method for monitoring exposure to LPG containing small amounts of 1,3-butadiene

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ABSTRACT

The validation of a sampling and analytical methodology is described for occupational exposure monitoring of liquefied petroleum gas (LPG) and its components including trace amounts of 1,3-butadiene. A detailed sampling and analytical method is included.

KEYWORDS

Liquefied petroleum gas, LPG, 1,3-butadiene, occupational exposure, monitoring method

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SUMMARY

A detailed method for the analysis of exposure to liquefied petroleum gas (LPG), including identification and quantification of single constituents, was required by CONCAWE to support LPG substance risk assessment. The single constituent of primary concern is 1,3-butadiene due to its carcinogen classification. 1,3-butadiene may be present in certain LPGs in small amounts.

The exposure monitoring method first selected was derived from the approach taken for gasoline vapour as described in CONCAWE report 8/02. Laboratory tests indicated however poor recovery of 1,3-butadiene from the adsorbent used for sampling. An alternative sorbent was tested and showed acceptable performance.

A detailed sampling and analytical method is provided as an appendix.

1.   INTRODUCTION AND SCOPE

Liquefied petroleum gas (LPG) is a mixture of mainly C_3 and C_4 hydrocarbons, and may contain trace amounts of several impurities, including 1,3-butadiene. For the purpose of substance risk assessment for LPG it may be necessary to conduct exposure monitoring in certain scenarios. Some exposure monitoring has been conducted in the past by CONCAWE member companies, however an agreed validated method did not appear to exist. From an oil product risk assessment perspective, it is important that the exposure monitoring methodology is adequate for quantification of the total substance, as well as important constituents from a toxicological point of view, in this case 1,3-butadiene. Work undertaken on the exposure monitoring method for gasoline vapour indicated that a suitable sorbent for C_3 and C_4 hydrocarbons might be Carbosieve SIII [1].

The method for gasoline vapour involves pumping a small flow of (workplace) air through a tube placed in the operator's breathing zone. The tube contains a sorbent which traps the gasoline vapour constituents. During analysis the gasoline vapour constituents are removed from the sorbent by a hot gas flow (thermal desorption) and analysed and quantified using gas chromatography with flame ionisation detection. A similar approach was envisaged for LPG.

Storage trials using 1,3-butadiene were conducted with the gasoline vapour method that showed decreasing recoveries, with storage times of up to 4 weeks and depending also on butadiene loading concentrations, to levels that do not satisfy standard performance requirements.

The storage trials were therefore repeated using Carbopack-X, a sorbent that had given good results for 1,3-butadiene in other trials. Storage of 1,3-butadiene for periods up to 4 weeks satisfied performance requirements.

Carbopack-X tubes were found to be suitable for the sampling of n-butane and other C_4 hydrocarbons but not for sampling propane. If this analyte is required then a sorbent tube combination of a Carbopack-X sampling tube in series with a Carbosieve SIII sampling tube should be used.

This report provides an overview of the method validation work conducted for LPG exposure monitoring and its results. Detailed results and a method statement are included as appendices.

2. MATERIALS AND METHODS

Initial work involved the validation of storage of 1,3-butadiene on sampling tubes containing Carbosieve SIII. The work was conducted in phases, advancing to the next phase only when a phase had been completed satisfactorily (**Appendix 1**). Sorbent tubes were spiked with 1,3-butadiene as described in **Appendix 2**. Experiments were conducted at a relative humidity of approximately 50%. Samples were loaded at an air flow rate of 50 ml/min.

Phase 1 - Initial checks and thermal desorption efficiency

The gas chromatographic retention time of 1,3-butadiene, n-propane and n-butane together with possible interferences in LPG were determined to ensure that no co-elution with 1,3-butadiene was occurring. Samples of LPG were analysed before being spiked with 1,3-butadiene to confirm that no co-elution was present. All the major peaks in the LPG sample were identified.

Two sets of 12 tubes were loaded with 1,3-butadiene, one with 56 μg 1,3-butadiene and the other set with 100 μg. The tubes were each desorbed three times in succession. The areas of the 1,3-butadiene peak were summed and the percentage of 1,3-butadiene on each desorption calculated.

Two sorbent tubes were connected in series and 25 litres of standard atmosphere sampled. Both tubes were desorbed to see if breakthrough had occurred.

Phase 2 - Stability study - 1,3 Butadiene only

The stability of 1,3-butadiene only was evaluated in Phase 2. The calibrant gas was 500 ppm v/v 1,3-butadiene in nitrogen. The sets of samples described below were prepared. Alternate samples from the gas loading rig were taken for each storage set. One set was stored at ambient temperature (20°C) whilst the other set was stored in a refrigerator (below 4°C). At the end of each storage period the samples were analysed by gas chromatography after thermal desorption. Calibration standards were prepared from the same standards cylinder of calibrant, the range of weights of 1,3-butadiene on the standard tubes being adjusted to cover the weights on the sample tubes. Repeat determinations were performed for two storage sample sets to check reproducibility.

12 tubes at 6 μg, to be kept for 28 days
12 tubes at 56 μg, to be kept for 28 days
12 tubes at 56 μg, to be kept for 14 days
12 tubes at 56 μg, to be kept for 7 days
12 tubes at 90 μg, to be kept for 28 days
12 tubes at 90 μg, to be kept for 14 days
12 tubes at 90 μg, to be kept for 7 days

Phase 3 - Breakthrough - 1,3 Butadiene only

Carbosieve SIII tubes, fitted with identical back-up tubes were loaded with 550 μg 1,3-butadiene by pumping 25 litres of 0.88 mg/m^3 1,3-butadiene in nitrogen at a rate of 100 ml/min. When analysis showed that breakthrough had occurred the test was repeated with the back-up tubes being changed on a regular basis.

Phase 2A - Stability study - 1,3 Butadiene only

When the analysis showed that storage stability of 1,3-butadiene on Carbosieve SIII did not satisfy standard performance requirements the stability study was repeated using Carbopack-X sorbent. The samples were prepared exactly as described in Phase 2. Repeat determinations were performed at one level to check reproducibility.

Phase 3A - Breakthrough - 1,3 Butadiene only

Using the Controlled Atmosphere Test Facility described in **Appendix 2** the breakthrough volume for 1,3-butadiene on Carbopack-X was determined.

Phase 4 - Stability study - Mixed gas

The stability of 1,3-butadiene in LPG was evaluated in Phase 2. Samples were prepared utilising the gas loading rig described in **Appendix 2**. The calibrant gas was 1,3-butadiene (~500 ppm), n-propane and n-butane in nitrogen (~2.5% each) in nitrogen. Preliminary trials were undertaken to establish if the large excess of propane and n-butane in the calibrant had an effect on the retention of 1,3-butadiene. When it was established that this was indeed the case the sample testing programme was modified; 10 µg 1,3-butadiene being loaded onto the sorbent tubes for storage evaluation. As before alternate samples from the gas loading rig were taken for each storage set. One set was stored at ambient temperature (20°C) whilst the other set was stored in a refrigerator (below 4°C). At the end of each storage period the samples were analysed as described in Section 11. Calibration standards were prepared from the same standards cylinder of calibrant, the range of weights of 1,3-butadiene on the standard tubes being adjusted to cover the weights on the sample tubes. Repeat determinations were performed at each level to check reproducibility. The sample sets used were:

12 tubes 10 μg of 1,3-butadiene using mixed gas standard, to be kept for 28 days
12 tubes at 10 μg of 1,3-butadiene using mixed gas standard, to be kept for 14 days
12 tubes at 10 μg of 1,3-butadiene using mixed gas standard, to be kept for 7 days

Phase 5 – Breakthrough test with mixed gas

As phase 3 but using a mixture n-propane, n-butane and 1,3-butadiene in nitrogen as a surrogate LPG.

