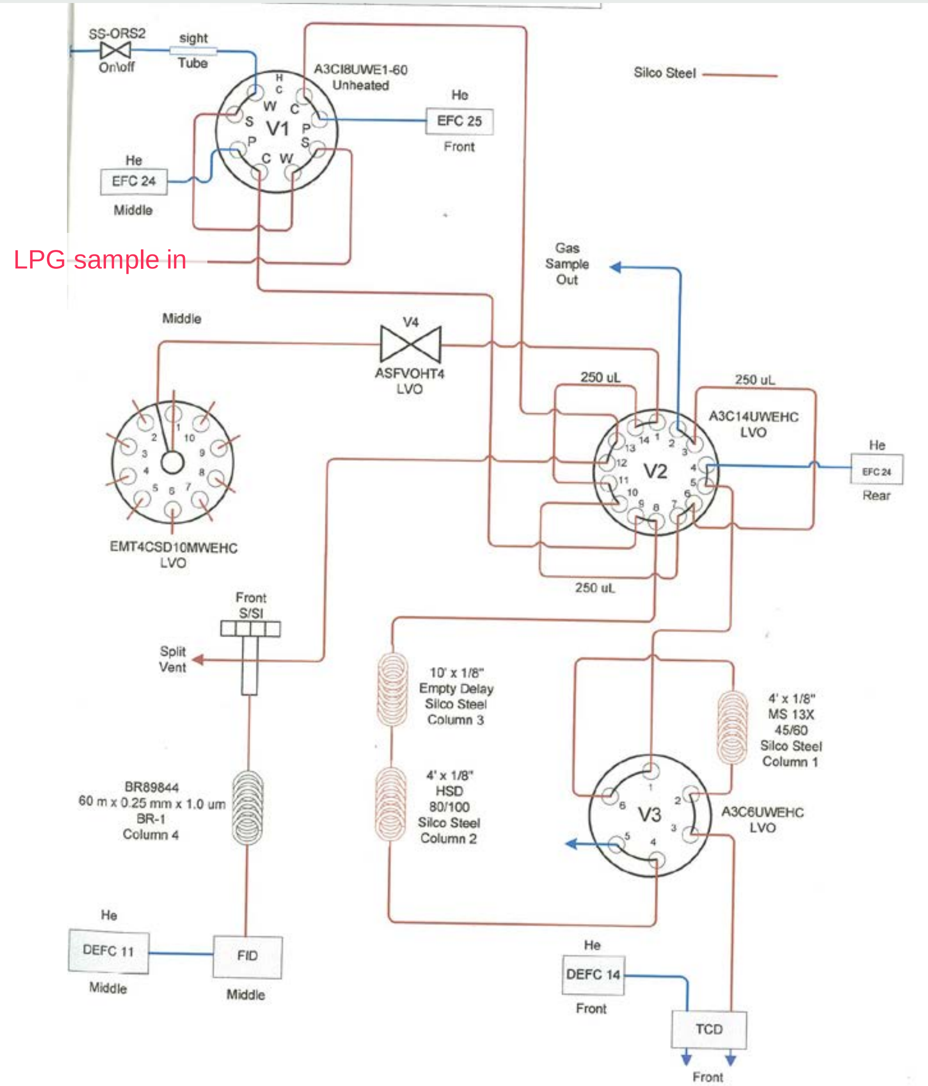


Verification and Certification
NGA with liquid injection capability

Certification was by GC-FID

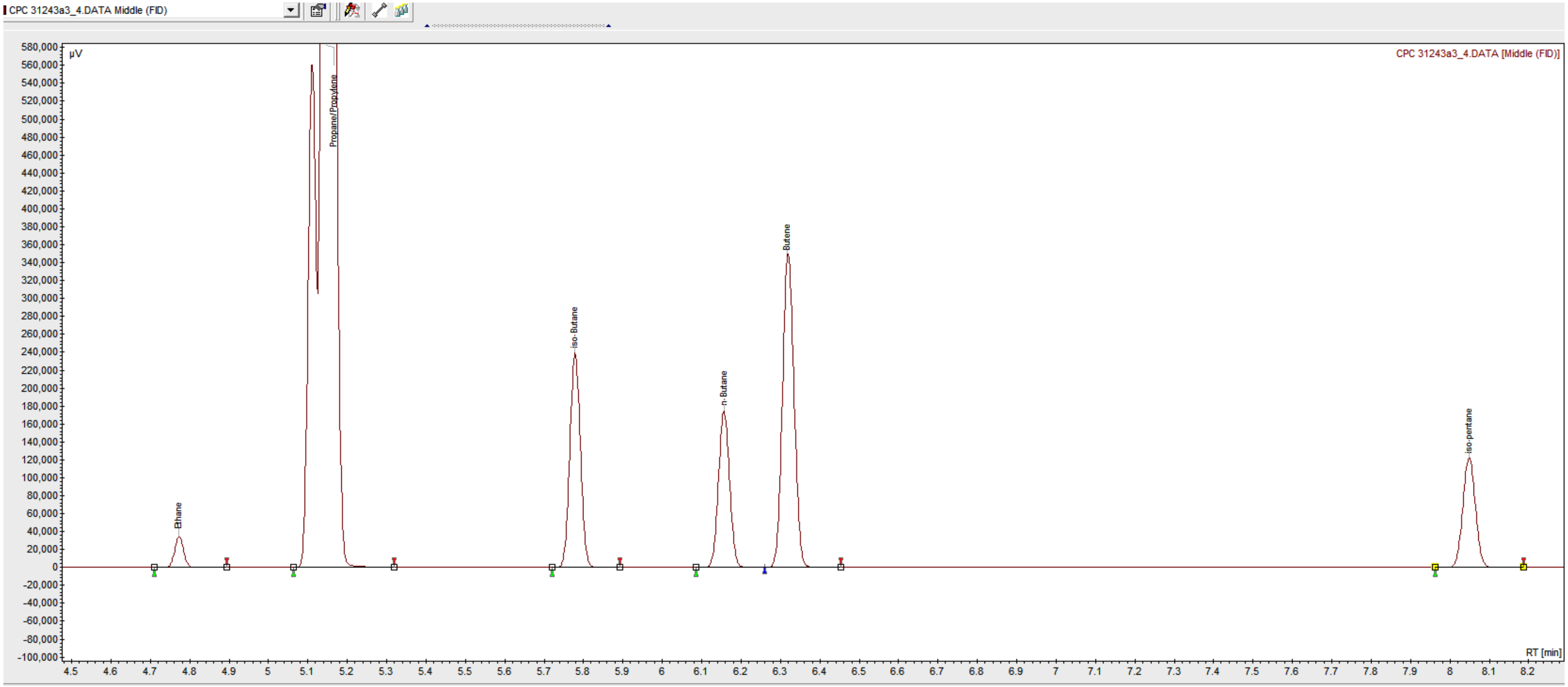
LPG injection was performed using liquid injection valve

