The Benefits of Thermal Desorption Coupled with Gas Chromatography for the Analysis of Hydrocarbon Residues in Liquefied Petroleum Gas

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Liquefied Petroleum Gas (LPG) is a hydrocarbon fuel produced from the refining of natural gas or the fractional distillation of crude oil. It is primarily a mixture of propane and butane that is used for a wide variety of field and industrial applications, including a fuel for motorised transport systems, a propellant for aerosols and as a gas for refrigeration purposes. Once produced, LPG is transferred to pipelines, ocean tankers or terminal delivery systems for long-distance distribution. Once at a distribution centre, LPG is typically transferred to a bulk truck or rail car for short-haul transport to a retail plant. From there, it is distributed in cylinders or bulk trucks for delivery to the retail customer. Figure 1 represents a simplified schematic of the LPG distribution Chain [1].

The transportation and delivery of LPG can lead to potential sources of contamination, which can be harmful to engines, motorised systems or industrial processes. For example, if gasoline or diesel fuel has been used in the transportation tankers, it can result in contamination of those components in the LPG. When compressors are used to pump the LPG into pressurised tanks, the oil can contaminate the LPG. And finally, phthalates and similar plasticisers can end up in the LPG from the delivery hoses used to fill pressurised cylinders.

ASTM International (ASTM) D1835 'Standard Specification for Liquefied Petroleum (LP) Gases' [2] designates ASTM Method D2158 'Standard Test Method for Residues in Liquefied Petroleum (LP) Gases' [3], as the referee method for residue measurement. However, residue contaminants in LPG using this evaporation/gravimetric procedure does not achieve the detection limits required by industry. Besides being time consuming and labour intensive, the sensitivity of the method is not sufficient for many of the more challenging applications of LPG including fuel cells and micro turbines, which require keeping the contaminants below 20 ppm (µg/g) for the process to work efficiently. In addition, Method D2158 can

