method for monitoring exposure to gasoline vapour in air – revision 2002

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ABSTRACT

An overview is provided of practical issues in relation to the assessment of occupational exposure to gasoline vapour, determined via complete compositional analysis. A detailed sampling and analytical method is presented. This report replaces guidance given previously by CONCAWE in report 8/86.

KEYWORDS

Gasoline, gasoline vapour, occupational exposure, monitoring method

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SUMMARY

A detailed method for the analysis of exposure to gasoline vapour, including identification and quantification of single constituents, was first developed and published by CONCAWE in 1986. Subsequent technical and procedural developments, including international standardisation of quality requirements for workplace assessment of exposure to hazardous agents, have prompted a revision of the recommended method.

The revision includes a change to one of the recommended sorbents for capturing airborne gasoline vapour components, and an assessment of the validation status in comparison with international standards requirements. A short description is provided of some practical issues that have been encountered during application of the method in a field survey of occupational exposures in the European oil industry.

The revised methodology is presented in **Appendix 1**.

1. INTRODUCTION

CONCAWE initiated an assessment in 1997 of available exposure data on gasoline in advance of the expected requirement for industry to provide such information in support of an EU Risk Assessment on gasoline. The assessment identified the need to undertake exposure monitoring in situations where data on gasoline were either deficient or significantly out of date. It was recognised that, in the light of experience and recent developments in the area of exposure sampling and analysis, it would be desirable to review the status of the CONCAWE method for monitoring gasoline [8]. This ‘Method for Monitoring Exposure to Gasoline Vapour in Air’ - CONCAWE Report 8/86 is referred to in short in this report as ‘method 8/86’.

An analytical working group was set up to conduct a review of method 8/86 and make recommendations to update the method in light of current international standards and state of the art technology. Subsequently, the modified method was used in a field survey in 1999-2001 of gasoline vapour exposure in a variety of situations. The survey results are reported under separate cover [9].

This report describes the revision of method 8/86 against current technological developments and validation requirements of international standards. The report cites modifications made to the method. The report also covers experiences gained in the use of the modified method for a large field study. Shortcomings in the methodology were identified and recommendations for further improvement are discussed. The final version of the modified method is reported in **Appendix 1**.

2. REVIEW OF METHOD 8/86

2.1. INTRODUCTION

The procedure of method 8/86 for monitoring of occupational exposure to gasoline vapour consisted of drawing air through two different sorbents, followed by thermal desorption and analysis via gas chromatography (GC) of up to 150 chemical components of gasoline. These components included those of concern on the basis of health hazard classification or occupational exposure limits (OELs).

A review was conducted of the method, which was originally developed and validated in 1986. The objective of the review was to agree the necessary revisions to the method in order for it to represent current good practice relevant to the monitoring and analysis of workplace exposures to gasoline vapour.

Method 8/86 has proved to be a robust and reliable method which, in many respects, was ahead of its time and has earned wide respect in the sampling and analytical communities [17]. However, it was recognised that many CONCAWE members did no longer use the method in its original format. It is a detailed and specific method and although inter-laboratory validation exists, it does not meet current international standards (e.g. EN 1076 [4]) for validation, although these standards have been principally developed for less complex agents. It was accepted however, that any modifications made to method 8/86 must yield at least equivalent performance in relation to the original objectives.

2.2. RECENT DEVELOPMENTS IMPACTING ON GASOLINE VAPOUR EXPOSURE MONITORING

Since 1986 there have been a number of significant developments, which have either increased overall performance requirements in the field of workplace exposure sampling and analysis, or specifically affected technical aspects of method 8/86:

a) In recent years the international standards bodies, and notably the European Committee for Standardisation (CEN), have produced detailed guidance concerning the performance requirements of methods used for monitoring exposures to workplace airborne contaminants. These often require a high degree of laboratory validation (see further Chapter 3 of this report).

b) A number of the OELs for components of gasoline have changed. In particular, the OEL for benzene has been reduced from 30 mg/m^3 or 10 ppm in several countries to 3.25 mg/m^3 (1 ppm) as a European binding limit value [11]. For the monitoring method, the consequences are that the limit of detection needs to change accordingly: it is commonly accepted that a method should be capable of detecting exposure levels as low as one tenth of the OEL. The lower limit of detection of method 8/86 for benzene is 0.2 mg/m^3 (approx. 0.1 ppm), but it was increased when sampling in conditions of high humidity and temperature.

c) The importance of laboratory quality control and involvement in suitable quality assurance schemes has become apparent in the last 10 years. A number of quality control schemes have now become established which are relevant to some key components of gasoline, such as benzene, toluene and xylene. Moreover, the interdependence of sampling and analytical procedures has been reinforced. Laboratory quality control schemes still, however, focus on single substances and not on complex mixtures. Indeed, no suitable inter-laboratory exchange scheme is known to exist for gasoline vapour. Consequently, the revised method should contain a quality control procedure.

d) Shift patterns have moved away from traditional 8-hour periods to more extended shift types, e.g. 10-12 hours. Method 8/86 was principally designed to address the 8-hour work shift. The consequence of this for sampling requirements is that the sampling period has increased by up to 50%, which impinges on parameters such as breakthrough volume and sample flow rate.

2.3. RECOMMENDED TECHNICAL CHANGES TO METHOD 8/86

The continued need was confirmed for a sampling and analytical method capable of distinguishing and quantifying the individual components of gasoline, as well as providing a measure of the total vapour exposure. It was considered that this updated gasoline vapour "reference method" should be based on method 8/86.

A number of recommended improvements were identified. The rationale for the changes is discussed below.

2.3.1. Sampling Mode

The two main modes of sampling currently available are pumped (active) and diffusive (passive). Diffusive techniques have the advantage of better dealing with the issues posed by increased shift times. However, while diffusive methods exist for hydrocarbon mixtures (e.g. MDHS 80 [15]), these methods of sampling have yet to be validated over the full exposure range for complex mixtures such as gasoline. Therefore, the established pumped mode of sampling used in method 8/86 was thought to be more suited to gasoline vapour.

2.3.2. Desorption Technique

The two main modes of desorption currently available are chemical (solvent) and thermal. Solvent desorption is not suitable for the analysis of gasoline components and the established technique of thermal desorption used in method 8/86 remains the preferred option. There are, however, equipment changes, which allow more efficient laboratory operations. Single stage desorbers, as specified in method 8/86, are not suitable for a high throughput of samples. Also, new improved systems are invaluable for identification of components when attached to a mass spectrometric (MS) detection system.

2.3.3. Sorbent System

Because of the wide range of hydrocarbons that make up gasoline, method 8/86 specified two sorbents to cover the full range of components. These sorbents consisted of a porous polymer (80-100 mesh Chromosorb 106 (C106)) to collect the higher boiling components (nC_5 to nC_{11} and higher), and activated charcoal (60-80 mesh Sutcliffe Speakman 607 Charcoal (SS607)) to collect the light end components (nC_3 to nC_5).

Although there are other potentially suitable sorbents available, it was decided to retain C106, as any advantages with the alternative sorbents were regarded as minimal. However, it was known that the fine 80-100 mesh material caused problems in some thermal desorbers (e.g. PE ATD 400) and so the 60-80 mesh version was recommended for the new method.

SS607 is no longer commercially available and so an alternative sorbent had to be found. Also, reports have indicated that some activated charcoals are subject to profound absolute and batch-to-batch performance deficiencies for key gasoline components [10]. There are commercially available synthetic charcoals that are known not to suffer from these short-comings and which may provide better collection efficiencies. One of these, 60-80 mesh Carbosieve S-III (CS-III), was selected on the basis of supplier data and a laboratory break-through test with propane. In addition, CS-III is one of the options recommended in the CEN standard for ultra-volatile organic compounds [6].

2.3.4. Sample Tube System

For the configuration of the sorbents method 8/86 gave two options of either a single tube or two tubes joined together. The single tube system contained both sorbents packed sequentially with C106 in the front portion of the tube. The dual tube system contained the two sorbents in separate tubes but with the tubes joined together, with C106 in the front tube. The dual tube configuration is the preferred option for several reasons:

a) Larger quantities of sorbent can be packed into two tubes, thus increasing the safe sampling volume. This is important where extended shifts are being followed or where 'light end' exposures are anticipated to be elevated.

b) It allows more appropriate desorption conditions. High temperature desorption of C106 can cause degradation and generation of artefacts, whereas activated and synthetic charcoals require high temperatures for adequate desorption efficiency.

To minimise sample break-through and increase the safe sampling volume for extended sampling times (up to 12 hours) the recommended quantity of C106 was increased from 200 mg to 300 mg. CS-III was found to be of higher density than SS607, hence it was possible to recommend 600 mg of 60-80 mesh for the back tube.