BR-1 column used for natural gas analysis



Verification and Certification
NGA with liquid injection capability

Propylene was not separated from propane

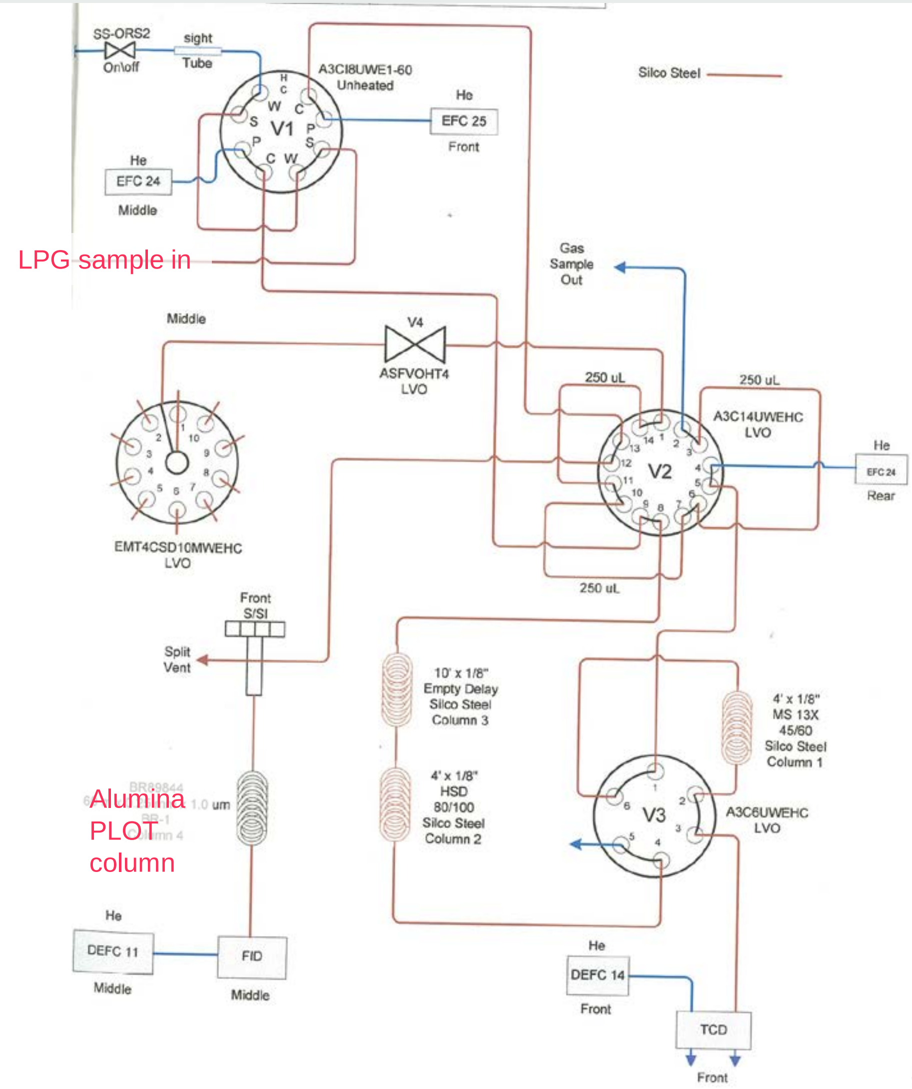