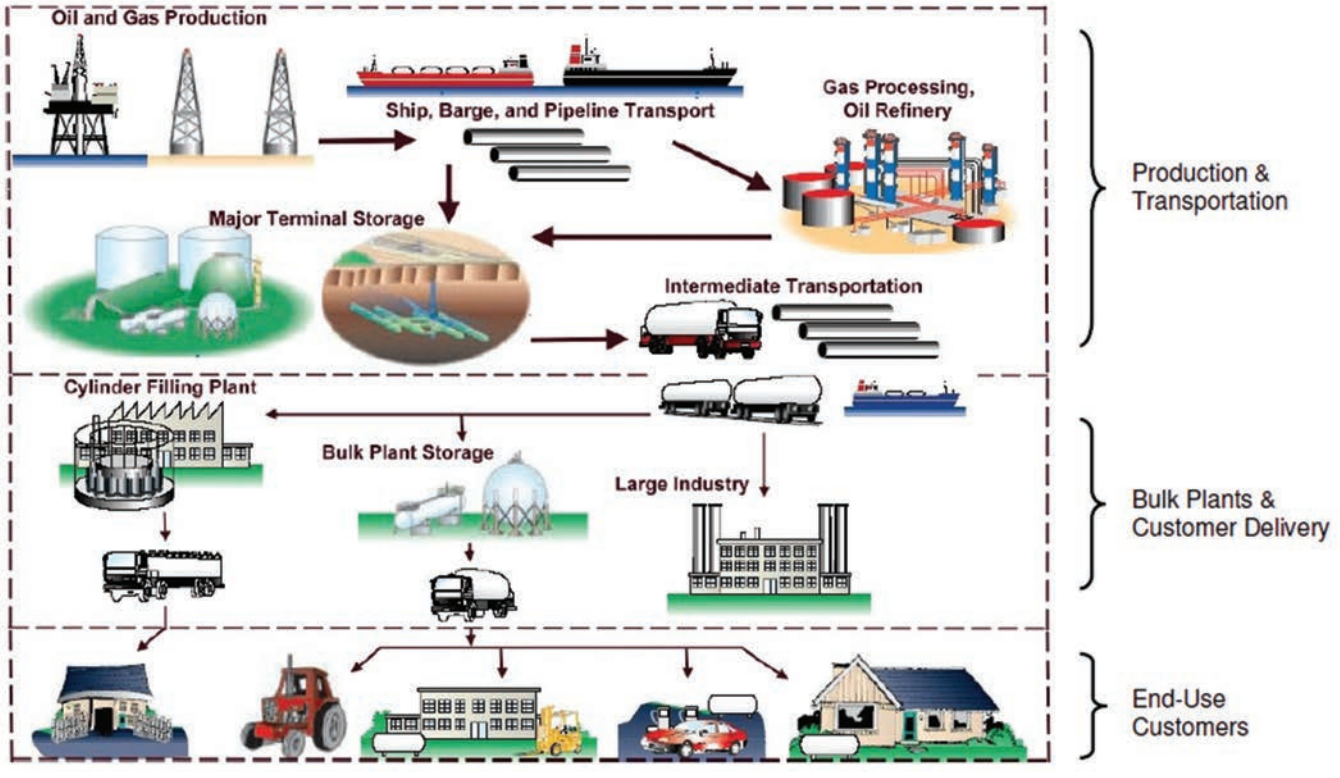

Figure 1: Simplified schematic of the LPG distribution Chain [1]

also produce inaccurate results, because low boiling point compounds are lost during the evaporation stage. In addition, the method does not generate any information about the source of the contaminating residue, which is useful for troubleshooting purposes.

This study will therefore describe a new method using Automated Thermal Desorption (ATD) coupled with gas chromatography (GC), for the measurement of residue in LPG down to 5µg/g, as well as yielding the hydrocarbon range of the contaminants, to give an understanding about the source of contamination. This methodology has since become a new ASTM Method D7828, 'Standard Test Method for Determination of Residue Composition in Liquefied Petroleum Gas (LPG) Using Automated Thermal Desorption/Gas Chromatography (ATD/GC)' [4].

Standard Test Method for Residues in Liquefied Petroleum Gases

ASTM D1835 states that besides the four main constituents of, methane, ethane, propane and butane, the residue contaminants, particularly longer chain hydrocarbons C_6-C_{40}, should be kept to an absolute minimum, because they can lead to problematic deposits in liquid feed and vapour withdrawal systems utilised in end-use applications of LPG. These residues also have the potential to be carried over and can foul up regulating equipment, and over time, the ones that remain can accumulate, and could contaminate additional components.

ASTM Method D2158 involves taking a 100-mL sample of liquefied petroleum gas, which is evaporated at 38°C in a customised centrifuge tube, cooled with a condensing coil and cooling bath. The volume of residue remaining is weighed, measured and recorded. This test method has been used to verify heavy contaminants in propane and LPG products for many years. However, in addition to being time-consuming, labour-intensive, and often dangerous with harmful vapours escaping into the atmosphere, the test has precision limitations. Therefore, besides not being sensitive enough to protect some equipment from operational problems or increased maintenance, it also cannot identify the source of residue.

In fact, D2158 states that if the LPG is specifically being used for certain applications such as micro turbines, a new electricity generation technology being designed for stationary energy applications, or fuel cells, which are used to convert hydrogen/hydrocarbon gases into electricity using proton exchange membrane (PEM) technology, a more sensitive test is required. It has been estimated that to use LPG for these kinds of applications, a residue detection capability of < 20 µg/g is required in order to ensure the efficiency and trouble-free operation of the technology.

Thermal Desorption Coupled with Gas Chromatography

To meet the detection requirements of these innovative new technologies, it was decided to investigate the use of Thermal Desorption (TD) coupled with Gas Chromatography (GC) and flame ionisation detection (FID). The objectives of the study were to:

- Achieve acceptable recoveries of hydrocarbons from C_6 to C_{40}
- Not retain compounds lighter than C_6 to minimise interferences
- Ensure the pressurised LPG enters the tube as a liquid
- Achieve a detection capability of less <10µg/g and a dynamic range of 3 orders of magnitude
- Prove accuracy through an LPG quality control sample
- Attain acceptable repeatability
- Offer the potential of identifying the individual residue component or hydrocarbon profile for troubleshooting purposes
- Enable sampling in the field, so the sorbent tubes can be sent to a laboratory for analysis, saving significant transportation costs associated with shipping pressurised cylinders
- Reduce costs associated with cleaning (labour and solvents) and purchasing cylinders
- Make it rugged enough to be a standardised ASTM method