Once packed with sorbent and conditioned, sample tubes may be re-used repeatedly in a cycle of cleaning, sampling and analysis.

2.3.5. Conditioning and Desorption Temperatures

At desorption temperatures of 250°C and higher C106 can produce artefacts, which can interfere with the analysis of some components of gasoline, including benzene. Also, if the analysis temperature is higher than the conditioning temperature, gross interference can occur. Experience has indicated that provided the same desorption temperatures are maintained over the tube life, the effects of degradation can be significantly reduced.

To minimise degradation of the sorbent and ensure interference is kept to a minimum, the following conditions for handling C106 are recommended:

- Sorbent pre-conditioning: prior to the tubes being packed the C106 should be heated under nitrogen to 250ºC for 18 hours.
- Packed tube pre-conditioning: a temperature of 220ºC was chosen for initial conditioning of the tube.
- Packed tube use: after sorbent and tube pre-conditioning, the temperature of the tube should never be taken above 200ºC. This includes cleaning, certification and analysis of the tubes.
- An extended desorption time of 10 minutes ensures complete desorption of higher boiling analytes from the tube, e.g. C_3/C_4-alkylated aromatics.

Synthetic charcoals such as CS-III do not suffer from high temperature degradation and in fact must be desorbed at temperatures above 250°C. A temperature of 280ºC is recommended for CS-III sorbent pre-conditioning and 250ºC for packed sample tube conditioning, certification and analysis. A 5 minute desorption time is recommended which should be adequate for full recovery of C_3 to C_5 hydrocarbons.

2.3.6. Cold Trap

For the sorbent in the cold trap of the desorption unit there are potentially suitable alternatives, but these would still require more extensive validation. The continued use of C106 is recommended due to its proven good performance.

Past experience indicates that the amount of sorbent in the trap (40 mg) does not need to be changed. It is recommended, however, that the mesh size is changed from 80-100 to 60-80 to provide consistency with the sampling tubes.

For older models of thermal desorbers (e.g. PE ATD 250) the time of desorption is fixed. However, for more modern desorbers (e.g. PE ATD 400 or Turbomatrix) desorption time and rate of desorption can be varied and the conditions shown in **Table 2.1** are recommended.

Table 2.1 Recommended conditions for thermal desorption

Sorbent	Cold trap low	Cold trap high	Cold trap high temperature held	Rate of temperature increase
C106	- 30 °C	+ 220 °C	3 minutes	Fast
CS-III	- 30 °C	+ 250 °C	3 minutes	Fast

2.3.7. Transfer Line Temperatures

The temperature of 150°C of the transfer line between desorption unit and gas chromatograph, specified in method 8/86, can yield a slight loss of heavier species with subsequent sample 'carry-over' problems. Operating at 170-200°C can prevent this. Therefore a temperature of 200°C for both valve and line operation is recommended.

2.3.8. Split Ratios

Method 8/86 predates recent changes to splitting technologies, which now include both cold trap inlet and outlet splits. Any changes should ensure that desorption flows are not < 20-30 ml/min through the cold trap. Generally, this is achievable for most ATD/GC combinations in use. A lower split ratio of 50:1 was recommended to allow for the increased sensitivity required for lower detection limits. However, it should be noted that the final split ratio is dictated by the sensitivity and range of the detector.

2.3.9. Column

The gas chromatograph should be fitted with a capillary column suitable for the separation of the components of gasoline. The recommended column for this method is a 50 m long by 0.2 mm diameter column coated to 0.5 µm with unbonded OV 1701. Newer and more stable alternatives exist, but at least equivalent separation and identification of gasoline components needs to be demonstrated. Some laboratories have successfully used a column coated with BP1.

2.3.10. Detector

Flame ionisation detection (FID) is adequate for detecting and quantification of gasoline components. However, GC/MS should be used where specific confirmation of components is desired or critical.

2.3.11. Calibration

Method 8/86 recommended 6 calibration standards using 10 components of gasoline over the range 2.5 – 250 µg tube loading. It was recommended to change this to 0.5 - 125 µg to avoid possible overload of the column or detector at the reduced split ratio of 50:1. Any upward or downward extension of the calibration range is acceptable where the analyst can demonstrate that the analytical system is linear over the range and is sensitive enough for the reporting limit.

However, it was recognised that calibration standards were necessary for the CS-III tubes in the C_3 to C_4 hydrocarbon range. It was recommended that calibration tubes should be prepared using n-butane taken from the gas phase. 1,3-butadiene was excluded from the suite of components, because of uncertainties about the stability on the sorbents and the generally very low levels in gasoline.

2.4. NEW METHOD REQUIREMENTS

2.4.1. Quality Assurance

It is now highly recommended that laboratories working on gasoline vapour exposure monitoring samples have a quality management system, which provides a minimum standard equivalent to applicable European Standards (e.g. [7]), and preferably have obtained accreditation.

Laboratories should participate in at least one proficiency testing scheme relevant to the analytes and substrates of interest, and demonstrate satisfactory performance.

One such scheme is the Workplace Analysis Scheme for Proficiency (WASP), administered by the UK Health and Safety Executive (HSE).

For large studies, a set of independently produced quality assurance sorbent tubes should be ordered from a recognised Certified Reference Materials laboratory. The tubes should be loaded with known quantities, relevant to the calibrated range (e.g. 1 to 100 µg) of 4 components - benzene, toluene, p-xylene, and n-hexane. A sufficient number of tubes should be purchased such that one tube can be analysed for each ATD run (i.e. typically one QA tube per 30 samples).

Laboratories should be staffed by trained personnel. The thermal desorption and gas chromatography activities for gasoline vapour air samples should be guided or supervised by individuals with e.g. a minimum of 5 years experience with method 8/86 and other oil industry hydrocarbon analysis.

2.4.2. Quality Control

A number of requirements for quality control were defined:

Laboratories should be able to demonstrate linear performance across the calibration range and for the full range of anticipated exposure concentrations.

Two travel blanks should accompany each exposure monitoring batch. Blank results should be reported separately and not subtracted from the sample results.

All tubes should be engraved with a unique sample number. They should be sealed for transport with brass Swagelok end-caps, fitted with one-piece PTFE ferrules.

All calibration standards should be of the highest possible purity and traceable. A full 6 point calibration (including a separate run for the gas calibration for n-butane), with 2 tubes per concentration level, should be carried out at least once per month for calculation of the results.

Two sets of 2 liquid calibration check samples (of different levels) should be included within each sample run (i.e. one carousel batch on an ATD 50 or ATD 400) as a check of the system integrity, one set before the sample batch and one set after the sample batch.

Each calibration or sample set should be preceded by at least one analytical blank (metal or glass tube) to check the cleanness of the system.

The secondary trap sorbent, if C106, should be changed every 3 months.

All run conditions should be recorded. Back-up and archive procedures should be in place for all computer records.

3. COMPARISON OF THE REVISED METHOD WITH INTERNATIONAL STANDARDS

3.1. INTRODUCTION

Since 1986 international standards bodies, and notably the European Committee for Standardisation (CEN), have produced detailed guidance concerning the competence of laboratories. They have also produced detailed performance requirements for methods used for monitoring exposures to workplace airborne contaminants. There is a much higher expectation of quality assurance for both sampling and analytical procedures, as well as a high degree of validation.

For laboratories participating in workplace air monitoring a minimum standard equivalent to ISO/IEC/EN 17025:2000 [7] and preferably accreditation to this standard should be required. In order to meet these requirements, methods used need to be validated to CEN standards developed specifically for workplace atmosphere monitoring. A summary of these standards is given in Table 3.1 below, including comments on their relevance to the current method recommended by CONCAWE for gasoline vapour. The standards contain requirements for both sampling and analytical performance.

Table 3.1 International Standards Impacting on the CONCAWE Gasoline Vapour Monitoring Method (revision 2001)

Number/date of CEN Standard	Title of CEN Standard	Association of CEN Standard to CONCAWE Method
EN 482:1994 [1]	Workplace atmospheres – General requirements for the performance of procedures for the measurement of chemical agents	Performance requirements (validation) general to workplace atmospheres
EN 1076:1997 [4]	Workplace atmospheres – Pumped sorbent tubes for the determination of gases and vapours – Requirements and Test Methods	Performance requirements (validation) specific to pumped sampling.
EN ISO 16017-1:2000 [6]	Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/ thermal desorption/ capillary gas chromatography – Part 1: Pumped sampling	Methodology similar to that used by CONCAWE with reference to validation criteria available at time of publication
EN ISO/IEC 17025: 2000 [7]	General requirements for the competence of testing and calibration laboratories	Quality assurance requirements to attain accreditation in sampling and analysis

3.2. VALIDATION STATUS OF REVISED METHOD

EN 482 and more specifically EN 1076 cover the performance requirements for methods used for monitoring workplace airborne contaminants using pumped sorbent tubes. The revised method has been reviewed against the requirements of EN 1076. The validation status is summarised in **Table 3.2**.