Verification and Certification
NGA with liquid injection capability

Certification was by GC-FID

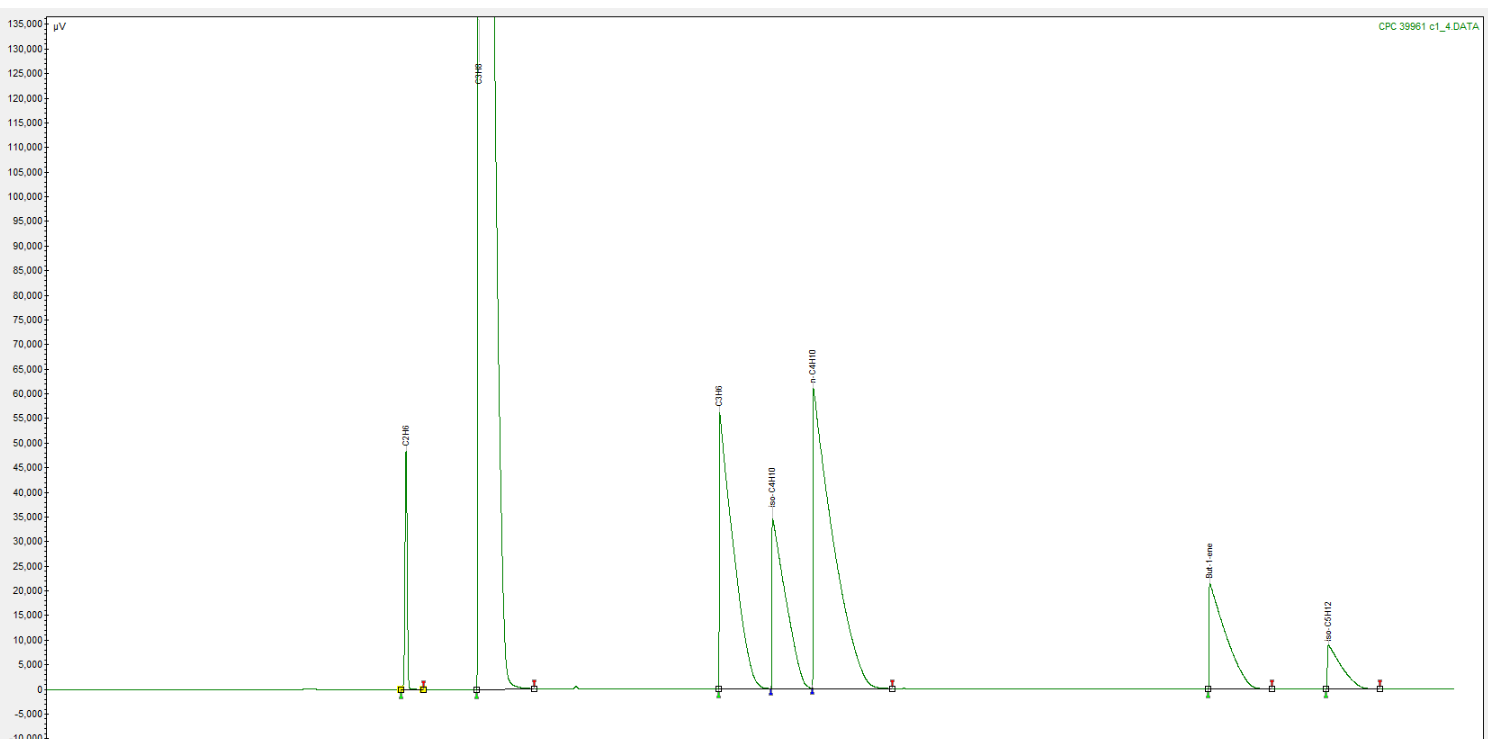
LPG injection was performed using liquid injection valve