Thermal desorption is well-recognised as being an accurate and precise technique for the sampling and analysis of volatile and semi-volatile compounds by gas chromatography. It has become the industry standard for analysing soil gases, studying healthy building syndrome, fenceline monitoring, indoor/outdoor air analysis as well as addressing industrial hygiene concerns [5]. Sorbent tubes are small and light, making them easy to transport, and when applied to LPG samples at a remote site, it can result in reduced shipping costs compared to other sampling techniques. In addition, the tubes are easily cleaned during the desorption process, rendering them available for immediate re-sampling, which can be verified with a rapid GC analysis.

Summary of New Methodology

A sample of LPG is captured on a sample loop, which is maintained at a pressure above its bubble point as it is released directly onto the hydrocarbon selective absorbent tube material, thereby trapping the C_6- C_{40} hydrocarbon residue. After the sorbent tube is sampled, it is brought or shipped to the laboratory for analysis by

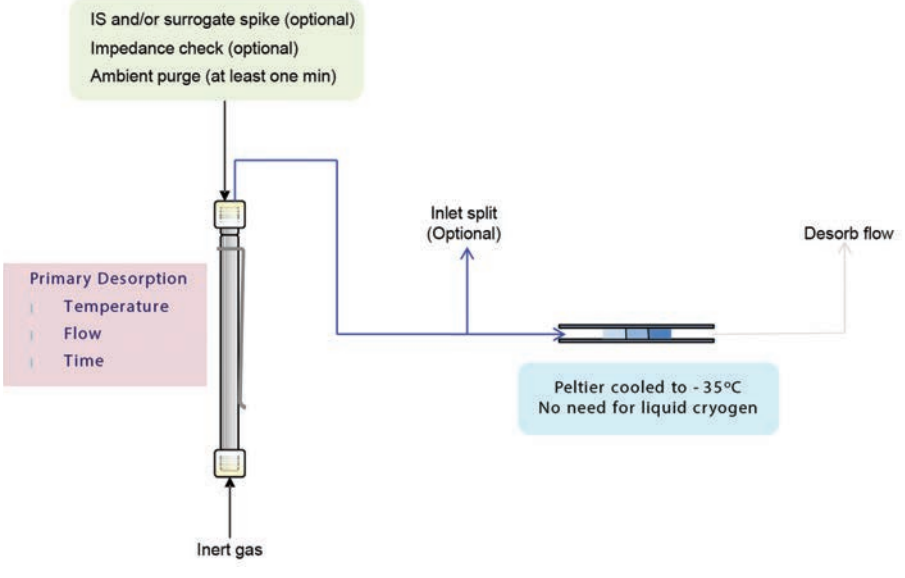

Figure 2: Sample Tube Primary Desorption

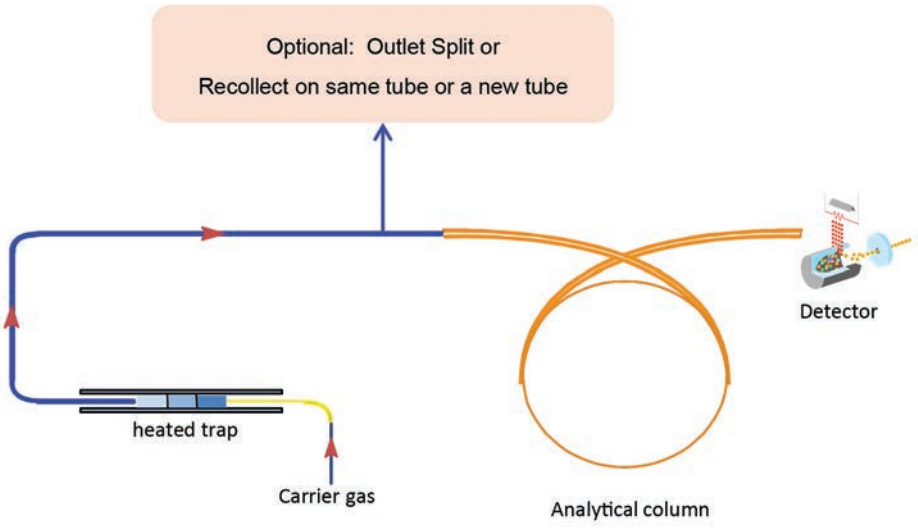

Figure 3: The secondary desorption step

Sample Tube	Desorb for 18 min @ 375°C @ 30mL/min
Concentrator Trap	Trap Low 5°C; Trap high 380°C; Trap Hold 14min
Pneumatics	inlet split 50mL/min; Outlet split 30mL/min; Column flow 0.8mL/mim
Purge	Purge for 3min @ ambient temp @ 50mL/min
Transfer Line	290°C