3.   RESULTS

Gas chromatographic analysis of the LPG sample and subsequent analysis of a sample spiked with 1,3-butadiene showed that 1,3-butadiene did not elute with any other analyte. Desorption efficiency tests with Carbosieve SIII showed that >99.5% of the loaded 1,3-butadiene was desorbed during the first desorption. Analysis of the linked tubes, loaded using an atmosphere of 0.088 mg/m^3 showed that all the loaded analyte was retained on the first tube. Subsequent loading tests using an atmosphere of 0.88 mg/m^3 1,3-butadiene showed that breakthrough occurred between 330 and 380 litres.

Analysis of the storage stability samples showed that losses of 1,3-butadiene occurred in the monitoring tubes (**Appendix 3**). The losses increased as the storage duration increased and were also higher for the samples that were stored at ambient temperature than for those stored in a refrigerator. For 56 µg samples stored for 7 days the average recovery from samples stored cold was 92.92% whilst for samples stored at ambient temperature the average recovery was 82.97%. When the samples were stored for 28 days the average recoveries from cold and ambient stored samples were 66.27% and 51.85% respectively. The results from the 90 µg samples showed a similar pattern, although the recoveries were slightly higher than those obtained from the 56 µg samples.

As the storage of Carbosieve SIII samples did not satisfy standard performance requirements [2] another sorbent, Carbopack-X that had been showing promise in other trials was investigated. The series of storage tests was repeated. Recoveries of 1,3-butadiene from stored samples of this sorbent were significantly improved (**Appendix 4**). The 56 µg samples showed no significant difference between the recoveries for both the cold and the ambient samples for all storage periods. All recoveries were in excess of 95%. The 90 µg samples gave better than 95% recoveries for the 7 and 14 day storage period for both cold and ambient samples. Storage of 1,3-butadiene for 28 days gave recoveries of 89.5% for cold samples and 87.2% for samples stored at ambient temperatures. Two batches of Carbopack-X were tested giving essential similar results.

Storage of 1,3-butadiene in LPG produced similar results (**Appendix 5**). 10 µg 1,3-butadiene was loaded onto several batches of Carbopack-X tubes. Recoveries better than 95% were on average obtained for storage durations of 7 and 14 days for both cold and ambient storage. As was found with 1,3-butadiene on its own storage for 28 days resulted in increased losses, recoveries of about 90% being found for both cold and ambient storage.

All average results of the storage experiments with both sorbents are presented graphically in **Appendix 6**.

Appendix 7 presents the results of breakthrough experiments with a mixture of 1,3-butadiene (12.7 mg/m^3), propane and n-butane (2.5% each) as a surrogate LPG. These tests gave rise to the observation that propane broke through the Carbopack-X very easily and thus would not be quantitatively retained, necessitating a back-up of Carbosieve SIII or similar carbon molecular sieve. Selected results presented in **Appendix 7** for 1,3-butadiene and n-butane show that approximately 18 µg of 1,3-butadiene can be retained on the Carbopack-X tubes when presented as a mixture. At that point n-butane was seen breaking through in some of the tubes.

A detailed sampling and analytical method was prepared and is included as **Appendix 8**. The principles and format of the method are similar to a generic European standard EN ISO 16017:1 of November 2000 for sampling and analysis of volatile organic compounds in indoor, ambient and workplace air [3]. The limit of detection for 1,3-butadiene was set at three times the analytical noise level or 0.5 µg per sample tube, corresponding to an ambient concentration of 0.05 mg/m^3 for a 10-litre air sample.

4.   CONCLUSIONS

1.   Carbopack-X is the preferred sorbent for pumped sampling of LPG containing small amounts of 1,3-butadiene.

2.   Exposed tubes should be stored cold and preferably analysed within two weeks of exposure.

3.   If quantitation of propane and n-butane are required Carbopack-X and Carbosieve SIII tubes in series should be used.

5. REFERENCES

1.   CONCAWE (2002) Method for monitoring exposure to gasoline vapour in air - revision 2002. Report No. 8/02. Brussels: CONCAWE

2.   CEN (2000) General requirements for the competence of testing and calibration laboratories. EN ISO/IEC 17025. Brussels: Comité Européen de Normalisation

3.   CEN (2000) Indoor, ambient and workplace air – sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 1: Pumped sampling. EN ISO 16017-1. Brussels: Comité Européen de Normalisation

APPENDIX 1

VALIDATION PROTOCOL OF CARBOSIEVE S-III FOR ANALYSIS OF 1,3-BUTADIENE IN LPG

Phase 1 - Initial checks and thermal desorption efficiency

- Set up and determine the retention time (RT) of 1,3-butadiene (BDE) and components in Propane and Butane gas standards. Identification of any peaks interfering with that of BDE and optimise conditions as necessary. Check area obtained for BDE to that for n-Butane.
- Obtain LPG sample and spike with BDE to ascertain that BDE can be separated from other components present.
- Order standard, containing Propane and n-Butane (50/50) and trace amount BDE. Concentration to be finalised in consultation with CONCAWE (typically 0.1-1%).
- Determine thermal desorption efficiency (DE) by analysing 10 freshly spiked tubes, 3 times each to determine remainder left on tube after desorption. Perform at two levels - 56 μg and 100 μg.
- If phase 1 is successful move onto phases 2 and 3.

Phase 2 - Stability study - 1,3-Butadiene only

- Cleaning and spiking of tubes for stability study. Samples to be analysed with 6 freshly spiked tubes. Half of each batch to be refrigerated and the other half stored at room temperature
    - 12 tubes at 6 μg using BDE, to be kept for 28 days
    - 12 tubes at 56 μg (25 litre*2.2 μg) using BDE, to be kept for 28 days
    - 12 tubes at 56 μg using BDE, to be kept for 14 days
    - 12 tubes at 56 μg using BDE, to be kept for 7 days
    - 12 tubes at 90 μg using BDE, to be kept for 28 days
    - 12 tubes at 90 μg using BDE, to be kept for 14 days
    - 12 tubes at 90 μg using BDE, to be kept for 7 days

Phase 3 - Breakthrough - 1,3-Butadiene only

- Spike 6 tubes, with back-up tubes, with mixed standard with amount equivalent to 550 μg (25 litre*22 μg) of BDE.
- Draw through known amounts of lab air. Analyse and alternate backing tubes to determine if breakthrough has occurred.
- If phases 2 and 3 are successful move onto phases 4 and 5.