Columns were Alumina Plot with KCl or Na_2SO_4



Verification and Certification
NGA with liquid injection capability

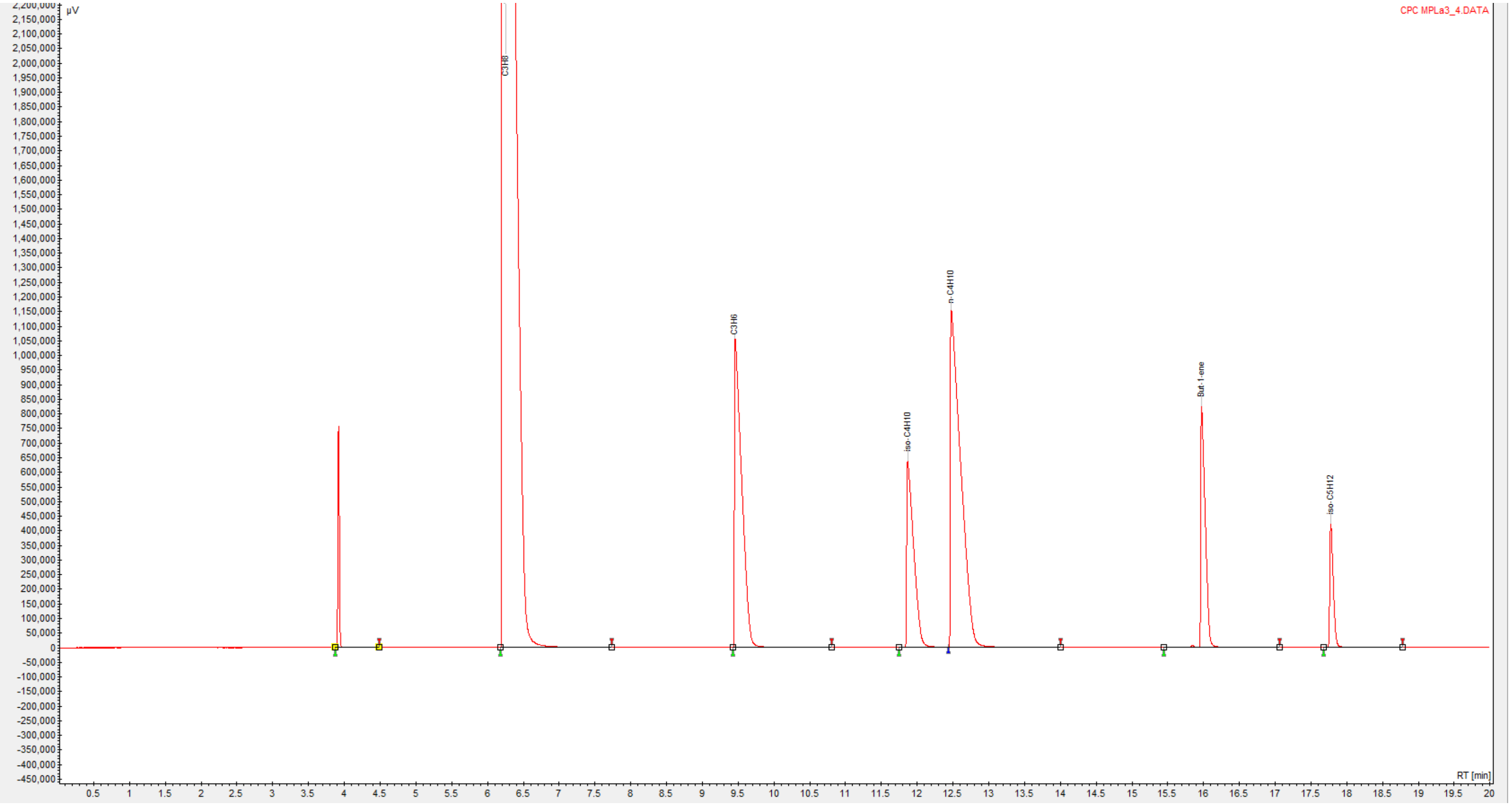
- Liquid injection valve delivered a fixed volume of 5 µL. The volume was too large and lead to overloading of the column.
- Smaller volume rotors will be incorporated in future certifications