Valve Temp	260°C
GC Cycle Time	34 min

Table 1: Thermal Desorber Parameters

Column	non-polar stationary phase 100% dimethyl polysiloxane: dimensions 20 m × 0.18 mm × 0.2 µm was used in this research
Carrier Flow Rate	0.4mL/min
Oven	35°C for 4min, ramp 15°C/min to 230°; ramp 10°C/min to 330°C and hold for 3min
GC Run Time	30 min
Detector temp	340°C

Table 2: Gas Chromatographic Parameters

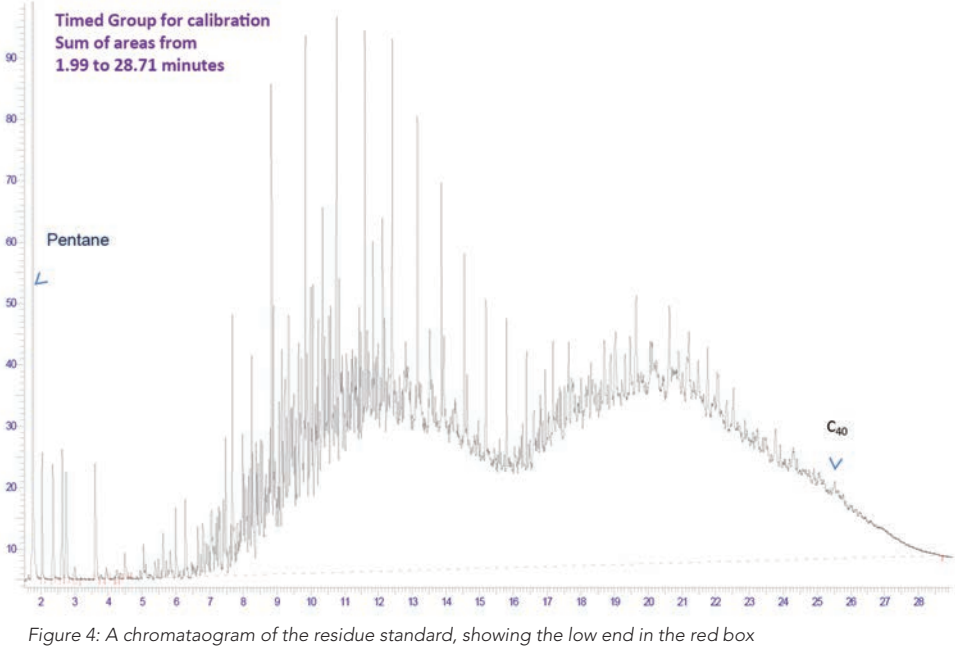

Figure 4: A chromataogram of the residue standard, showing the low end in the red box

ATD/GC/FID. The tubes are placed on the autosampler and the operator starts the instrument, which initiates the process of moving the tube from the carousel into the primary desorption flow path. This process is shown schematically in Figure 2.

The residue is desorbed from the sorbent tube using heat, inert gas flow and time. The effluent from the tube is focused onto a secondary (cold) trap. After residue recovery from the tube to the focusing trap is complete, the trap heats very rapidly to volatilise the components from the trap and the inert gas flow brings the effluent onto the analytical column of the gas chromatograph for separation and onto the FID for detection. This secondary desorption step is exemplified in Figure 3.

This acquired (raw) data is stored in the data handling system for processing. The processing method, which contains the response factor (RF) and integration parameters from standards previously analysed, is applied to the sample, and the mass of residue in the sample is calculated.