Phase 4 - Stability study - Mixed gas

- Cleaning and spiking of tubes for stability study. Samples to be analysed with 6 freshly spiked tubes. Half of each batch to be refrigerated and the other half at room temperature
    - 12 tubes 6 μg of BDE using mixed gas standard, to be kept for 28 days
    - 12 tubes 56 μg (25 litre*2.2 μg) of BDE using mixed gas standard, to be kept for 28 days
    - 12 tubes at 56 μg of BDE using mixed gas standard, to be kept for 14 days
    - 12 tubes at 56 μg of BDE using mixed gas standard, to be kept for 7 days
    - 12 tubes at 90 μg of BDE using mixed gas standard, to be kept for 28 days
    - 12 tubes at 90 μg of BDE using mixed gas standard, to be kept for 14 days
    - 12 tubes at 90 μg of BDE using mixed gas standard, to be kept for 7 days

Phase 5 - Breakthrough - Mixed gas

- Spike 6 tubes, with back-up tubes, with mixed standard with amount equivalent to 550 μg (25 litre*22 μg) of BDE.

Draw through known amounts of lab air. Analyse and alternate back-up tubes to determine if breakthrough has occurred.

APPENDIX 2

CONTROLLED ATMOSPHERE TEST FACILITY (CATFAC)

The CATFAC is an aerodynamic wind tunnel at NPL that was employed to generate VOC traceable atmospheres (including 1,3-butadiene) at specified known concentrations. Determination of the VOC concentrations employed gas chromatography together with NPL primary gravimetric gas standards for calibration the concentration. The table below summarises the wider range of environmental conditions that are available in the Facility.

Summary of Environmental Parameters

Environmental Parameter	Range
Temperature	5°C to 40°C
Humidity	0% to 80% Relative Humidity
Wind Speed	0 $m.s^{-1}$ to 5 $m.s^{-1}$
Flow Conditions	Laminar or Turbulent

Pumped samplers, connected to dedicated ports on the CATFAC, were used to determine the breakthrough volume for 1,3-butadiene on Carbopack-X sorbent.

APPENDIX 3

STORAGE RESULTS FOR 1,3-BUTADIENE LOADED ONTO TUBES CONTAINING 700 mg CARBOSIEVE SIII

Table A3.1   **Experiment at loading level 6 μg stored for 28 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	μg	μg	%	%
Cold	6.45	4.38	67.91	69.25 ± 4.96
	5.08	3.23	63.58	
	5.03	3.72	73.96	
	5.22	3.84	73.56	
	5.34	3.90	73.05	
	5.69	3.61	63.44	
Ambient	5.63	2.36	41.92	38.12 ± 4.23
	5.37	1.96	36.50	
	5.60	2.36	42.14	
	4.41	1.58	35.83	
	5.66	2.31	40.81	
	5.62	1.77	31.49	

Table A3.2   **Experiment at loading level 56 μg stored for 7 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	μg	μg	%	%
Cold	62.05	57.43	92.55	92.92 ± 2.28
	63.28	59.45	93.95	
	61.07	55.11	90.24	
	63.33	60.41	95.39	
	60.80	57.81	95.08	
	57.50	51.92	90.30	
Ambient	61.99	47.83	77.16	82.97 ± 6.31
	71.64	64.28	89.73	
	56.85	41.82	73.56	
	63.38	53.92	85.07	
	66.04	58.10	87.98	
	49.39	41.65	84.33	

Table A3.3   **Experiment at loading level 56 µg stored for 14 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	**µg**	**%**	**%**
Cold	60.81	49.03	80.63	77.44 ± 6.33
	68.49	53.99	78.83	
	58.24	45.29	77.76	
	60.45	39.25	64.93	
	59.95	47.98	80.03	
	60.99	50.29	82.46	
Ambient	64.37	48.29	75.02	72.03 ± 3.28
	58.97	40.97	69.48	
	62.51	48.07	76.90	
	59.02	40.50	68.62	
	58.89	42.33	71.88	
	60.52	42.52	70.26	

Table A3.4   **Experiment at loading level 56 µg stored for 28 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	**µg**	**%**	**%**
Cold	54.07	39.87	73.74	66.27 ± 7.79
	51.90	29.92	57.65	
	51.11	35.62	69.69	
	50.29	35.53	70.65	
	47.70	26.32	55.18	
	52.77	37.31	70.70	
Ambient	51.54	28.28	54.87	51.85 ± 5.65
	51.18	22.94	44.82	
	56.55	32.73	57.88	
	52.74	30.13	57.13	
	54.44	27.47	50.46	
	50.73	23.30	45.93	

Table A3.5   **Experiment at loading level 90 µg stored for 7 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	91.54	88.70	96.90	
	91.96	89.49	97.31	
	87.78	81.39	92.72	93.02
	96.32	89.75	93.18	± 3.73
	92.88	83.90	90.33	
	94.15	82.54	87.67	
Ambient	88.50	67.10	75.82	
	92.41	81.97	88.70	
	93.35	86.55	92.72	87.11
	88.79	75.78	85.35	± 6.04
	85.49	76.55	89.54	
	85.39	77.33	90.56	

Table A3.6   **Experiment at loading level 90 µg stored for 14 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	93.72	92.49	98.69	
	92.93	92.58	99.62	
	91.21	86.04	94.33	94.82
	89.57	87.40	97.58	± 7.08
	90.19	88.32	97.93	
	90.26	72.91	80.78	
Ambient	89.55	77.75	86.82	
	97.82	75.43	77.11	
	91.34	70.88	77.60	78.12
	96.78	57.54	59.45	± 9.92
	91.37	75.95	83.12	
	93.86	79.39	84.58	

Table A3.7   **Experiment at loading level 90 µg stored for 14 days (Repeat)**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	93.06	86.59	93.05	91.91 ± 4.02
	91.58	89.47	97.70	
	94.40	82.13	87.00	
	97.57	86.40	88.55	
	91.69	86.93	94.81	
	92.80	83.86	90.37	
Ambient	94.00	69.70	74.15	81.29 ± 8.61
	92.69	86.40	93.21	
	97.27	86.98	89.42	
	90.97	68.52	75.32	
	92.46	67.24	72.72	
	96.18	79.74	82.91	

Table A3.8   **Experiment at loading level 90 µg stored for 28 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	92.01	96.64	105.03	97.46 ± 6.49
	93.44	80.86	86.54	
	96.42	96.29	99.87	
	91.32	92.49	101.28	
	92.42	90.74	98.18	
	92.70	86.99	93.84	
Ambient	95.25	50.73	53.26	68.29 ± 19.66
	94.48	86.36	91.41	
	92.48	75.62	81.77	
	92.06	50.63	55.00	
	91.91	77.10	83.89	
	95.33	42.34	44.41	

Table A3.9   **Experiment at loading level 90 µg stored for 28 days (Repeat)**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	92.86	76.87	82.78	76.70 ± 11.50
	90.93	75.99	83.57	
	89.49	67.19	75.08	
	90.90	74.92	82.42	
	91.30	49.38	54.09	
	93.69	77.06	82.25	
Ambient	92.79	63.86	68.82	66.61 ± 8.55
	96.87	74.52	76.93	
	95.45	65.56	68.69	
	91.22	46.45	50.92	
	99.48	65.64	65.98	
	93.48	63.87	68.32	

Table A3.10   **SUMMARY OF STORAGE TEST RESULTS FOR 1,3-BUTADIENE LOADED ONTO TUBES CONTAINING 700 mg CARBOSIEVE SIII**

6 µg Loaded			
Storage Period	**Batch**	**Mean Recovery Cold**	**Mean Recovery Ambient**
28 DAY	B1	69.25	38.12
56 µg Loaded			
Storage Period	**Batch**	**Mean Recovery Cold**	**Mean Recovery Ambient**
7 DAY	B1	92.92	82.97
14 DAY	B1	77.44	72.03
28 DAY	B1	66.27	51.85
90 µg Loaded			
Storage Period	**Batch**	**Mean Recovery Cold**	**Mean Recovery Ambient**
7 DAY	B1	93.02	87.11
14 DAY	B1	94.82	78.12
	B2	91.91	81.29
28 DAY	B1	97.46	68.29
	B2	76.70	66.61