Alumina Na_2SO_4 column

Verification and Certification
NGA with liquid injection capability

- Preferred method



Alumina KCL column

Verification and Certification
GC with alumina PLOT column to a TCD

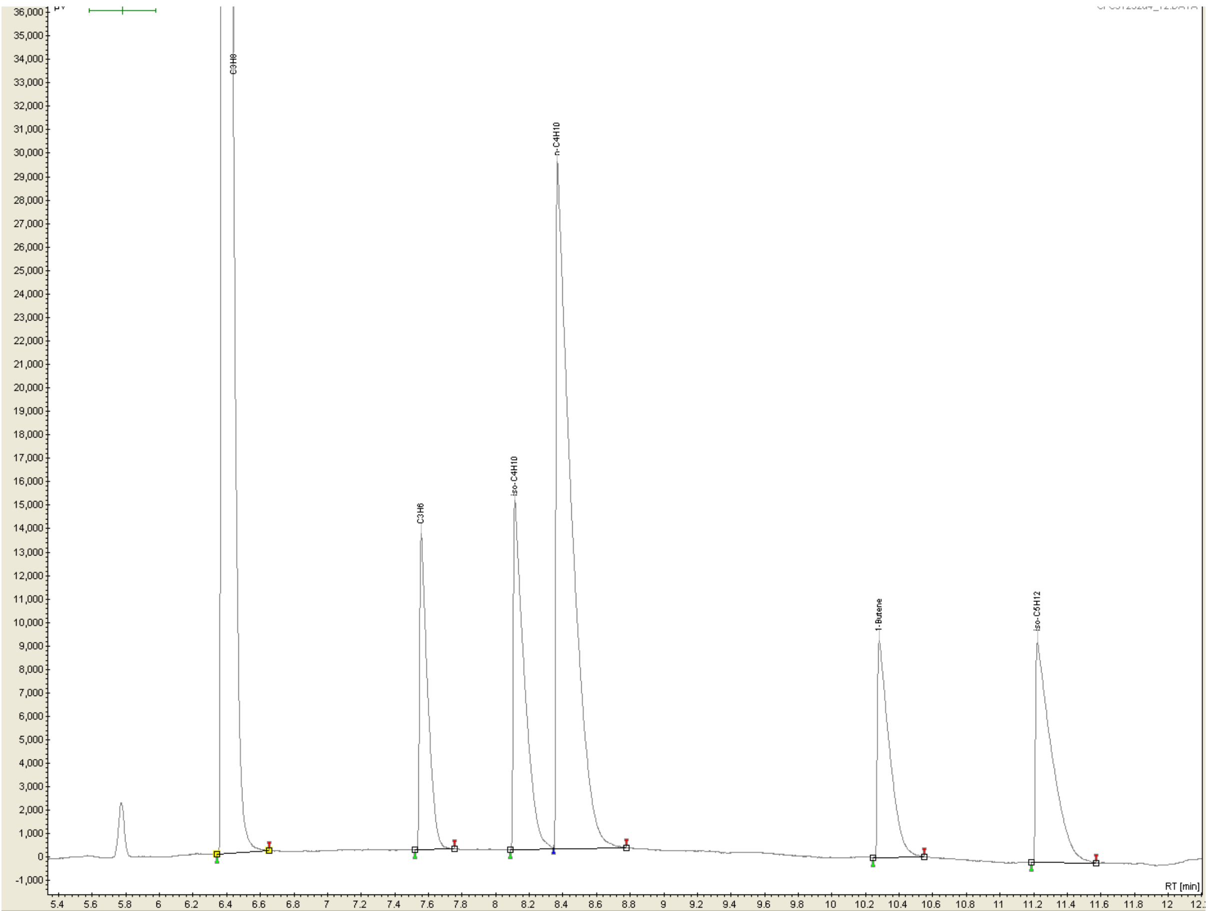