Operating Conditions

Parameters for the thermal desorption process are shown in Table 1, while the GC operating conditions are shown in Table 2.

Recovery Validation

The performance comparison between direct injection into a split/splitless (S/SL) injector port and an injection into the ATD was investigated to ensure recovery of the residue boiling point range by the ATD and to validate the sorbent tube injection technique. The inlet injection method was carried out by injecting a standard directly into the split/splitless injector of the GC, while with the thermal desorption technique, this standard was spiked onto a tube, and the analytes were desorbed onto the GC column. The results of the two injection techniques were compared.

To ensure recovery with no discrimination, a hydrocarbon standard was prepared representing the residue range. This is considered a recognised and valid test, since these targets have approximately the same response factor in an FID at the same component concentration. Percent (%) recoveries of the conventional liquid injection technique compared to thermal desorption are shown in Table 3, using the response factor for C_{22} as a reference. It

can be seen that there is no discrimination (within experimental error) using the ATD approach for this residue range.

Calibration and Chromatographic Separation

To cover the full residue range, a calibration standard containing a mixture of hexane, heptane, iso-octane, and toluene was used for the lower boiling point region (gasoline range), while diesel was used for the mid-range and compressor oil was used for the higher boiling point region.

In order to demonstrate that the gasoline surrogate components could be separated from each other and in particular, that the hexane could be separated from pentane, and the diesel and compressor groups were distinquishable, a chromatogram of the residue standard containing the gasoline surrogate components, diesel and compressor oil was collected using the set up previously described. This was done by making up a stock solution in pentane and then diluting with LPG in a cylinder. The chromatogram of the residue standard is shown in Figure 4, while an expanded view of the low end (red box) showing the lighter components is seen in Figure 5. It can be clearly seen that the pentane peak is well resolved from hexane, and there is also no interference from propane or butane.

A calibration plot was then generated by transfering fixed amounts of the standard residue dissolved in pentane onto the sorbent tubes, which represented 11 concentrations in total, ranging from 3 to 1500 µg. Figure 6 shows this calibration plot, which gave a correlation coefficient of 0.9990. For calibration, a timed group area of the residue is used as shown in Figure 4, which is the response of each standard, taken from the time immediately after the elution of pentane (C_5) through to the end of the elution of the compressor oil (C_{40}).

Breakthrough Experiment

The prevention of breakthrough is a very important aspect of any adsorbent. According to the EPA, it is defined as the volume sampled when the amount of analyte collected in a backup sorbent tube reaches 5% of the total amount collected by both sorbent tubes (6). Therefore a breakthrough experiment was performed to ensure the adsorbent was able to retain the target analyte range of residue, by connecting two sorbent tubes together while sampling the LPG. If breakthrough does not occur, the

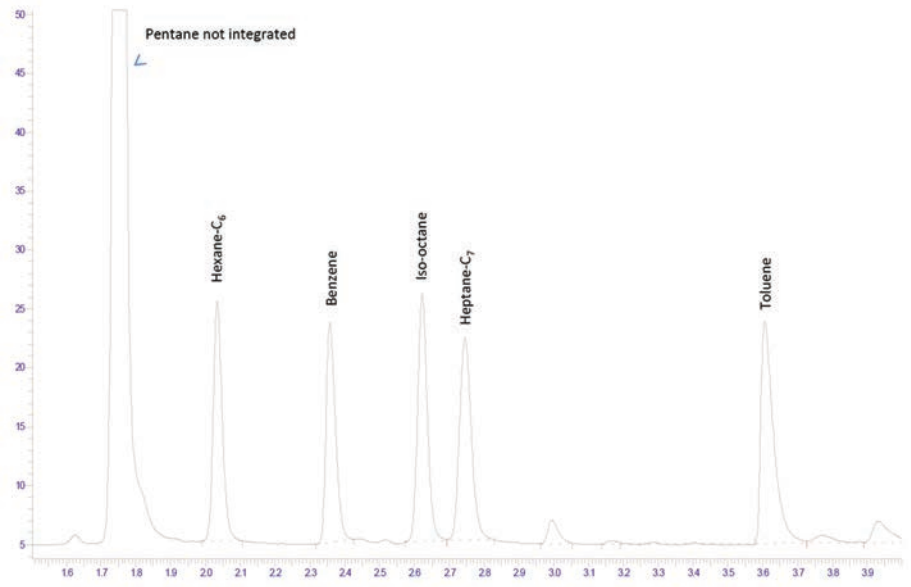

Figure 5: An expanded view of the low end (red box) showing the ligher hydrocarbon components are well-separated from the pentane solvent (for safety reasons, benzene was used for separation purposes, but not for calibration)