Although method 8/86 predates EN 1076 and was not fully validated to EN 1076 requirements, it contributed significantly to ISO 16017-1:2000 which uses identical techniques. The revised method should be read in conjunction with ISO 16017-1:2000 since many of the procedures and references support the method.

The method does not fully satisfy the requirements for Level 1 evaluation, although there are supporting data. The method is analogous to EN ISO 16017-1, which is a generic, validated method for sampling and analysis of volatile organic compounds, and which itself does not fully satisfy the requirements of EN 1076.

For the revised method to become an industry standard for monitoring of gasoline vapour in workplace atmospheres, Level 1B validation would be necessary, using upper and lower homologues. In addition, priority pollutants such as benzene should be validated to Level 1A.

Table 3.2 Validation Requirements of EN 1076 and status of revised gasoline vapour method

Section from EN 1076	**Validation Requirement from EN 1076**	**Status of revised method**
5.2 Desorption Efficiency	Desorption efficiency shall be >0.95 with a coefficient of variation of not more than 0.1 at each loading	Validated for 11 components of gasoline covering the hydrocarbon range n-C_4 to n-C_{10} and BTX over the concentration range 0.1 to 100 µg - data to support criteria in: CONCAWE 8/86 [8] MDHS 72 [13] EN ISO 16017-1 [6]
5.3 Storage	The mean recovery after storage shall not differ by more than 10% from the value before storage. See section 7.7.1 for details of test	Not fully validated – data to support criteria in: CONCAWE 8/86 [8] EN ISO 16017-1 [6] Neither of the tests involved the required spiking of the tubes with an equivalent amount of water to represent an exposure to air at 80% relative humidity and at a temperature of 20ºC.
5.4 Overall uncertainty (OU)	Test in accordance with section 7.5 and 7.6 the OU, calculated in accordance with 7.12 shall be as specified in EN482: i.e. Measuring range 0.1 to 0.5 OEL: < 50% Relative Overall Uncertainty (ROU) Measuring range 0.5 to 2 OEL: < 30% ROU	Not fully validated – data to support criteria in: MDHS 72 [13] EN ISO 16017-1 [6]

Table 3.2 Cont'd Validation Requirements of EN 1076

5.5 Blank value	Test in accordance with 7.3 the blank value shall be less than one third of the calculated mass collected by the sampler during 30 min exposure to 0.1 LV at 10 ml/min	Blank samples are routinely analysed, but current reporting limit is higher than required maximum blank value
5.6 Leak test	Test in accordance with 7.8 (expose sealed samplers to atmosphere of 2 OEL for 4hr) any additional analyte determined above the blank value shall be less than one third of the calculated mass collected by the sampler during 30 min exposure to 0.1 LV	Perkin Elmer tubes with Swagelok end caps tested by UK HSE-Reference not available
5.7 Flow resistance	19 out of 20 tubes shall not exceed 5kPa at a flow rate of 300ml/min	No data but test should form part of the method
5.8 Instructions for use	a. Breakthrough volume b. Designated use/measuring range/level of validation c. Directions for the proper handling of the sorbent tubes including opening and closing d. General information on the system e.g. sorbents (can be given in additional literature). e. The levels at which other gases and vapours including water, are likely to interfere to the extent of increasing the OU above the level in the standard i.e. 30% or 50%. f. Information on calculation of results including the evaluation of reading and correction factors for temperature, pressure and desorption efficiency, if applicable g. Information on transport and storage h. Desorption Efficiency i. Information on desorption method	Method meets all the criteria (Appendix 1)
5.9 Sample ID	Tube to have room for sample id by the user	Tubes engraved with unique number
8. Levels of Evaluation	There are 3 levels of evaluation: Level 1: a) 1A – An evaluation as per main text b) 1B – An evaluation of an analogue within an homologous series both upper and lower members as tested to 1A Level 2: An evaluation to Level 1 plus Annex C (i.e. Field tests – paired comparisons Level 3: An evaluation to Level 2 plus Annex D (i.e. Field tests – multiple comparisons	Method meets some of the performance requirements of Levels 1A and 1B but will require further validation to fully meet the Level 1 criteria

4. FIELD AND LABORATORY EXPERIENCES USING THE REVISED METHODOLOGY AND FINAL RECOMMENDATIONS

A field study of occupational exposure to gasoline vapour was carried out by CONCAWE member companies during the period 1999 – 2001, using the revised methodology. Over 250 samples were collected and analysed in 19 different surveys. A single laboratory was contracted to prepare the sample tubes and analyse the samples. Sample tube distribution and receipt were also handled by a single office. This arrangement was intended to ensure a high degree of consistency and quality control. The sample tubes, along with any external quality control samples, were returned to the analytical laboratory as blind samples. The study protocol also required that bulk gasoline samples were taken. The survey results from this study are reported under separate cover [9].

This section deals with the experiences gained using the revised method. Shortcomings were identified and recommendations were made to improve the procedures for both the sampling and analytical methods.

The current version of the revised CONCAWE monitoring method for gasoline vapour is provided in **Appendix 1** and incorporates the recommended changes where these could be justified.

4.1. FIELD EXPERIENCE

4.1.1. Sampling Package

On at least two occasions higher boiling components were detected on the back tube but were absent on the front tube. This suggested that the tubes had been connected to the pump in the wrong orientation, i.e. with the front tube connected nearest to pump. As with any sampling tube or tube combination, it is possible that they are used in the wrong orientation or sequence by mistake. In the case of the gasoline vapour method, an incorrect sequence will lead to loss of data, because the desorption of high boiling components from CS-III will be incomplete. The C106 and CS-III tubes were supplied to the participants in two separate tins, which were clearly marked. Also, clear instructions with diagrams were given via a detailed sampling protocol. The problem appeared to be simple human error, which would have been even more difficult to detect if the sorbents had been packed into a single tube. Since this error constituted less than 1% of the samples, no change in the method is envisaged or recommended.

On a number of occasions the sample tubes were returned to the laboratory with loose end caps. This may have resulted in sample contamination or some loss of analytes during storage and transportation. Conversely, on one occasion, bent tubes were returned to the laboratory. This suggested that excessive force had been applied to the end caps when tightened and made it difficult to mount them on the desorber. On another occasion the end caps were missing altogether, which pointed to a fundamental lack of understanding of the procedures. These problems are most efficiently addressed via adequate training and instruction.

Sorbent loss from the back section of one sample tube was observed during sampling, in the form of sorbent in the plastic tube connecting the tubes to the pump. As the loss was from the back of the back tube, this could have lead to an underestimation of components of the gasoline vapour in the C_3 to C_5 range. However, since the loss of sorbent was from the back of the tube, the error would most likely be minimal. Since all tubes are checked for sorbent loss prior to certification and again before dispatch, the most likely cause of the problem was excessive shaking of the sample tubes during transportation. Therefore it is recommended that:

a) The tubes are tightly packed in the sealed tins prior to transportation

b) Sorbent loss should be checked prior to sampling. This can be done by gently tapping the end of the sample tube on a suitable surface. A white surface should be used for the back tube (sorbent is dark) and a black surface for the front tube (sorbent is white). If sorbent loss is observed the sample tubes should be removed from the study and returned to the laboratory.

4.1.2. Contamination

Field blanks in one survey were found to contain gasoline components in detectable quantities. Since the laboratory blanks were found to be contamination free, the likely cause was one of the following:

a) Sample tubes were stored or transported in a contaminated atmosphere

b) The field blanks were exposed to the atmosphere during sampling i.e. the end cap or caps were removed for the duration of the survey.

If the sample tubes were correctly stored in the sealed tins provided and the caps were replaced correctly then the most likely cause for the contamination would be b). The problem would appear to point to not carefully following the protocol instructions.

On one occasion the sample tubes were actually transported in the same package as bulk gasoline samples. If the tubes were capped properly and effectively sealed in the tins provided, then the contamination should have been minimal. The sample results were treated as suspect, due to the heightened risk of contamination, though the field blanks were clean. The revised method contains a clear statement “that under no circumstances should sample tubes be stored or despatched with bulk gasoline samples”. It is further stated “that it is advisable to dispatch the sample tube package and the bulk gasoline package on separate days, so that they are not combined by the courier or postal service used”.

In order to avoid these contamination problems the following recommendations are made:

a) The sampling organisation should be accredited to EN ISO/IEC 17025 and demonstrate competence in workplace air sampling (occupational hygiene) through the appropriate organisation.

b) Definition of a detailed sampling protocol should form part of any study and must be included in training of personnel.