GC with alumina PLOT column to a TCD

Alumina PLOT columns with KCl or Na_2SO_4 were trialed.

LPG injection was performed using a gasifier

Gasifier

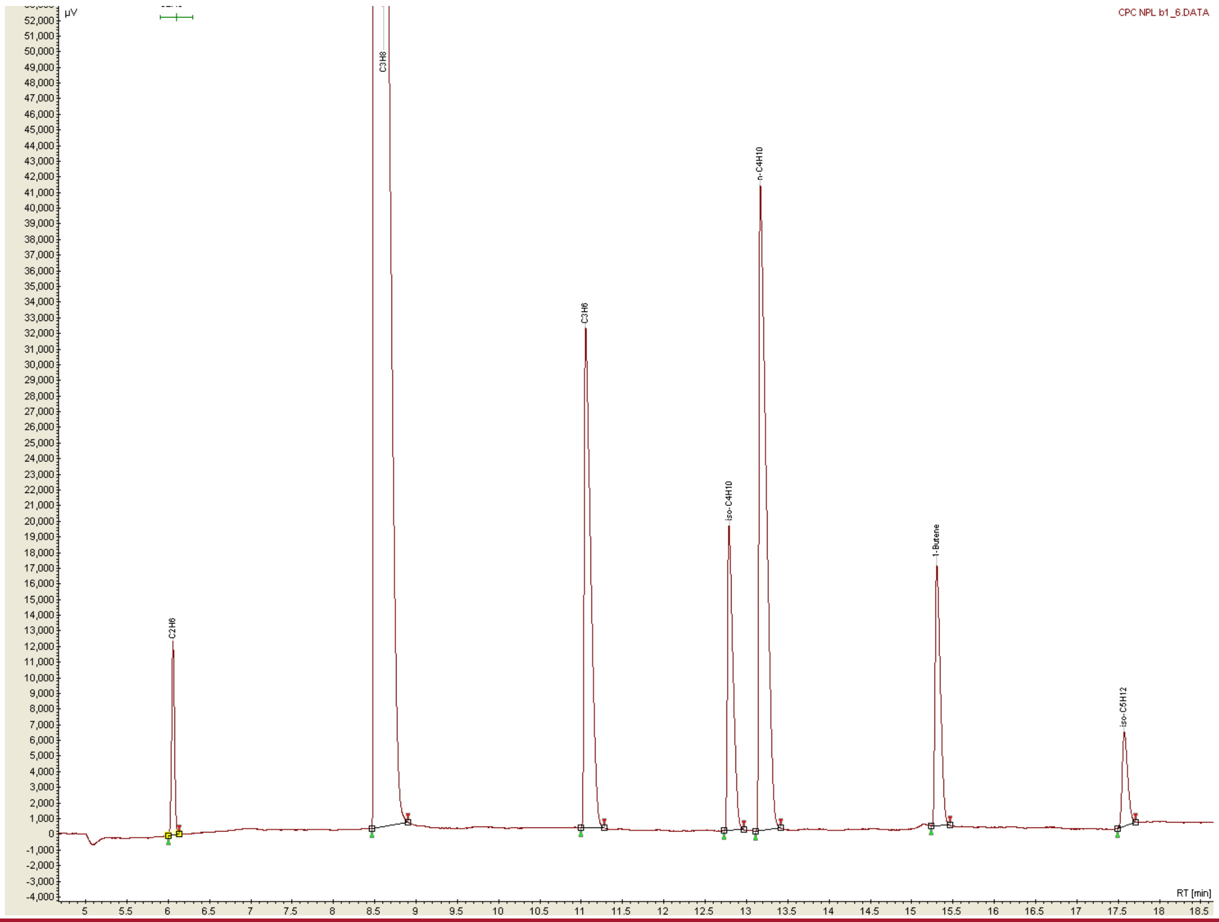
Verification and Certification
GC with alumina PLOT column to a TCD