	Liquid Injection	Thermal Desorber Injection
Compound	% Recovery	% Recovery
n-Hexane	99.8	94.2
Iso-octane	105.2	99.5
n-Heptane	104.3	100.3
Toluene	113.2	104.2
C_{22}	100.0	100.0
C_{30}	108.9	112.2
C_{36}	105.7	106.9
C_{40}	105.5	102.7

Table 3: Recoveries (%) of the hydrocarbon standard using conventional liquid injection compared to thermal desorption.

second tube in line will be blank (or less than 5%) because the front tube was able to retain the residue. Figure 7 exemplifies the result from that breakthrough experiment. The chromatogram of the first tube is seen in black, which shows all the residue hydrocarbon peaks. Whereas the chromatogram of the second tube is seen in blue, which shows an absence of all the signature peaks except for the pentane

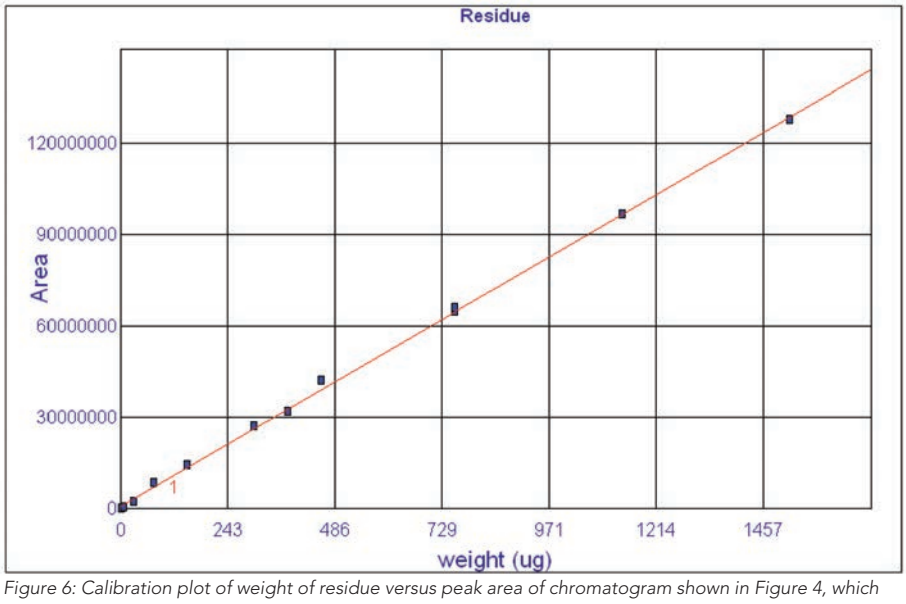

Figure 6: Calibration plot of weight of residue versus peak area of chromatogram shown in Figure 4, which gave a correlation coefficient of 0.9990