4.1.3. Safe Sampling Volumes

An evaluation was made of the amount of material detected on the back tube in comparison with the front tube for two reasons:

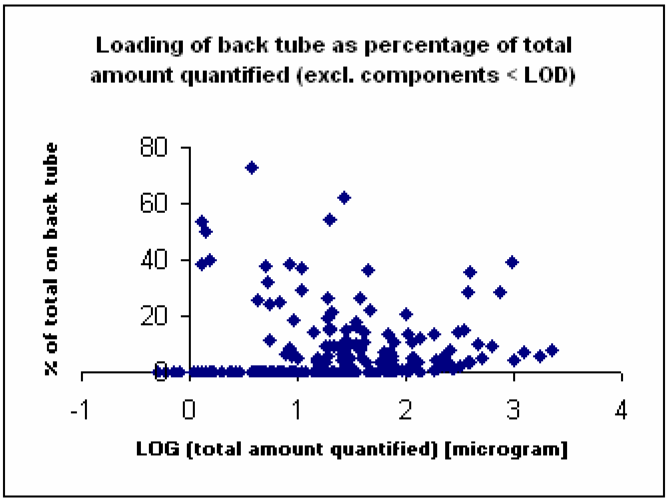
- It has been noted that most published studies of exposure to gasoline vapour and components typically did not use a sorbent such as CS-III for the very volatile components and consequently may not have captured these components completely. The current field data were used to quantify this possible underestimation.
- Propane on the back tube is the determining factor for the Safe Sampling Volume. If this were changed to n-butane, for example, then a larger volume would be allowed, improving the detection limits for priority components, or reducing the number of samples needed to cover work shifts under unfavourable conditions of temperature and relative humidity.

The calculated average value for the amount on the back tubes was 7.7% of the total detected quantity (on both tubes). This suggested that any systematic error due to not having a back tube would not be very large. However, there was considerable variation, as exemplified by the standard deviation of 12.7(%) and maximum value of 73% (see also **Figure 1**). Therefore, on occasion the underestimation could be significant. There was no apparent relationship with the total adsorbed quantity, suggesting this was not a simple break-through phenomenon.

Propane was often not detected at all, and was never among the components detected in highest quantities in the air samples. The median and 90th percentile values propane in bulk product were 0.1 and 0.4%, respectively (n = 26). Propane is also not a priority component hazardous to health, and therefore the safe sampling volume for gasoline vapour may not need to be based on propane.

In conclusion, the back tube was found to be important for ensuring that all airborne components are captured, but the safe sampling volume does not have to be set for propane.

Figure 1 Loading of back tube as percentage of total amount quantified (excl. components < LOD)



Care should be taken, however, if n-butane were selected to determine the safe sampling volume of the method. Although the safe sampling volume would be considerably increased (see Appendix 2 for the safe sampling volumes of propane and n-butane on CS-III), consideration must then be given to the components collected on C106. For example the safe sampling volume of benzene on 300 mg of C106 is 28 litres. If this is reduced by a factor of 3 for a 15ºC rise in temperature (35ºC), and a factor of 2 for high humidity (80% RH) the safe sampling volume for benzene on 300 mg of C106 is reduced to 4.7 litres. This is lower than the safe sampling volume for n-butane on CS-III under the same environmental conditions.

4.2. ANALYTICAL EXPERIENCE

4.2.1. Range of Method

Analytical system overload of C_4 components was reported on several occasions, which was attributed to detector overload. The method was intended to account for the total hydrocarbon concentration as the sum of the 150 individual components. This overload problem reduces the ability of the method to meet this objective.

Conversely, it was observed on a number of occasions that some of the priority pollutants, notably benzene, were not detectable down to a satisfactory concentration, i.e. one tenth of the OEL.

The analytical range of the revised method had been reduced to 0.5-125 μg per component (i.e. 0.2 mg/m³ to 50 mg/m³ for a 2.5 litre sample) to avoid overload of the detection system during calibration. However, even this reduction of the upper limit caused overload at a split ratio of 50:1, so the ratio was changed to between 250:1 and 300:1 for the analytical systems used in the study. At this split ratio, overload of the detection system was not observed and the method was deemed satisfactory for the study.

Similarly, under normal sampling conditions (with typically a 2.5 litre sample), the reporting lower limit of the method (i.e. 0.2 mg/m³) was deemed to be satisfactory (i.e. below one tenth of the OEL) for all the priority pollutants in gasoline. However, when the sample volume was reduced to accommodate conditions of high humidity and temperature and avoid breakthrough of propane, then the detection limit for benzene became higher than one tenth of the OEL. (e.g. 0.8 mg/m³ for a 0.6 litre air sample versus an OEL of 3.25 mg/m³).

In summary, if the priority pollutants such as benzene are the focus of the study under all environmental conditions of sampling, then it is recommended that the method should be modified in one of the following ways:

a) Retain the safe sampling volumes but reduce the split ratio of the analytical method and risk overload of the detection system.

b) Increase the sampling volume and risk overload of the detection system and breakthrough of sampling package due to loss of propane.

c) Fix the sampling volume at 2.5 litres for all environmental conditions as discussed above in section on safe sampling volume.

If option b) or c) is taken then analytical costs can be reduced, since less samples will be needed for a full shift, but some propane may be lost.

4.2.2. Identification of Components

The OV-1701 column, specified in method 8/86, was retained, because of the large number of compounds which have been identified with assigned retention times or relative retention times. However, when known analytes were analysed for the 1999-2001 study, it was found that relative retention times were different from those in report 8/86. Furthermore, it was found that retention times shifted slightly during analysis, and that in those cases where the analyte pattern was not typical for gasoline, assigning true identification was difficult. Identification was further complicated when unknowns were present in the sample, for example as a result of the worker also having handled petroleum products other than gasoline. Some example plots of chromatograms are provided in **Appendix 3**.

To assist with the determination of retention times and identification of components, a number of steps are recommended as follows:

a) A bulk gasoline sample collected during the survey should be analysed by GC-MS using an OV-1701 column.

b) GC-FID analysis of the bulk samples will also help to confirm identification of the significant peaks.

c) A retention time vapour standard of known analytes (11 calibration compounds, propane, and methyl-*tertiary*-butyl-ether (MTBE)) should be run alongside the samples. These qualitative standards should be prepared as vapour and spiked onto the sorbent to eliminate any effect of the cyclohexane solvent on the retention times. A butane/propane standard should also be run with the front tubes to enable accurate determination of propane and n-butane retention times.

   These steps will assist in identification when retention times have shifted slightly or when the samples are atypical or unknowns are present which are not from gasoline vapour.

   Information about possible potential interfering contaminants should be submitted with the samples to assist in assigning identification of unknown components.

d) For proof of identification of unknown compounds it will be necessary to use GC/MS for airborne samples collected during the survey. Therefore some samples should be collected in duplicate and one set analysed by GC/MS for identification purposes.

e) Any further review of the method should consider alternative columns such as bonded BP1, which may exhibit better properties regarding retention time stability.

4.2.3. Oxygenated Components

Due to the large number of samples and diversity of sources of the samples of the field study, it was not always possible to know whether oxygenates were present in the samples. The most commonly encountered oxygenated component was MTBE. However, in several surveys it had not been possible to obtain bulk samples. Consequently calibration of the analytical system for oxygenates was not always carried out.

For this study an MTBE calibration was either carried out before the samples were run or retrospectively if MTBE was detected. Occasionally, the MTBE response factor had to be estimated. This was carried out by using n-Hexane response factors and comparing these with MTBE response factors from samples where the MTBE calibration had been carried out.

To minimise any uncertainty it is recommended that MTBE should be included in the calibration standards. Stability of these MTBE standards, however, needs to be assessed.

It is also recommended that the bulk gasoline is analysed by GC/MS and GC/FID prior to analysis of the sample tubes. A sample of the bulk vapour should be spiked onto a C106 tube and analysed alongside the standards to identify any oxygenates and significant hydrocarbons.

Other oxygenates should be included in the calibration blend if they are found to be present.

4.2.4. Component Carry-over

The specification for the acceptability of carry-over from the cold trap in the ATD system, is quoted by the manufacturer as < 2%. This study has shown that carry-over of the components used for calibration does not occur for masses of < 50 μg. However, carry-over may occur for higher boiling components (e.g. BTX, Octane, Nonane, and Decane) at masses > 50 μg.

For example, when analysing a blank tube after a 125 μg standard, ~0.08% (0.1 μg) of m-Xylene and ~0.05% (0.06 μg) of Octane and Toluene was found due to cold trap retention of these compounds. This carry-over is below the reporting limit of 0.5 μg and is not likely to influence the results greatly. Also, the components that are most likely to be retained by the cold trap are the least likely to be present, at high concentrations, in the air samples.