Alumina Na_2SO_4 column

Verification and Certification
GC with alumina PLOT column to a TCD

- Preferred method on this GC



Alumina KCL column

Verification and Certification

- ***Concerns:***
  - LPG standards were made as gas mixtures in gas cylinders. Four gas mixtures were manufactured.
  - These mixtures could not be used for the certification of liquid LPG samples, as the gas samples gave biased LPG compositions
    - For one GC, this could be explained by the injection of a different volume through a gas sampling valve vs a liquid sampling valve.
    - For the other GCs using a gasifier, the difference could not be explained.

Component	Amount fraction (cmol/mol)	Amount fraction (cmol/mol)	Bias
	CPC Standard	Gas Standard	% relative
Ethane	1.81	1.54	-15
Propane	71.53	69.98	-2
Propene	8.68	7.80	-10
iso-butane	3.79	3.84	1
n-butane	10.06	10.48	4
But-1-ene	3.12	3.50	12
iso-pentane	1.02	2.99	194

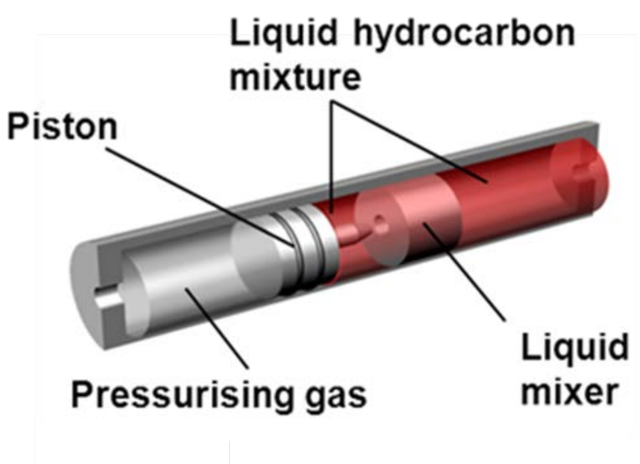
International Comparisons on Energy Gases
Key Comparison K119 on LPG

LPG – Liquefied Petroleum Gas. CCQM-K119

In mid 2015 the NMI certified an LPG mixture supplied by NPL.

Certification was against LPG standards made by the NMI in constant pressure cylinders (CPC).

Participants: NPL (UK), KRISS (South Korea), NMIA, VNIIM (Russia), VSL (Netherlands)



	Amount fraction (cmol/mol)
Ethane	2
Propane	71
Propene	9
iso-butane	4
n-butane	10
But-1-ene	3
iso-pentane	1

International Comparisons on Energy Gases Key Comparison K119 on LPG

Normalization was used.

Calculation of Uncertainty:

Component	Reference LPG (% relative)	Analysis (% relative)	Stability and Instrument Drift (% relative)
Ethane	***50***	33	17
Propane	9	82	8
Propene	23	55	21
iso-butane	26	60	14
n-butane	12	68	20
But-1-ene	19	68	13
iso-pentane	***37***	48	15

International Comparisons on Energy Gases
Key Comparison K119 on LPG

Reported results:

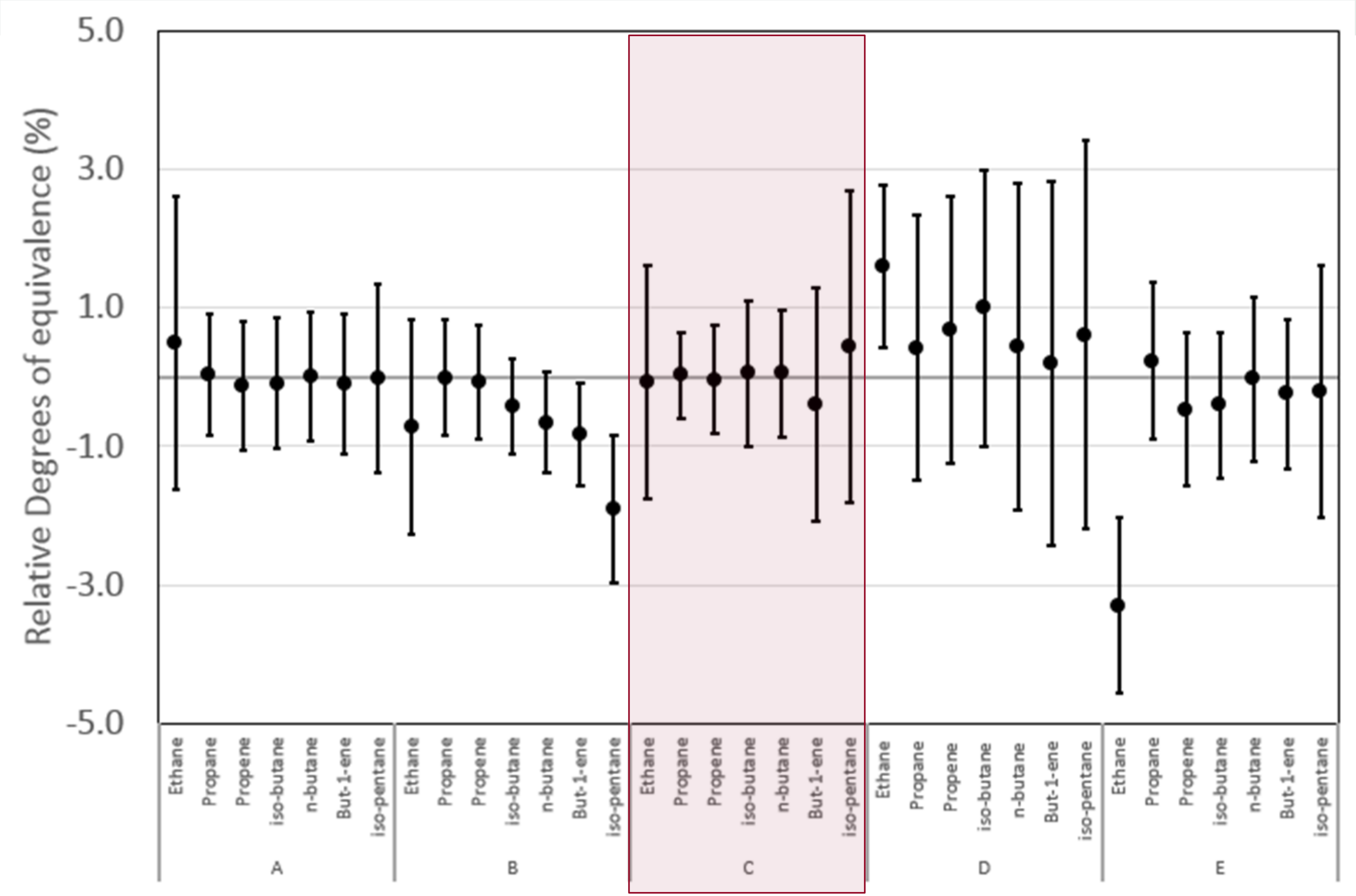
Component	Amount fraction (cmol/mol)	Expanded uncertainty (cmol/mol)
Ethane	1.814	0.028
Propane	71.531	0.257
Propene	8.676	0.051
iso-butane	3.791	0.034
n-butane	10.057	0.076
But-1-ene	3.116	0.049
iso-pentane	1.015	0.023

Concerns:

We compared our uncertainties to the values in the Euramet bilateral comparison 1195 on LPG – our measurement uncertainties were much larger than those reported in that comparison.

We were concerned that our uncertainties would be much larger than the other participants in the key comparison.

Results: Key Comparison K119 on LPG



LPG – New services

- PT studies were developed with the LNG industry.
- LPG is a bi-product of the LNG industry, along with condensate

LPG – New services

- In 2017 new PT studies for LPG will be delivered by the NMI

1. Heating (Propane)

   Q1 2017

   Composition:

   - Propane: 99.6 cmol/mol
   - Ethane: 0.2 cmol/mol
   - *n*-Butane: 0.2 cmol/mol

LPG – New services

2. Transport (Butane)

   Q3 2017

Composition:

- *iso*-Butane: 35 cmol/mol
- *n*-Butane: 62 cmol/mol
- Propane: 1.5 cmol/mol
- *n*-Pentane: 1.5 cmol/mol

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