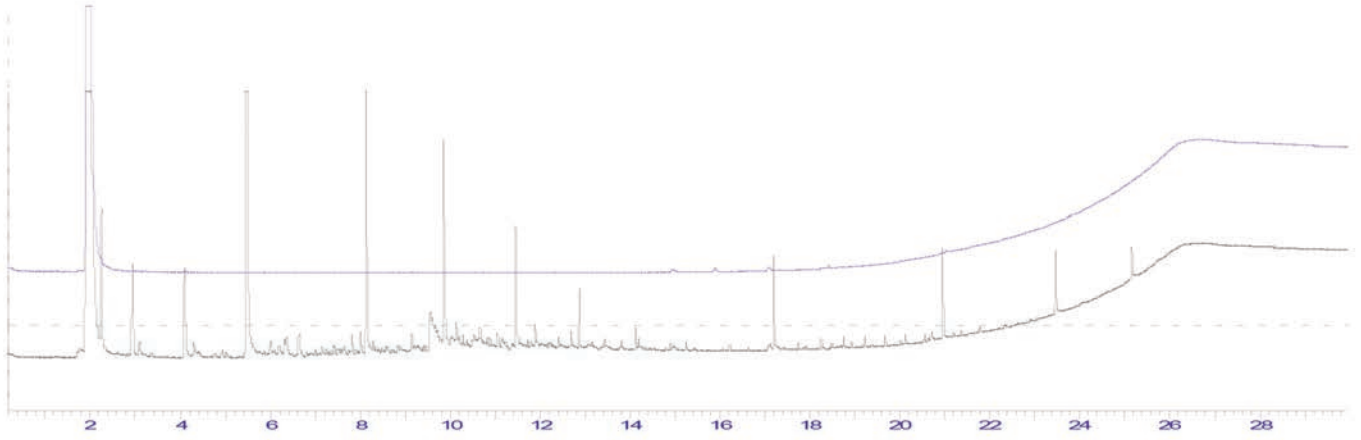

Figure 7: Result of the breakthrough experiment, showing no significant residue was in the 2nd thermal desorption rube

solvent. This demonstrates that non-detectable breakthrough of the residue occurred even for hexane, the most volatile component.

Quantitative Results

There are no certified reference materials (CRM) for the quantitation of hydrocarbon residue (C_6 plus) in LPG; therefore, a Quality Control (QC) sample was prepared in LPG and quantitated from the calibration curve created in pentane. To demonstrate the accuracy and precision of this new gas chromatography method and sampling technique, six separate injections of the QC standard were made onto six tubes, and the masses recorded. The results in µg/g in the LPG are shown in Table 4. The accuracy (% deviation) is demonstrated by the difference between the actual and the calculated result, while the repeatability of the injection technique and method is shown by the average of the six results and the standard deviation. Based on this data set, it can be seen that the recoveries are all very acceptable, while the detection limit for total residues in LPG is on the order of 10 µg/g. However, it was observed that there was a slight loss in targets above C_{34} (diesel and compressor oil) for the results using LPG as the solvent, which can be explained by pentane having greater solvation capability for these high boiling point components

Analyte		Hexane			Iso-Octane			Heptane		
	LPG Sample Weight (g)	Calculated Amount (µg/g)	Actual Amount (µg/g)	% Dev	Calculated Amount (µg/g)	Actual Amount (µg/g)	% Dev	Calculated Amount (µg/g)	Actual Amount (µg/g)	% Dev
	0.4088	2.00	1.8	11.1	1.6	1.6	0	1.7	1.7	0.00
	0.4140	2.06	1.8	14.4	1.6	1.6	0	1.7	1.7	0.00
	0.4317	1.93	1.8	7.2	1.5	1.6	-6.25	1.6	1.7	-5.88
	0.4269	2.00	1.8	11.1	1.5	1.6	-6.25	1.7	1.7	0.00
	0.4274	1.98	1.8	10.0	1.5	1.6	-6.25	1.7	1.7	0.00
	0.4143	2.00	1.8	11.1	1.5	1.6	-6.25	1.7	1.7	0.00
Std Dev	0.0093	0.0418			0.0516			0.0408		
Average	0.4205	1.9950			1.5333			1.6833		
% RSD	2.21	2.10			3.37			2.43		
		Toluene			Diesel and Compressor Oil					
	LPG Sample Weight (g)	Calculated Amount (µg/g)	Actual Amount (µg/g)	% Dev	Calculated Amount (µg/g)	Actual Amount (µg/g)	% Dev			
	0.4088	1.8	1.8	0.0	114	132	-14			
	0.4140	1.8	1.8	0.0	113	132	-14			
	0.4317	1.7	1.8	-5.6	102	132	-23			
	0.4269	1.7	1.8	-5.6	107	132	-19			
	0.4274	1.7	1.8	-5.6	104	132	-21			
	0.4143	1.8	1.8	0.0	108	132	-18			
Std Dev	0.0093	0.0548			4.7749					
Average	0.4205	1.7500			108					
% RSD	2.21	3.13			4.4					

Table 4: Quantitative data for six separate tube injections of a QC sample made in LPG

compared to LPG.