However, to safeguard samples it is recommended that a “dummy blank tube” is analysed after high calibration standards, check standards or quality control samples (i.e.> 50 μg) to ensure that carry-over problems do not affect any field samples or blanks. Any significant carry-over should be investigated and rectified immediately.

5. CONCLUSIONS

1. A considerable number of procedural and technical changes were needed to adapt the CONCAWE recommended method for the monitoring of occupational exposure to gasoline vapour, originally published in 1986, to current standards of technology and occupational hygiene practice. The changes have been documented and a rationale provided.
2. The revised method has been reviewed against the validation criteria of the European Standards. Whilst the revised method meets a number of the criteria, others are not met or not met in full.
3. The revised method is considered adequate for monitoring full-shift exposures to total and individual components of gasoline vapour in air, as low as 0.2 mg/m^3 per component under moderate environmental conditions. Under unfavourable conditions of temperature and humidity, the method limitations will not allow quantification at one tenth of the future European Occupational Exposure Limit for benzene. However, by fixing the sample volume, this issue can be resolved, whilst keeping the loss of very light components, such as propane, to a minimum.
4. Some further recommendations for improvement of the sampling and analysis method have been made on the basis of experiences gained in a large, multi-centre field study. Where justified, these recommendations were incorporated into the method. Other recommendations require further experimental assessment before they can be incorporated.

6. REFERENCES

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APPENDIX 1

MONITORING EXPOSURE TO GASOLINE VAPOUR IN AIR – CONCAWE METHOD (REVISION 2002)

CONTENTS

1. SCOPE

This method describes a procedure for the sampling and analysis of gasoline vapour in a wide range of workplace activities. The method is suitable for both personal and fixed location monitoring for periods up to 12 hours by appropriate adjustment of the sampling flow rate. When the effect of temperature or humidity reduces the sampling time to less than 12 hours then more than one sample must be taken to cover the full period. 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. For a twelve hour period, it may be appropriate to take 6 samples, each with a sampling period of 2 hours.

This method is appropriate for a range of hydrocarbons from propane to dodecane and, if present, oxygenated compounds such as methyl *tertiary*-butyl ether (MTBE). Two specific sorbents are recommended for the sampling of these volatile organic compounds (VOCs), namely Carbosieve S-III (CS-III) for C_3 to C_5 hydrocarbons and Chromosorb 106 (C106) for C_5 to C_{12} hydrocarbons and MTBE. This method uses two tubes in series, with the C106 tube acting as the front tube to collect the less volatile hydrocarbons and the CS-III tube acting as the backup tube to collect the more volatile hydrocarbons.

The method is applicable to the measurement of individual gasoline components on the tube in the concentration range of approximately 0.5 to 125 μg per component. This is equivalent to airborne hydrocarbon vapours in the range 0.2 mg/m³ to 50 mg/m³ of individual components for a 2.5 litre sample.

The method is suitable for atmospheres up to 95% relative humidity and temperatures up to 40°C provided the recommended sampling volumes are used. However, it is possible that breakthrough, hence loss of lighter hydrocarbons such as propane may occur under extreme conditions.

2. NORMATIVE REFERENCES

CEN (1997) Workplace atmospheres - Pumped sorbent tubes for the determination of gases and vapours - Requirements and test methods. EN 1076:1997. Brussels: Comité Européen de Normalisation

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3. TERMS AND DEFINITIONS

Measuring procedure:

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

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.

Flow rate:

Volume of (workplace) air drawn through the sampling medium per unit of time; usually expressed in millilitres per minute (ml/min).

Sorbent tube:

A stainless steel tube containing either C106 or CS-III sorbent through which sampled air is passed at a rate controlled by the air- sampling pump.

Sorbent tube combination:

For the purpose of this method two tubes are joined together with the front tube containing C106 and the back tube CS-III.

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.

Breakthrough volume:

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

Safe sampling volume:

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

Desorption efficiency:

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

Method Validation:

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

Limit value:

Reference value for the concentration of a chemical agent or agents in air.

Bias:

Constant deviation of the results of a measurement process from the true value of the concentration of a chemical agent in air.

Precision:

The closeness of agreement of results obtained by applying the method several times under prescribed conditions.

True value:

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

Overall uncertainty:

Quantity used to characterise as a whole the uncertainty of the result given by a measuring procedure.

Loading:

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

4. PRINCIPLE

A measured volume of air is drawn through two sorbent tubes in series. The front tube is packed with C106 and the back tube contains CS-III. The front tube retains the gasoline vapour in the hydrocarbon range C_3 to C_{13} though some of the C_3 to C_5 hydrocarbons may pass straight through. These hydrocarbons are retained on the Carbosieve S-III tube. The collected gasoline components 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 liquid or vapour spiking of the sorbent tube using a selection of hydrocarbons over the range of concentration and carbon number. The quantified gasoline components, expressed in micrograms and the volume of air sampled, expressed in litres are used to calculate the concentration of gasoline components in the sampled atmosphere, expressed in milligram per cubic metre.

5. REAGENTS AND MATERIALS

Sorbents:

Chromosorb 106 60-80 mesh (Polystyrene):

Should be preconditioned at 250°C for 18 hours under a flow on nitrogen.

Carbosieve S-III 60-80 mesh (Carbon molecular sieve):

Preconditioned at 280°C for 18 hours under a flow of nitrogen.

Note: To prevent recontamination of the sorbents, they should be kept in a clean atmosphere during cooling to room temperature, storage and packing into the tubes.

Note: The analytical desorption temperature MUST always be kept below the conditioning temperature to prevent production of artefacts or contamination interference.

Volatile organic compounds:

All reagents used should be Analar grade and should at least include the liquids listed in **Table 1**.

Solvents:

Cyclohexane:

The cyclohexane must be free of components used for the calibration and should be checked before use. C106 tubes, which have been spiked with up to 2.5 µl of the solvent should be analysed under the same conditions as the calibration standard tubes. If the solvent is found to contain more than 10 ng/µl of any components that might interfere with the calibration then this bottle should not be used. Fresh bottles of solvent should be checked in the same way before use.

Note: A suitable grade can be purchased from Rathburn Chemicals which is produced on specially decontaminated equipment and checked by the manufacturer prior to delivery.

Gases:

Certified (traceable to primary standards of mass or volume) cylinder of butane and propane (~ 1% mass of each) in nitrogen.

Note: Suitable gas blends can be purchased from Linde Gas.

6. APPARATUS

Sorbent tubes:

Sorbent tubes are made of stainless steel tubing (6.3 mm OD, 5 mm ID and 90 mm long). 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 in the tubes by stainless steel gauzes and/or un-silanised glass wool plugs.

The front tube should be packed with 300 mg of C106 and the back tube with 600 mg of CS-III. The tubes should be cleaned, conditioned and certified prior to each use as described in **Section 7**.

Sorbent tube end caps:

Metal screw-caps, such as Swagelok, with PTFE seals.

Metal screw-caps with 1mm hole (for use when sampling with flow rates < 5 ml/min).

Metal sorbent tube unions, such as Swagelok, with PTFE seals.

Syringes:

Precision liquid syringes to cover the range 1 to 5 µl readable to 0.1 µl. Precision gas tight syringes to cover the range 25 µl to 5 ml and readable to 0.1 µl or 0.01 ml as appropriate.

Sampling pump:

The pump should fulfil the requirements of EN 1232 or equivalent and shall be in accordance with local safety regulations, e.g. certified as intrinsically safe.

Tubing:

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.

Clips:

Suitable clips to hold the tubes and tubing in place.

Calibrated flow meter:

Soap bubble meter or other suitable gas flow meter calibrated/certified and traceable to national standards.

Gas Chromatograph:

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

Thermal Desorption Apparatus:

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. A Perkin Elmer ATD 400 is suitable.

7. SAMPLE TUBE CONDITIONING AND CERTIFICATION

C106 packed tubes are initially cleaned / conditioned at 220°C for 1 hour and then a further hour at 200°C, before first use. Thereafter the tubes are cleaned at 200°C for 30 minutes.

CS-III packed tubes are cleaned /conditioned at 250°C for 1 hour. Thereafter tubes are cleaned at 250°C for 30 minutes for each use.

Cleaning/conditioning can be carried out using the automated desorber e.g. ATD 400 in mode 1 or use of a Tube Conditioner.

Every tube should be certified before each use. This can be achieved by analysing each tube under the conditions used for analysis (**Tables 4 and 5**) and comparing the area of any peaks found 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, then the tube should be re-conditioned or re-certified by repeating the procedure. Tubes should be sealed with screw caps fitted with PTFE ferrules as soon possible after certification and stored in an airtight container. The container should be stored in a solvent free atmosphere, such as a refrigerator in which only sampling tubes have been stored.