"Cold" means below 4°C

APPENDIX 4

STORAGE RESULTS FOR 1,3-BUTADIENE LOADED ONTO TUBES CONTAINING 300 mg CARBOPACK-X

Table A4.1   **Experiment at loading level 56 µg stored for 7 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	54.24	52.55	96.88	97.30 ± 1.92
	52.92	51.37	97.07	
	69.59	66.04	94.90	
	55.01	54.98	99.95	
	60.80	58.30	95.89	
	67.94	67.35	99.13	
Ambient	61.87	59.54	96.23	96.76 ± 5.06
	55.08	51.02	92.63	
	63.13	60.18	95.33	
	54.49	57.75	105.98	
	58.33	57.29	98.22	
	62.63	57.71	92.14	

Table A4.2   **Experiment at loading level 56 µg stored for 14 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	58.94	57.33	97.27	96.78 ± 2.09
	60.41	59.17	97.95	
	66.26	66.31	100.08	
	60.01	56.87	94.77	
	52.85	49.99	94.59	
	62.45	59.96	96.01	
Ambient	58.41	55.94	95.77	95.28 ± 2.42
	64.31	60.87	94.65	
	57.51	57.00	99.11	
	65.22	60.67	93.02	
	61.92	57.32	92.57	
	57.72	55.72	96.53	

Table A4.3   **Experiment at loading level 56 µg stored for 28 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	60.52	59.41	98.17	
	62.67	lost		
	53.75	53.17	98.92	98.55
	66.37	64.03	96.47	± 1.73
	71.66	72.11	100.63	
Ambient	57.20	54.83	95.86	
	55.86	54.62	97.78	
	62.90	61.58	97.90	98.03
	56.47	57.19	101.28	± 1.87
	58.23	56.32	96.72	
	55.22	54.47	98.64	

Table A4.4   **Experiment at loading level 90 µg stored for 7 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	104.64	101.64	97.13	
	93.05	91.68	98.53	
	98.34	100.84	102.54	99.37
	93.73	94.49	100.81	± 2.07
	102.29	99.72	97.49	
	95.28	94.99	99.70	
Ambient	99.80	92.60	92.79	
	96.48	93.17	96.57	
	99.31	97.80	98.48	98.05
	93.29	95.27	102.12	± 3.18
	84.92	84.94	100.02	
	106.21	104.40	98.30	

Table A4.5   **Experiment at loading level 90 µg stored for 14 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	97.41	93.03	95.50	
	94.73	89.06	94.01	
	95.51	90.44	94.69	95.50
	92.38	86.31	93.43	± 1.83
	92.85	90.43	97.39	
	91.74	89.85	97.94	
Ambient	90.07	82.98	92.13	
	91.22	85.82	94.08	
	92.32	81.14	87.89	91.98
	91.59	80.18	87.54	± 3.57
	93.47	90.05	96.34	
	90.97	85.44	93.92	

Table A4.6   **Experiment at loading level 90 µg stored for 14 days (Repeat)**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	96.79	94.78	97.92	
	95.56	93.70	98.05	
	99.04	97.22	98.16	99.61
	92.36	92.07	99.69	± 2.08
	91.48	92.03	100.60	
	89.22	92.13	103.26	
Ambient	94.99	91.46	96.28	
	102.48	100.73	98.29	
	98.74	99.19	100.46	99.73
	98.40	100.11	101.74	± 2.13
	94.71	94.60	99.88	
	96.61	98.29	101.74	

Table A4.7   **Experiment at loading level 90 μg stored for 28 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	μg	μg	%	%
Cold	97.12	87.04	89.62	
	111.52	100.83	90.41	
	78.21	67.96	86.89	89.53
	91.82	84.60	92.14	± 1.74
	92.81	82.45	88.84	
	96.40	86.06	89.27	
Ambient	95.89	82.55	86.09	
	100.78	86.66	85.99	
	94.14	84.45	89.71	87.16
	91.70	77.39	84.39	± 2.00
	99.03	87.14	87.99	
	94.59	83.98	88.78	

Table A4.8   **SUMMARY OF STORAGE TEST RESULTS FOR 1,3-BUTADIENE LOADED ONTO TUBES CONTAINING 300 mg CARBOPACK-X**

56 μg Loaded			
Storage Period	**Batch**	**Mean Recovery Cold**	**Mean recovery Ambient**
7 DAY	B1	97.30	96.76
14 DAY	B1	96.78	95.28
28 DAY	B1	98.55	98.03
90 μg Loaded			
Storage Period	**Batch**	**Mean Recovery Cold**	**Mean recovery Ambient**
7 DAY	B1	99.37	98.05
14 DAY	B1	95.50	91.98
	B2	99.61	99.73
28 DAY	B1	89.53	87.16

"Cold" means below 4°C

APPENDIX 5

STORAGE RESULTS FOR 1,3-BUTADIENE (1%) IN LPG, LOADED ONTO TUBES CONTAINING 300 mg CARBOPACK-X

Table A5.1   Experiment at loading level 10 µg stored for 7 days

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	9.67	10.83	112.00	98.69 ± 7.49
	10.22	10.31	100.88	
	9.28	8.85	95.37	
	10.66	9.55	89.59	
	10.27	9.96	96.98	
	9.84	9.58	97.36	
Ambient	11.93	11.22	94.05	99.07 ± 5.85
	11.28	11.46	101.60	
	10.40	11.16	107.31	
	10.22	10.43	102.05	
	10.75	10.56	98.23	
	10.33	9.42	91.19	

Table A5.2   Experiment at loading level 10 µg stored for 7 days (Repeat)

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	10.08	10.17	100.89	99.46 ± 2.81
	10.33	10.31	99.81	
	9.94	9.37	94.27	
	10.05	10.19	101.39	
	9.73	9.91	101.85	
	10.18	10.03	98.53	
Ambient	10.45	10.32	98.76	100.14 ± 4.18
	10.47	10.91	104.20	
	10.00	9.51	95.10	
	10.12	10.60	104.74	
	10.11	9.90	97.92	

Table A5.3 **Experiment at loading level 10 µg stored for 7 days (Repeat)**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	10.39	10.80	103.95	104.05 ± 2.75
	10.34	10.51	101.64	
	10.00	10.15	101.50	
	10.20	10.48	102.75	
	10.07	10.93	108.54	
	10.26	10.87	105.95	
Ambient	10.24	10.27	100.29	99.37 ± 1.80
	10.30	10.27	99.71	
	10.08	9.90	98.21	
	10.04	9.74	97.01	
	10.42	10.59	101.63	

Table A5.4 **Experiment at loading level 10 µg stored for 14 days**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	9.73	10.15	104.32	102.27 ± 1.44
	9.67	9.94	102.79	
	9.62	9.85	102.39	
	9.56	9.62	100.63	
	9.65	9.77	101.24	
Ambient	10.43	10.79	103.45	102.22 ± 1.62
	9.56	9.85	103.03	
	9.51	9.81	103.15	
	9.57	9.79	102.30	
	11.75	12.06	102.64	
	9.52	9.43	99.05	