Investigating the Source of Residue Contamination

As mentioned previously, an added benefit of gas chromatography/FID is that it provides information of the hydrocarbon range of the residue, which can then be used as a troubleshooting tool to investigate the source of the contamination. For this part of the study, an investigation was carried out to determine if there are losses or discrimination of the light boiling point contaminants of the residue by Method D2158 which could lead to erroneous data. This was done by taking the residue material in the graduated tube left over from Method D2158, dissolving it in a solvent and analysing it by GC/FID via liquid injection. The resultant chromatogram is shown on the left in Figure 8. The same sample was also analysed by this new gas chromatography method. However, instead of an FID, the analysis was performed by GC-MS so that specific components, such as the phthalates and other compounds, could be identified with a high degree of certainty. It's important to emphasise that the hydrocarbon profile using GC-MS will be consistent with FID detection. The total ion chromatogram (TIC) is displayed on the right of Figure 8. The results of this experiment demonstrate the discrimination of the lighter components using Method D2158 which could possibly lead to inaccurate results. In addition, it will not provide the speciation data available with the chromatographic method.

Conclusion

All objectives of the thermal desorption investigation have been met, with good accuracy, precision, recoveries and detection capability being achieved for all hydrocarbons from C_6 to C_{40} on a single tube. Additionally, it has been shown that there are no interferences of compounds below C_5 since the majority of C_5 minus is not retained thus allowing for the quantitation of C_6 plus. It offers the added benefit of the tubes being portable and very easy to transport back to the lab for analysis. This means remote sampling in the field can be carried out with more convenience and safety and, as discussed, a more cost effective solution than the traditional way of sampling LPG cylinders. As a result, this methodology has proved itself to be rugged enough that it is now been designated as ASTM Method D7828. Additionally, if there is a need to detect lower levels below 10 µg/g, the ASTM test method can be modified to achieve a 50x enhancement, or a detection capability of 0.2 µg/g.

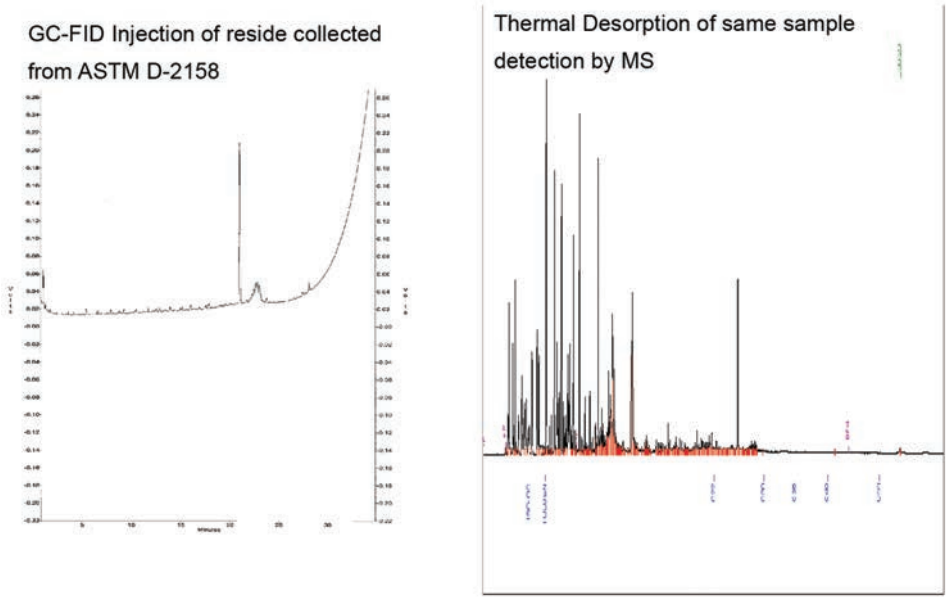

Figure 8: Comparison of the chromatogram of a GC injection of the residue after the evaporation procedure described in ASTM Method D2158 (left) and a chromatogram of the thermal desorption sample introduction approach of the same sample measured by GC-MS (right)

Acknowledgement

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Further Reading

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