8. PREPARATION OF STANDARDS

Standard CS-III tubes:

Clean CS-III tubes are spiked in duplicate with a blend obtained from Linde Gas containing accurately known proportions of butane (~1% m/m) and propane (~1% m/m) as shown in **Table 3**.

Note: The propane is used only as a retention time marker.

The cylinder manifold should be purged with the calibration gas before taking an aliquot. The syringe should also be purged with the calibration gas before the required amount is spiked slowly on to the front of the tube whilst a pump draws 80-120 ml/min of clean laboratory air through the tube. The pump should be kept on for 20-30 seconds before the tubes are capped. The standards should be analysed within a day of being prepared.

The concentration of butane is converted to mg/m^3 using the following equation:

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

Where:
ppm = % m/m x 10000
Molecular mass for butane = 58
Molar volume of air at 25 °C = 24.45 litres

The exact mass (µg) of butane spiked, at each level, should be calculated and used for the calibration.

Standard C106 tubes:

Solutions for spiking onto C106

Multi-Component Blend

"Concentrated" Calibration Blend (50 µg/µl):

This should be prepared by accurately weighing (to the nearest 0.01 g) approximately 2.5 g of each component (starting with the higher boiling components) into a 50 ml volumetric flask containing about 10 ml of cyclohexane. The 10 liquid components are listed in **Table 1**.

After the last component has been added, the blend should be made up to the mark with cyclohexane and the flask stoppered and thoroughly mixed.

"Diluted 1" blend (5 µg/µl):

This should be prepared by pipetting 5 ml of the "concentrated" blend into a 50 ml volumetric flask containing between 20 and 40 ml of cyclohexane. The blend should be made up to the mark with cyclohexane, stoppered and thoroughly mixed.

"Diluted 2" blend (0.5 µg/µl):

This should be prepared by pipetting 5 ml of the "Diluted 1" blend into a 50 ml volumetric flask containing between 20 and 40 ml of cyclohexane. The blend is made up to the mark with cyclohexane and the flask stoppered and thoroughly mixed.

The liquid standards can be kept in a suitable refrigerator for three months or longer unless internal quality control procedures indicate that the solutions have deteriorated.

Clean C106 (300 mg) tubes should be spiked, in duplicate, with the various volumes and concentrations of the multi-component blend, as shown in **Table 2**. The front end of the tube should be spiked slowly with a micro syringe containing the appropriate standard, whilst air, at a flow rate of 80-120 ml/min is pulled through the tube by a pump connected to the back of the tube. The pump should kept on for a further 20 and 30 seconds after injection. The tubes should then be sealed with Swagelok end caps and kept at least overnight before analysis.

The exact mass (µg) of each component spiked, at each level, should be calculated and used for the calibration.

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 at a flow rate of 2 - 20 ml/minute and be capable of stable operation throughout the sampling period.

Note: To achieve these low flow rates on some pumps a flow splitter may need to be used.

Sampling pumps should be calibrated before commencement of, and on completion of sampling utilising a portable gas flow meter system capable of measuring an air flow in the range of 1-20 ml/min and accurate to ± 2%. Pump calibration and flow checks must be made with the tandem sample tubes included in the sample train.

Note: To achieve these low flow rates on some pumps a flow splitter may need to be used.

Calibration/certification of the gas flow meter used should be traceable to national standards.

Pump flow rates should be checked periodically during the sampling period and in particular if/when a battery pack is changed.

10. SAMPLING

Prior to use, sampling tubes should be tested for flow resistance. This should be done, by connecting a differential pressure gauge (manometer) between the pump and the tubes and measuring the pressure drop. At least 19 out of 20 tube combinations tested shall not exceed 5kPa at a flow rate of 300 ml/min

The sample tubes and connections supplied by the laboratory should be kept sealed in the storage can provided, refrigerated ideally at below -4°C and away from any contamination. Each sample tube has been certified as to its suitability for monitoring gasoline and 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.

The sampling package consists of two separate metal tubes, and each batch is supplied with special connections. Tubes are capped when supplied. 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.

The maximum recommended sample volume is 2.5 litres at 20° C and relative humidity below 80%. In sample volumes greater than this, there may loss of the lower boiling components of gasoline (e.g. propane and butanes). This volume should be reduced by a factor of 2 for every 10 degree C increase above 20°C.
Key factors influencing the breakthrough volume (litres) and therefore the sampling rate (ml/min) 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 a factor of 10 for high humidity. However, it is not

just a question of maintaining a 'very low' air sampling rate, because diffusion begins to play a contributory role when the pumped air 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 includes 'peak samples', taken over gasoline handling tasks of a duration shorter than the full work shift. In some instances it may be necessary to take two or more consecutive samples to cover the work shift or task of interest.

Surgical gloves should be worn when handling the tubes. Touching of the ends of the tubes, or the ferrules with contaminated fingers, should be avoided. This may cause contamination which may interfere with subsequent analysis.

Before start of sampling a set of two tubes should be combined after removing the brass end caps, using two spanners of the correct size. Note the location of the grooves on each of the tubes. The correct direction of flow is into the tube containing C106 from the grooved end. This tube has an engraved number and a designation indicating "Chromosorb106".

When sampling at flow rates of less than 5 ml/min, fit a brass Swagelok nut with a 1 mm hole on to the grooved end of the C106 tube. This will minimise the effect due to diffusive sampling at these low sampling rates.

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

All connections using Swagelok fittings should be made hand tight and then ¼ turn using a spanner or wrench.

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.

Sampling pumps must be calibrated in a clean atmosphere with the tandem sampling tubes included in the sampling train.

Prior to taking each sample record:

- Sample tube numbers for each combination of sampling tubes
- Personnel ID (optional and for company use only).
- Date of sampling
- Location of sampling
- Nature of Task
  Position the sampling head in the breathing zone of the operator being monitored with the tube combination in a vertical, downward position and fixed securely.
  Locate the pump on the person in an appropriate position ensuring that any flexible tubing is not restricted in any way.
  Turn sampling pumps on and record:
- Sample start time (hh:mm)
- Initial pump flow rate (ml/min)
  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)

- Volume of air sampled (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)
- Atmospheric pressure (mm Hg) (optional)
- Relative humidity (%)
- Precipitation (yes/no, time period)
- Cloud cover (octiles) (optional)

Draw a simple plot plan and mark location of operators and sources of product release. Additional information required includes:

- Gasoline throughput (preferably during sampling period)
- Any relevant observations, e.g. control measures

Immediately after sampling, carefully separate the tubes and fit the end caps

Take extreme care to ensure that the front and back tubes are positively identified as one sample set. When submitting the sample record form to the analytical laboratory log tube numbers in sequential order, e.g. Sample I front tube No. xxx , back tube No. xxx

A minimum of two 'field blank' (tandem tubes) samples should be submitted for each 10 field samples submitted.

Field blank tubes 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. All samples, including field blanks, should be clearly labelled and details entered on a sample submission form.

Samples tubes should be despatched by the quickest route available, together with a copy of the information required.

NOTE: UNDER NO CIRCUMSTANCES SHOULD SAMPLE TUBES BE STORED OR TRANSPORTED WITH BULK GASOLINE SAMPLES.

When bulk samples are being collected, great care should be taken to ensure that loss of low boiling components is minimised and, during sampling, ensure that all sources of ignition are excluded.

Representative samples of handled products should be taken where possible. In the case of service stations, it may be more convenient to obtain the bulk samples from the distribution terminal from which deliveries are made to the service stations being monitored.

Although only 5 ml of bulk products is required for analysis, it is often easier to take larger samples (e.g. 1 litre volume). Also, small samples are liable to evaporate if in larger containers. Containers should conform to relevant international or European legislation, as appropriate. Shipping regulations will need to be adhered to in terms of volumes and packaging.

NOTE: IT IS ADVISABLE TO DISPATCH SAMPLE TUBES AND BULK SAMPLES ON SEPARATE DAYS SO THAT THEY ARE NOT COMBINED BY THE COURIER OR POSTAL SERVICE USED.

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 components of gasoline 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 a cold trap containing C106. This pre-concentration stage, 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 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 the components of gasoline collected onto the sorbent tubes used for sampling. A Perkin Elmer ATD 400, for example, is suitable for this type of analysis. The desorption parameters for the complete recovery of components from the two types of tube are given in **Table 4**.

The gas chromatograph should be fitted with a capillary column suitable for the separation of the components of gasoline. The recommended column for this method is a 50 m long by 0.2 mm diameter column coated to 0.5 µm with unbonded OV 1701 or BP1. The column should be connected to the thermal desorber according to the manufacturer 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 gasoline and the parameters required for this analysis are given in **Table 5**.

The gas chromatograph and thermal desorption unit should be operated according to the manufacturer instructions and conditions given in **Tables 4 and 5**.