Table A5.5 Experiment at loading level 10 µg stored for 14 days (Repeat)

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	10.54	10.73	101.80	98.25 ± 4.49
	10.63	11.10	104.42	
	10.68	10.53	98.60	
	10.54	10.21	96.87	
	10.47	9.59	91.60	
	10.60	10.20	96.23	
Ambient	10.52	9.76	92.78	95.82 ± 4.08
	11.03	11.21	101.63	
	10.77	10.09	93.69	
	10.71	9.72	90.76	
	10.73	10.56	98.42	
	11.53	11.26	97.66	

Table A5.6 Experiment at loading level 10 µg stored for 28 days

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	10.54	10.40	98.67	95.00 ± 6.45
	11.59	12.18	105.09	
	9.40	8.41	89.47	
	9.38	8.19	87.31	
	11.04	10.59	95.92	
	10.01	9.36	93.51	
Ambient	10.65	10.02	94.08	94.62 ± 1.87
	9.43	8.92	94.59	
	10.38	10.11	97.40	
	9.48	8.72	91.98	
	13.59	13.04	95.95	
	9.87	9.25	93.72	

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Table A5.7   **Experiment at loading level 10 µg stored for 28 days (Repeat)**

Loading & Storage Conditions	Butadiene Loaded	Butadiene Recovered	Percentage Recovered	Mean Recovery ± Standard Deviation
	µg	µg	%	%
Cold	10.52	7.08	67.30	85.78 ± 15.05
	10.54	7.68	72.87	
	10.56	8.12	76.89	
	10.54	10.56	100.19	
	10.50	10.24	97.52	
	10.54	10.53	99.91	
Ambient	10.49	6.98	66.54	86.47 ± 16.12
	10.52	7.28	69.20	
	10.54	8.66	82.16	
	10.49	10.46	99.71	
	10.96	11.28	102.92	
	10.54	10.36	98.29	

Table A5.8   **SUMMARY OF STORAGE TEST RESULTS FOR 1,3-BUTADIENE (1%) IN LPG LOADED ONTO TUBES CONTAINING 300 mg CARBOPACK-X**

Storage Period	Batch	Mean Recovery Cold	Mean Recovery Ambient
7 DAY	B1	101.51	98.96
	B2	93.21	100.69
	B3	101.35	99.54
	B4	98.69	99.07
	B5	100.49	100.00
	B6	104.05	99.37
14 DAY	B1	102.27	102.02
	B2	98.25	95.82
28 DAY	B1	95.00	94.62
	B2	85.78	86.47

"Cold" means below 4°C

APPENDIX 6

GRAPHICAL REPRESENTATION OF AVERAGE STORAGE RESULTS

A comparison of the mean percentage recoveries on storage for 56 µg 1,3-butadiene using the sorbents Carbopack-X (CX) and Carbosieve SIII (HSU)
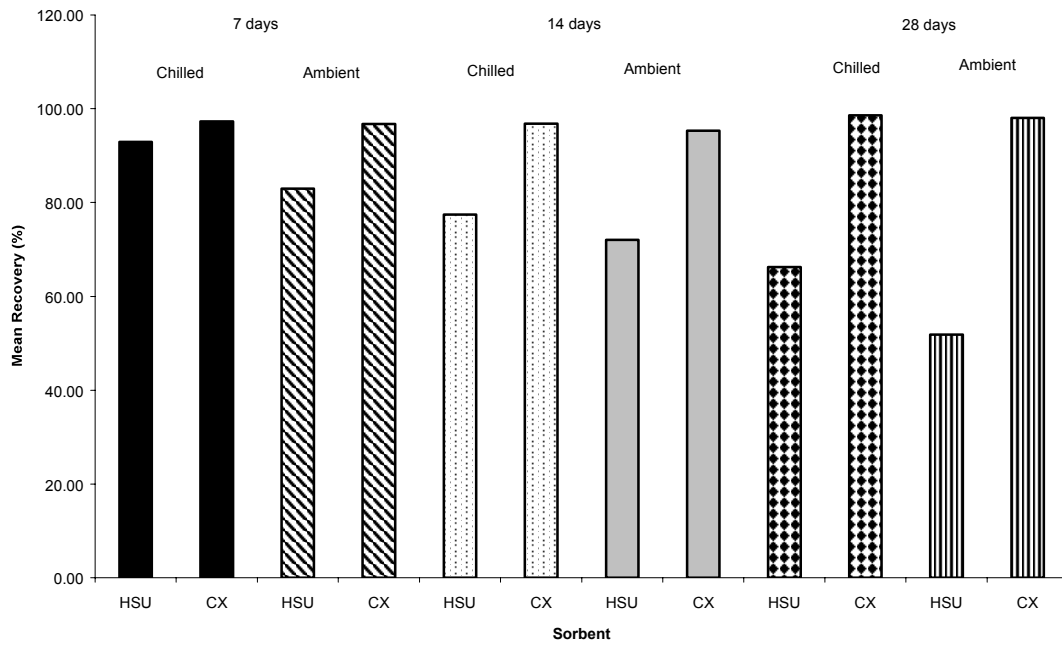
A comparison of the mean percentage recoveries on storage for 90 µg 1,3-butadiene using the sorbents Carbopack- X (CX) and Carbosieve SIII (HSU)

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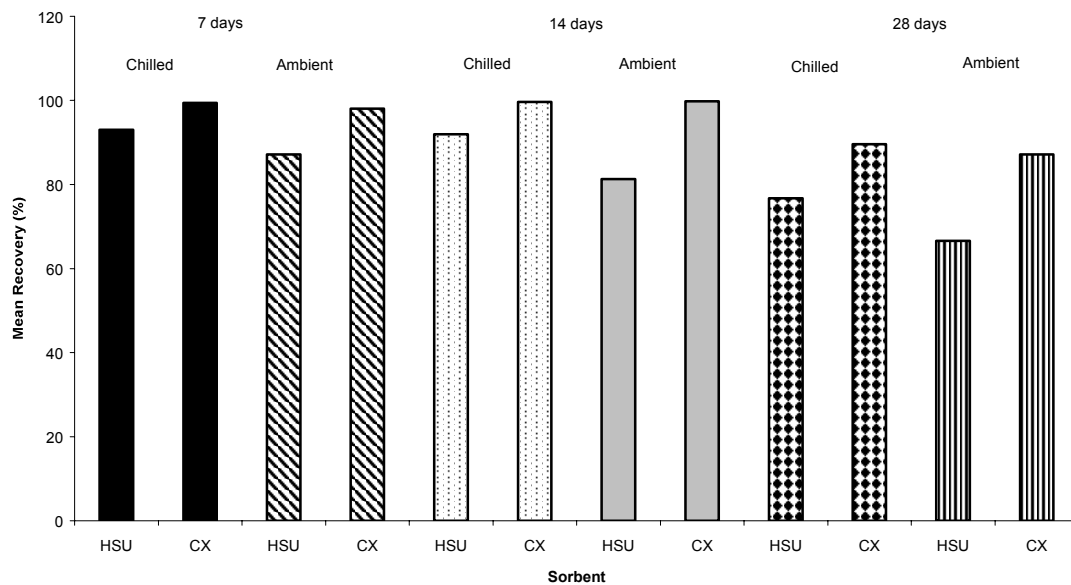
APPENDIX 7