11.3 Calibration

The gas chromatograph/thermal desorption unit system must be calibrated before any samples are analysed. Each calibration tube should be analysed according to the conditions given in **Tables 4 and 5**.

11.3.1 Calibration of Front Tubes (C106)

The gas chromatograph should be calibrated before the samples are committed to analysis by use of the multi-component blend solutions spiked on to C106 tubes as shown in **Table 2**. The calibration tubes should be analysed in duplicate for each level (total 7 level over the range 0.5 to 125 µg). An internal quality control (IQC) sample should also be run to check the accuracy of the calibration. The IQC results must be within 10% of the expected results before samples are analysed. If the IQC

is outside this range then a second IQC sample should be analysed. If the second IQC sample is also outside 10% then an investigation should be carried out and the instrument re-calibrated.
"Dummy blank tubes" tubes should be run after each pair of standards and QC samples to prevent carry-over into other standards or samples.

For each component a calibration plot is generated which should display linearity i.e. correlation coefficient >0.999. The exact mass (μg) of each component spiked, at each level, should be calculated and used for the calibration. The gas chromatographic data system will give a series of response factors for each component and a mean response factor may be calculated from these or a gradient may be determined from the calibration plot. The response factor or gradient are used to determine the mass of components in the samples. For each of the components reported a suitable calibrant will be assigned as shown in Table 1, e.g. n-hexane used for all non-aromatic hydrocarbons containing six carbon atoms. The full range of the calibration is from 0.5 to 125 μg per component.

11.3.2 Calibration of Back Tubes (CS-III)

The Gas Chromatograph should be calibrated before the samples are committed to analysis by use of the butane standard spiked on to CS-III tubes as described in **Section 8**. The calibration tubes should be analysed in duplicate for each level (5 levels over the range 0.5 to 100 μg).

The calibration plot generated should display linearity, i.e. correlation coefficient >0.999. A mean response factor or gradient should be derived in the same way as for C-106 (see above) for butane and used to determine the mass of components in the samples. The butane mean response factor or gradient should be used to calculate the masses of all components found on the back tube. The full range of the calibration is from 0.5 to 100 μg of butane.

Note: Calibration Standards containing butane should be analysed within one day of preparation.

11.4 Identification of Sample Components

To correctly identify the components present a range of hydrocarbons should be obtained and analysed to determine the absolute retention time and retention time relative to toluene. These times can vary, even when using identical columns.

Retention time standards of known analytes (11 calibration compounds, propane, and MTBE) should be run alongside the samples. These qualitative standards should prepared as vapour and spiked onto the sorbent to eliminate the effect of cyclohexane solvent on the retention times.

A butane/propane standard should also be run with the front tubes to enable accurate determination of propane and n-butane retention times.

These steps will assist in identification when retention times have shifted slightly or when the samples are atypical or unknowns are present which are not from gasoline vapour. To further assist with the identification of the components, GC-FID analysis of the bulk gasoline samples collected during the survey should be undertaken to help confirm identification of the significant peaks. Also the bulk gasoline sample can also be analysed by GC-MS using an identical column.

With the data from the procedures described above it should be possible to accurately identify most of the components found on the tubes. A list of the components of gasoline is given in **Table 6**.

11.5 Determination of Desorption Efficiency

The ratio of the slope of the calibration graph of the substance of interest relative to that of n-hexane should be the same as the relative response factor for that compound. If the ratio of the slope of the calibration graph does not agree within 10% then, the desorption parameters, should be checked and changed accordingly.

12. CALCULATIONS

Calculate the concentration c_m of each component in the sampled air, in milligrams per cubic metre by means of the following equation:

$$c_m = m_f \cdot 1000/V$$

m_f is the mass of analyte found on the tube (or the sum from both tubes) in milligrams

V is the volume of sample taken in litres.

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 or cleaning temperature. All cleaned and certified tubes should be stored in sealed containers in a clean, solvent free atmosphere before and after sampling prior to analysis.

Contamination of the tubes can occur if the tubes are transported with the bulk gasoline samples. To minimise the risk of the samples being transported in the same package, the sample tubes and bulk gasoline sample should be sent on different days.

Organic compounds in the same boiling range as gasoline will interfere with the analysis. Any known or potential interferents encountered during the survey should be reported with the sample details.
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 storage and blank levels can be found in EN/ISO 16017-1:2000. The safe sampling volume for propane and butane is given in **Table 7**.

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.

16. QUALITY CONTROL

A minimum standard equivalent to EN/ISO/IEC 17025:2000 and preferably accreditation to this standard should be employed.

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) relevant to the analytes (e.g. WASP benzene, toluene and xylene on Tenax) and where possible substrates of interest should be undertaken and a satisfactory performance attained.

Internal quality control (IQC) samples should be run prior to any field samples being analysed. These IQC samples should be prepared independently of the laboratory, 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 detected on the laboratory blanks should be investigated and eliminated prior to any further analysis of samples.

Check standards covering the range of concentration should be included within each batch of samples analysed to check the system integrity. These check standards can be used to recalibrate if conditions have been shown to alter slightly since the initial calibration. If a major shift in conditions occurs then the analysis should be stopped immediately and the reasons investigated and rectified.

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 1 Relationship between calibration components and sample components

Calibration component	Related hydrocarbon
n-Butane	C_3 to C_5
n-Pentane	C_5 (non aromatic)
n-Hexane	C_6 (non aromatic)
n-Heptane	C_7 (non aromatic)
n-Octane	C_8 (non aromatic)
n-Nonane	C_9 (non aromatic)
n-Decane	C_{10}-C_{13} (non aromatic)
Benzene	C_6 (aromatics)
Toluene	C_7 (aromatics)
Xylene	C_8 (aromatics)
Isopropyl benzene	C_{9+} (aromatics)

Table 2 Calibration Standards for Preparation of Standard Chromosorb 106 Tubes using multi-component blend

Level	Standard Solution	Volume (μl)	Approx. Mass (μg)
1	Diluted 2	0.5	0.25
2	Diluted 2	1.0	0.5
3	Diluted 1	0.5	2.5
4	Diluted 1	1.0	5.0
5	Diluted 1	2.0	10
6	Concentrated	1.0	50
7	Concentrated	2.5	125

Table 3 Calibration Standards for Preparation of Standard Carbosieve S-III Tubes using Butane Gas Standard (~1.0%)

Level	Volume (ml)	Approx. Mass (μg)
1	0.025	0.5
2	0.25	5.0
3	0.5	10
4	2.5	50
5	5.0	100

Table 4 Desorption Parameters for Analysis of tubes used to sample Gasoline components (based on Perkin Elmer ATD400 capabilities)

Function	Chromosorb 106	Carbosieve S-III
Desorption mode (ATD400)	2	2
Primary desorption temperature °C	200	250
Primary desorption flow rate ml/min *	18-24	18-24
Primary desorption time min	10	5
Valve/transfer line temperature °C	200	200
Cold trap sorbent	C106 (40 mg)	C106 (40 mg)
Inlet split flow ml/min *	70-80	70-80
Outlet split flow ml/min *	70-80	70-80
Cold trap low °C	-30	-30
Cold trap high °C	220	250
Cold trap high time min	3	3
Cold trap high rate of heating	Fast	Fast
Carrier gas	Helium	Helium
Split ratio *	200 to 250:1	250 to 300:1

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

Table 5 Gas Chromatographic Conditions (applicable to both types of tubes)

Parameter	Conditions
Capillary Column	50m long by 0.2mm diameter coated to 0.5µm with unbonded OV 1701
Column oven temperatures	
Initial temperature	10°C Held for 10mins
Final temperature	200°C Held for 10min
Ramp rate	8°C/min
FID temperature	300°C
Carrier gas Flow rate through column	Helium ~ 1.5 ml/min

Table 6 List of Components and Calibrant Information (C106 only)