BREAKTHROUGH TRIALS FOR GAS MIXTURE CONTAINING TRACE OF 1,3-BUTADIENE

Tube set (front and rear)	Butadiene loaded (μg)	Butadiene breakthrough onto rear tube (%)	Butane breakthrough onto rear tube (%)
0 (blank)	0.00	nd	nd
1	18.72	nd	0.009
2	17.99	nd	0.006
3	18.82	nd	0.15
4	18.81	nd	0.003
5	18.91	0.25	8.8
6	18.84	0.28	9.6
7	19.10	0.35	10.5
8	18.85	nd	0.003
9	19.51	nd	0.002
10	19.05	nd	0.002
11	18.83	0.16	7.7
12	18.83	nd	0.003
13	18.84	nd	0.002
14	18.80	nd	0.002
15	18.77	nd	0.003
16	19.31	nd	0.002
17	18.80	nd	0.002
18	18.82	nd	0.002
19	18.83	nd	0.002

nd = not detected

APPENDIX 8

METHOD FOR MONITORING EXPOSURE TO LPG CONTAINING SMALL AMOUNTS OF 1,3-BUTADIENE (VERSION 2004)

1.   SCOPE

Liquefied Petroleum Gas (LPG) is a mixture of mainly C_3 and C_4 hydrocarbons and may contain trace amounts of several impurities, including 1,3-butadiene. From a risk assessment point of view it is important that the exposure monitoring methodology is adequate for quantification both of the total mixture and, from a toxicological point of view, key components in this case 1,3-butadiene.

The method describes a procedure for the sampling and analysis of 1,3-butadiene in LPG. The method is suitable for both personal and fixed point monitoring for periods up to 12 hours by appropriate adjustment of the sampling flow rate. When samples have to be taken under extreme conditions i.e. >80% relative humidity and 30 to 40°C it may be necessary to take consecutive short-term samples.

When used for 1,3-butadiene in air the method is applicable for the range 0.5 to 90 µg 1,3-butadiene on the tube, equivalent to airborne 1,3-butadiene in the range 0.05 to 9.0 mg/m^3 for a 10 litre sample. When used for 1,3-butadiene in LPG the method is applicable for the range 0.5 to 16 µg 1,3-butadiene on the tube, equivalent to 0.05 to 1.6 mg/m^3 for a 10 litre sample.

When used for n-butane in LPG the method is applicable for the range 0.5 to 300 µg n-butane on the tube, equivalent to 0.05 to 30 mg/m^3 for a 10 litre sample. Carbopack-X is not suitable for sampling propane. If measurement of propane is required a Carbosieve SIII tube should be connected sequentially.

2.   NORMATIVE REFERENCES

CEN (1997) Workplace atmospheres – Pumps for personal sampling of chemical agents – Requirements and test methods. EN 1232:1997. Brussels: Comité Européen de Normalisation

CEN (2000) General requirements for the competence of testing and calibration laboratories. EN ISO/IEC 17025:2000 Brussels: Comité Européen de Normalisation

CEN (2000) Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography – Part 1: Pumped Sampling (ISO 16017-1:2000). EN ISO 16017-1:2000. Brussels: Comité Européen de Normalisation

HSE (1991) Analytical quality in workplace air monitoring. MDHS 71. London: Health and Safety Executive

3.   TERMS AND DEFINITIONS

3.1   Measuring Procedure

Method of sampling and analysis of one or more chemical agents in the air, including storage and transportation of the sample.

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3.2   Pumped Sampler

A device which is capable of taking samples of gases and vapours from the atmosphere and consisting of a sampling medium, such as a sorbent tube, and an air sampling pump.

3.3   Flow Rate

Volume of air drawn through the sampling medium per unit of time; usually expressed in millilitres per minute (ml/min). Flow rates and consequent sampled volumes refer to the volume of air at the temperature and pressure during sampling, not corrected to standard temperature and pressure.

3.4   Sorbent Tube

A stainless steel tube containing sorbent medium through which the sampled air is passed at a controlled rate by an air-sampling pump.

3.5   Retention Volume

The elution volume at peak maximum of a small aliquot of a vapour eluted from the tube by atmosphere or chromatographic carrier gas.

3.6   Breakthrough Volume

Volume of test atmosphere that can be passed through a sorbent tube before concentration of eluting vapour reaches 5% of the applied test concentration.

3.7   Safe Sampling Volume

Volume of test atmosphere that can be passed through a sorbent tube without loss of vapour. This volume is normally two thirds of the breakthrough volume.

3.8   Desorption Efficiency

The ratio of the mass of analyte desorbed from a sampling device to that theoretically collected.

3.9   Method Validation

The process of evaluating the performance of a measuring procedure and checking that the performance meets certain pre-set criteria.

3.10   Limit Value

Reference value concentration, set by an enforcement authority, for a chemical agent or agents in air.

3.11   True Value

The value, which characterises a quantity perfectly, defined in the conditions which exist at the moment when that quantity is considered.

3.12   Overall uncertainty

Parameter, associated with the result of a measurement that characterises the dispersion of the values that could reasonably be attributed to the measurement.

3.13   Loading

The product of concentration of vapour expressed as milligrams per cubic (mg/m^3) and sampled atmosphere volume (flow rate x sampling time).

4.   PRINCIPLE

A measured volume of air is drawn by a small portable pump through a sorbent tube filled with a sample medium that retains 1,3-butadiene and other C_3 to C_6 hydrocarbons. The collected hydrocarbon compounds are desorbed by heat and are transferred under inert carrier gas into a gas chromatograph, fitted with a flame ionisation detector, where they are analysed. Calibration of the chromatograph is achieved by means of vapour spiking of the sorbent tube using 1,3-butadiene over the expected range of concentrations.

5.   REAGENTS AND MATERIALS

5.1   Sorbents

Carbopack-X 40-60 mesh (Graphitised Carbon with porosity)
Preconditioned at 400°C for 4 hours under helium.

A carbon molecular sieve sorbent (Carbosieve SIII 60-80 mesh) was tested but showed decreasing recoveries, with storage times of up to 4 weeks and dependant on butadiene loading concentrations, to a stage that did not satisfy standard performance requirements. Unless samples are analysed very promptly, this type of sorbent is not suitable for exposure monitoring of LPG containing traces of 1,3-butadiene.

5.2   Gases

Certified (traceable to primary standards of mass or volume) cylinder of 1,3-butadiene in nitrogen (~500 ppm).

Certified (traceable to primary standards of mass or volume) cylinder of 1,3-butadiene (~500 ppm), n-propane and n-butane in nitrogen (~2.5% each) in nitrogen.

6.   APPARATUS

6.1   Sorbent Tubes

Sorbent tubes are made of stainless steel tubing (6.3 mm OD, 5 mm ID and 90 mm long; industry-standard size). Tubes are marked by a scored ring (groove) at about 10 mm from the front end of each tube. Tubes are packed with the appropriate preconditioned sorbent so that the sorbent will be within the desorber heated zone and a gap of at least 14 mm is retained at each end to minimise ingress of vapours due to diffusion when low pump flows are used. The sorbents are retained by stainless steel gauzes. An example of a suitable tube is the Perkin-Elmer ATD tube.

6.2 <u>Sorbent Tube End Caps</u>

Metal screw caps, such as Swagelock, with PTFE seals.

6.3 <u>Sampling Pump</u>

The pump should fulfil the requirements of EN1232 or equivalent and shall be in accordance with local safety regulations, e.g. certified as intrinsically safe.

6.4 <u>Calibration Chamber</u>

The calibration chamber typically comprises a stirred 5 litre glass vessel with a flat, flanged top. It is fitted with a stainless steel flange containing a calibrant gas inlet, exhaust gas outlet, temperature sensor and at least six sampling ports.

6.5 <u>Tubing</u>

Plastic or rubber tubing about 90 cm long and appropriate diameter to ensure a leak proof fit to both pump and sample tube. Tubing must not be used upstream of the sorbent to avoid possible contamination from the tubing.

6.6 <u>Calibrated flow meter</u>

Soap bubble meter or other suitable gas flow meter calibrated/certified and traceable to National Standards.

6.7 <u>Gas Chromatograph</u>

A Gas Chromatograph (GC) fitted with a flame ionisation detector (FID), which must be capable of operation with a capillary column and a thermal desorber (ATD).

6.8 <u>Thermal Desorption Apparatus</u>

A Thermal Desorption Unit capable of automatic two stage desorption with an inlet and outlet split facility and heated transfer line to the gas chromatograph (**Table A8.1**).

7. SAMPLE TUBE CONDITIONING AND CERTIFICATION

Carbosieve SIII tubes are initially cleaned / conditioned at 350°C for 4 hours under a flow of helium. Thereafter the tubes are cleaned under similar conditions.

Carbopack-X tubes are conditioned at 350°C for 2 hours, followed by 400°C for 2 hours, both under a flow of helium. Thereafter the tubes are cleaned at 400°C for 2 hours under a flow of helium. A representative number of tubes are certified before use by analysing the clean tubes under the conditions used for analysis **(Table A8.2)** and comparing the area of the butadiene peak found (if any) with that obtained from a calibration standard. Each peak found should be no greater than 10% of the reporting limit of the method. If the certification is unacceptable the tubes should be re-cleaned. Tubes should be sealed with screw caps as soon as possible after cleaning and pre-analysis and stored in a solvent-free atmosphere.

8.   **PREPARATION OF STANDARDS**

Clean Carbosieve SIII or Carbopack-X tubes are spiked with a diluted blend of 1,3-butadiene in air. The blend is prepared as detailed below.

Set up the calibration chamber so that the calibrant gas is mixed with the dry N_2 prior to entering the chamber. Measure the flows of calibrant gas and adjust to give a suitable flow, for example 50 ml/min of calibrant (500 ppm 1,3-butadiene in 2.5% propane, 2.5%-n-butane in nitrogen) and 4500 ml/min of nitrogen.

Purge the chamber for 30 min to ensure uniformity of the contents.

Fix clean packed sorbent tubes into the ports by removing the sealing caps on the chamber, inserting the ringed end of the tube into the chamber and tightening the retaining nut (fitted with PTFE ferrule). Attach the outer ends of each tube to a pump using silicone rubber tubing.

Sample the atmosphere in the chamber to give accurately known loadings using appropriate pump rates and times to produce a range of standards so that a calibration graph can be drawn for each set of samples analysed. Prepare two standards at each of at least six calibration levels.

The concentration of 1,3-butadiene in molar ppm is converted to mg/m^3 standardised to 1 atmosphere pressure and 25°C using the following equation:

(mg/m^3) = ppm x molar mass / molar volume

Where:
Molar mass for 1,3-butadiene = 54.09 grams
Molar volume of air at 25^oC = 24.45 litres

The exact mass of 1,3-butadiene spiked, at each level, should be calculated and used for the calibration. A calibration of at least six levels, covering the expected concentration range, must be performed for each set of samples analysed.

9.   **CALIBRATION OF SAMPLING PUMP**

The sampling pumps should be classified as intrinsically safe for use in flammable atmospheres and/or operated under an appropriate safe system of work.

The pumps used should have an accuracy of ± 5% or better, be capable of operating in the range of flow rates of 2 – 50 ml/min and be capable of stable operation throughout the operating period. The pumps should be calibrated regularly.

Calibration/certification of the gas flow meter should be traceable to National Standards.

10.   **SAMPLING**

The sample tubes should be kept sealed and away from any contamination whilst not in use. The shelf life of the tubes is estimated to be 3 months. If the shelf life period expires, then the tubes should be returned to the laboratory for re-certification.

Tubes are capped when supplied. Immediately after sampling the tubes must be re-capped to prevent contamination.

The maximum recommended sample volume is 10 litres at 20°C and relative humidity below 80%. With sample volumes greater than this, there may be loss of the 1,3-butadiene. This volume should be reduced by a factor of 2 for every 10°C increase above 20°C. Key factors influencing the breakthrough volume (litres) are air temperature (°C) and relative humidity (%RH). For example, the breakthrough volume decreases by a factor of approximately two for each 10°C increase in air temperature and by a factor of 10 for relative humidity close to 100%. However, the sampled volume can not be reduced simply by reducing the air sampling rate, because diffusion begins to play a contributory role when the pumped flow rate is ≤2 ml/min.

The acceptable flow rate in order to achieve the optimum sample volume should be calculated on the basis of the expected sampling duration and environmental conditions. This should consider periods when levels may be elevated and may necessitate the taking of several samples consecutively to encompass the work shift or activity being investigated.

Surgical gloves should be worn when handling the tubes. Touching the ends of the tubes, or the ferrules, with contaminated fingers should be avoided.

The non-grooved end of the tube should be connected to the sampling pump.

All connections using Swagelock fittings should be preferably made using a "Caplock" tool. Failing this, the fittings should be made hand tight then a ¼ turn using the appropriate spanners.

Note: Do not over tighten the fittings as this will cause the ferrule to distort the thin walls of the sampling tube which will result in the sample having to be rejected for analysis.

Note: Do not mark or attach labels to sample tubes, as this may interfere with the analysis of the samples.

Prior to taking each sample record:

- Sample tube numbers
- Personnel ID (optional and for company use only)
- Date of sampling
- Location of sampling
- Nature of Task

Position the sample tube in the breathing zone of the operator being monitored and fix securely. Locate the pump on the person in an appropriate way ensuring that any flexible tubing is not restricted in any way. Turn pump on and record:

- Sample start time (hh:mm)
- Initial pump rate (ml/min) and or counter reading

At the end of the sampling, turn off the sample pump and record:

- Sample finish time (hh:mm)
- Sampling duration (min)
- Final pump flow rate (ml/min) and or counter reading
- Volume of air (litres)

For each sample the following information is required to describe environmental conditions during the sampling period:

- Air temperature (°C)
- Wind speed and direction (m/s) (optional)
- Atmospheric pressure (mmHg) (optional)
- Relative humidity (%)

Draw a simple plot plan and mark the location of operators and details of activity and its duration. Record any other relevant information.

Immediately that the monitoring period has been concluded fit the end caps and secure carefully.

A minimum of two "field blank" samples should be submitted for each 10 field samples submitted. Field blanks are chosen arbitrarily from the supplied batch and treated in the same way as the sample tubes except that the end caps will not be removed at any time in the field. They should be returned along with the field samples. The field blanks are used to evaluate any contamination which may occur due to transit. All samples, including field blanks, should be clearly labelled and details entered on a sample submission or chain-of-custody form.

Samples should be despatched by the quickest route available, together with a copy of the information required. When the samples have been received by the analytical laboratory they should be stored in a refrigerator at a temperature below 4°C and analysed within 14 days of receipt.

Carbopack-X tubes are suitable for the sampling of n-butane and other C_4 hydrocarbons but are not suitable for sampling propane. If this analyte is required then a sorbent tube combination of a Carbopack-X sampling tube in series with a Carbosieve SIII sampling tube should be used. Immediately after sampling, the tubes must be separated and capped to prevent contamination and migration of the sampled material between the different adsorbents within the tubes.

11.   ANALYTICAL PROCEDURE

11.1   Safety Precautions

This part of the method does not address all the safety concerns associated with its use. It is the responsibility of the user of the method to establish the appropriate health and safety practices and the applicability of regulatory limitations prior to use.

11.2   Desorption and Analysis

For the recovery and analysis of 1,3-butadiene from the sample tubes a compatible thermal desorption unit and gas chromatographic system is required. The type of thermal desorption unit suitable for this analysis is a two stage desorber. The components desorbed from the sample tube are cryogenically focused onto an Air Toxics cold trap containing Carbopack-B and Carbosieve SIII. The pre-concentration stage, also known as cryogenic focusing is essential if a capillary column is being used. It also allows for extended primary desorption of the sample tubes at temperatures that prevent or minimise artefact generation from the sorbent. The concentrated components are then desorbed from the cold trap into a capillary column where they are separated.

The thermal desorption unit should be set up for complete desorption of 1,3-butadiene collected onto the sorbent tubes used for sampling. A Perkin-Elmer Turbomatrix or ATD-400, for example, are suitable for this type of analysis. The desorption parameters for the complete recovery of 1,3-butadiene are given in **Table A7.1.**

The gas chromatograph should be fitted with a capillary column suitable for the separation of 1,3-butadiene from other LPG components. The recommended column for this analysis is a PLOT Silica 60m x 0.53mm diameter column. The column should be connected to the thermal desorber according to the manufacturer's instructions. It is important that the capillary column, or a length of de-activated capillary tubing, should be as close as possible to the cold trap outlet. This can be achieved by threading the column or tubing back through the transfer line from the thermal desorption unit to the gas chromatograph. The gas chromatograph should be set up for the separation and detection of the components of Liquefied Petroleum Gas including 1,3-butadiene. The parameters for this analysis are given in **Table A7.2.**

11.3   Calibration

The gas chromatograph/thermal desorption unit system must be calibrated before any samples are analysed. At least six levels, covering the expected concentration range, should be utilised with one calibration standard from each level being analysed before the sample tubes and the second calibration standard from each level being run after the sample tubes.

A calibration plot is generated for 1,3-butadiene which should display linearity i.e. a correlation coefficient > 0.95. The exact mass (µg) of 1,3-butadiene spiked, at each level, should be calculated and used for the calibration. The gas chromatographic system will give the response factor or gradient for butadiene, which can be used to determine the mass of this analyte in the samples.

12.   CALCULATIONS

Calculate the concentration c_m of 1,3-butadiene in the sampled air, in milligrams per cubic metre by means of the following equation:

c_m = m_f1000/V

m_f is the mass of analyte found on the tube in milligrams

V is the volume of sample in litres

Other detected LPG hydrocarbons may be quantified by including them in the original calibrant gas and preparing standards (See Sections 8 and 11). The concentration of the individual hydrocarbons in the sampled air may be calculated using the above formula.

13.   INTERFERENCES

Artefacts can be generated by the sorbents and analytical system, so meticulous care and preparation at all times is essential. The analytical desorption temperature should never be greater than the sorbent conditioning temperature or cleaning temperature. All cleaned and certified tubes should be stored in a clean, solvent free atmosphere before and after sampling prior to analysis.

Atmospheres in excess of 80% relative humidity are likely to interfere with the safe sampling volume causing premature breakthrough of hydrocarbons from the sorbents. Excessive moisture collected on the sorbents is also likely to interfere with the analytical process and in extreme cases can extinguish the flame in the flame ionisation detector. To minimise the interference of moisture the volume of air should be reduced as outlined in **Section 10.**

14.   PERFORMANCE CHARACTERISTICS

Examples of performance characteristics including overall uncertainty, precision and blank levels can be found in EN/ISO 16017-1:2000. The safe sampling volume for 1,3-butadiene is 40 l/g on Carbopack-X. However when sampling butadiene in LPG atmospheres care must be taken to ensure that butadiene loadings on the tube do not exceed 10 µg.

15.   TEST REPORT

The report should contain at least the following information as required by EN/ISO/IEC 17025: 2000:

- Complete identification of the sample, which should include both the Laboratory and Customer sample number.

- Reference to this method used and any significant deviations from the method or other unusual features noted during the determination.

- The results including the units of measurement.

- The details of the work activity with durations.

16.   QUALITY CONTROL

Quality Control should be maintained through a standard equivalent to EN/ISO/IEC 17025:2000 and preferably accreditation to this standard should be achieved.

Guidance on an appropriate level of quality control can be found in UK HSE MDHS 71 – Analytical Quality in Workplace Air Monitoring. Participation in at least one proficiency testing scheme (e.g. UK Health and Safety Executive Workplace Analysis Scheme for Proficiency – WASP) should be undertaken and a satisfactory performance attained.

Internal quality control (IQC) samples should be run prior to any field samples being analysed, so that the accuracy of the analysis can be confirmed.

Laboratory and field blanks should be prepared so that for each set of 10 sample tubes at least 2 tubes are stored in the laboratory and 2 tubes accompany the samples in the field. The purpose of these blanks is to determine if contamination or interferences have occurred either due to transportation or storage. Any contamination detected should be reported with the results and not subtracted from the sample results. Any contamination on the laboratory blanks should be investigated and eliminated prior to any further analysis of samples.

Check standards are not required as a 1,3-butadiene calibration is performed with each batch of samples.

The safe sampling volume of the sorbent tubes should be re-tested periodically to ensure the performance of the tube has not deteriorated significantly. If the safe sampling volume falls below the acceptable collection volume then the tube should be repacked and reconditioned.

Table A8.1   Desorption Parameters for Analysis of Sorbent Tubes containing Carbopack-X, used to sample 1,3-Butadiene samples (based on Perkin Elmer ATD400 capabilities)

Function	
Desorption Mode (ATD400)	2
Primary Desorption Temperature ^{o}C	350
Primary Desorption Flow Rate ml/min*	6-10
Primary Desorption Time min	10
Valve/transfer line temperature ^{o}C	200
Cold Trap Sorbent	Air Toxics
Inlet split flow ml/min *	65-75
Outlet split flow ml/min *	45-50
Cold trap low ^{o}C	-30
Cold trap high ^{o}C	350
Cold trap high time min	2
Cold trap high rate of heating	Fast
Carrier gas	Helium
Split ratio	66:1

* Note: The split flows should be checked and recorded daily when the instrument is in use

Table A8.2   Gas Chromatographic Conditions

Parameter	Conditions
Capillary Column	PLOT Silica 60m long by 0.53 mm diameter
Column Oven Initial Temperatures	35°C Held for 5 minutes
First Ramp Rate	2°C/min
Intermediate Temperature	90°C Held for 0 minutes
Second Ramp Rate	30°C/min
Final Temperature	180°C Held for 2 minutes
FID Temperature	300°C
Carrier Gas	Helium
Flow Rate Through Column	~7.7 ml/min