Peak	Compound name	Type	Use RF for n-
1	Propane	n alkane	C5
2	Isobutane	alkane	C5
3,4,5	n Butane + Butene-1 + Isobutene	n alkane	C5
6	Trans butene-2	alkene	C5
7,12	cis But-2-ene + 1,3 Butadiene	alkene	C5
8	3 Methyl Butene-1	alkene	C5
9	Isopentane	alkane	C5
10	n Pentane	n alkane	C5
11	Pentene-1	alkene	C5
13	2 Methyl Butene-1	alkene	C5
14	Trans Pentene-2	alkene	C5
15	cis Pentene-2	alkene	C5
16,17	2 Methyl Butene-2 + 2,2 Dimethyl Butane	alkene	C6
18,21	Cyclopentene + Cyclopentane	alkene	C5
19	2,3 Dimethyl Butane	alkane	C6
20	2 Methyl Pentane	alkane	C6
22	2,3 Dimethyl Butene-1	alkene	C6
23	4 Methyl Pentene-2	alkene	C6
24	3 Methyl Pentane	alkane	C6
25,26	n Hexane + 2 Methyl Pentene-1	n alkane	C6
27	Trans Hexene-3	alkene	C6
28,29	cis Hexene-3 + trans Hexene-2	alkene	C6
30	2 Methyl Pentene-2	alkene	C6
31	cis 3 Methyl Pentene-2	alkene	C6
32	trans 4 Methyl Cyclopentene	alkene	C6
33,36	Trans 3 Methyl Pentene-2 + Methyl Cyclopentane	alkene	C6
34	cis Hexene-2	alkene	C6
35	2,4 Dimethyl Pentane + unidentified alkene	alkane	C7
37	2,3 Dimethyl Butene-2	alkene	C6
38,40	2 Methyl Hexane + Cyclohexane	alkane	C7
39	cis 4 Methyl Cyclopentene	alkane	C6
41	2,3 Dimethyl Pentane	alkane	C7
42	4 Methyl Hexene-2	alkene	C7
44	3 Methyl Hexane	alkane	C7
45	2,2,4 Trimethyl Pentane	alkane	C8
46	4 Methyl Hexene-1	alkene	C7
47,48	trans and cis 1,3 Dimethyl Cyclopentane	alkane	C7
49	trans 1,2 Dimethyl Cyclopentane	alkane	C7
50	Cyclohexene	alkene	C6
51	2 Methyl Hexene-1	alkene	C7
52	2,3 Dimethyl Pentene-2	alkene	C7
53	n Heptane	n alkane	C7
54	3 Methyl Hexene-1	alkene	C7
55	3 Methyl Hexene-3	alkene	C7
56	cis 1,2 Dimethyl Cyclopentane	alkane	C7
57	Heptene-3	alkene	C7
58	Benzene	aromatic	Benzene
59	2 Methyl Hexene-2	alkene	C7
60	Heptene-2	alkene	C7

Table 6 List of Components and Calibrant Information (C106 only) (cont'd)

61	3 Methyl Hexene-2	alkene	C7
62	C_7 Olefin	alkene	C7
63	Methyl Cyclohexane	alkane	C7
64	2,5 Dimethyl Hexane	alkane	C8
65	2,4 Dimethyl Hexane	alkane	C8
66	Ethyl Cyclopentane	alkane	C7
67	1,2,4 Trimethyl Cyclopentane	alkane	C8
68	2,3,4 Trimethyl Pentane	alkane	C8
69	2,3,3 Trimethyl Pentane	alkane	C8
70	2,3 Dimethyl Hexane	alkane	C8
71	2 Methyl Heptane	alkane	C8
72	4 Methyl Heptane	alkane	C8
73	3,4 Dimethyl Hexane	alkane	C8
74	3 Methyl Heptane	alkane	C8
75	trans 1,3 Dimethyl Cyclohexane	alkane	C8
76	cis 1 Ethyl 3 Methyl Cyclopentane	alkane	C8
77	trans 1 Ethyl 3 Methyl Cyclopentane	alkane	C8
78	N Octane	n alkane	C8
79	C_8 Olefin	alkene	C8
80	trans 1,2 Dimethyl Cyclohexane	alkane	C8
81	2,4 Dimethyl Heptane	alkane	C9
82	Toluene	aromatic	Toluene
83	2,6 Dimethyl Heptane	alkane	C9
84	3,5 Dimethyl Heptane	alkane	C9
85,86	2 Methyl Octane + 4 Methyl Octane	alkane	C9
87	3 Methyl Octane	alkane	C9
88	n Nonane	n alkane	C9
89	Ethyl Benzene	aromatic	m Xylene
90,91	m and p Xylene	aromatic	m Xylene
92	Dimethyl Octane	alkane	C10
93	O Xylene	aromatic	m Xylene
94	4 Methyl Nonane	alkane	C10
95	2 Methyl Nonane	alkane	C10
96	Trimethyl Heptane	alkane	C10
97	Isopropyl Benzene (IPB)	aromatic	IPB
98	3 Methyl Nonane	alkane	C10
99	n Decane	n alkane	C10
100	n-Propyl Benzene	aromatic	IPB
101,102	1 Methyl 3 Ethylbenzene + 1 Methyl 4 Ethylbenzene	aromatic	IPB
103	1,3,5 Trimethyl Benzene	aromatic	IPB
104	C_{11} Paraffin	alkane	C10
105	C_{11} Paraffin	alkane	C10
106	1 Methyl 2 Ethyl Benzene	aromatic	IPB
107	1,2,4 Trimethyl Benzene	aromatic	IPB
108	sec Butyl Benzene	aromatic	IPB
109	C_{11} Paraffin	alkane	C10
110	Aromatic	aromatic	IPB
111	1,2,3 Trimethyl Benzene	aromatic	IPB
112	n Undecane	n alkane	C10

Table 6 List of Components and Calibrant Information (C106 only) (cont'd)

113	C_{11} Paraffin	alkane	C10
114	1 Methyl 3 Propyl Benzene	aromatic	IPB
115	n Butyl Benzene	aromatic	IPB
116	1,3 Dimethyl 5 Ethyl Benzene	aromatic	IPB
117	1 Methyl 2 Propyl Benzene	aromatic	IPB
118	1,4 Dimethyl 2 Ethyl Benzene	aromatic	IPB
119	1,3 Dimethyl 4 Ethyl Benzene	aromatic	IPB
120	1,2 Dimethyl 4 Ethyl Benzene	aromatic	IPB
121	C_{10} Aromatic	aromatic	IPB
122	C_{12} Paraffin	alkane	C10
123	Indene	Indene	IPB
124	C_{12} Paraffin	alkane	C10
125	1,3 Dimethyl 2 Ethyl Benzene	aromatic	IPB
126	1,2,4,5 Tetramethyl Benzene	aromatic	IPB
127	1,2,3,5 Tetramethyl Benzene	aromatic	IPB
128	n Dodecane	n alkane	C10
129	C_{11} Paraffin	alkane	C10
130	C_{10} Aromatic	aromatic	IPB
131	C_{11} Aromatic	aromatic	IPB
132	Indene	Indene	IPB
133	C_{11} Aromatic	aromatic	IPB
134	2,3 Dihydro 4 Methyl Indene	Indene	IPB
135	Dimethyl Propyl Benzene	aromatic	IPB
136	C_{11} Aromatic	aromatic	IPB
137	2,3 Dihydro 1,3 Dimethyl Indene	Indene	IPB
138	C_{11} Aromatic	aromatic	IPB
139	C_{11} Aromatic	aromatic	IPB
140	n Tridecane	n alkane	C10
141	2,3 Dihydro 1,6 Dimethyl Indene	Indene	IPB
142	Naphthalene	napht.	IPB
143	2,3 Dihydro 4,7 Dimethyl Indene	Indene	IPB
144	Dihydro Dimethyl Indene	Indene	IPB
145	1 Methyl Naphthalene	napht.	IPB
146	2 Methyl Naphthalene	napht.	IPB
150	Methyl Tertiary Butyl Ether	ether	MTBE

Table 7 Safe Sampling Volumes (22-24°C) for Propane and Butane on tube packed with 600mg Carbosieve S-III

Gas	Propane (litres)	Butane (litres)
Safe Sampling Volume (SSV)	33.3	141
SSV high temperature (32-34°C)	16.7	70
SSV high temperature (32-34°C) High humidity (95%RH)	1.7	7

APPENDIX 2 PROPANE AND N-BUTANE SAFE SAMPLING VOLUMES

PROPANE

Report of breakthrough test of propane on Carbosieve S-III.

Propane used: 60 ppm in dry air (approximately 110 mg/m^3).
Amount of sorbent in thermal desorption tube: 600 mg.

Test set up: 2 identical tubes in series. Analysis of both tubes to determine when breakthrough of front tube occurs.
Definition of breakthrough: quantity of analyte on back tube is 5% or more of quantity on front tube.

First experiment: No propane detected after passing 39.0 l of test gas through tube
Quantity on back tube compared to front tube after passing 44.1 litre: 0.002%
Quantity on back tube compared to front tube after passing 49.3 litre: 0.08%
Quantity on back tube compared to front tube after passing 54.3 litre: 13.0%

Second experiment: No propane detected after passing 22.8 l of test gas through tube
Quantity on back tube compared to front tube after passing 42.3 litre: 0.008%
Quantity on back tube compared to front tube after passing 45.8 litre: 0.21%
Quantity on back tube compared to front tube after passing 49.2 litre: 0.65%
Quantity on back tube compared to front tube after passing 52.0 litre: 17.9%

Estimated breakthrough volume: 50 litre.

Calculation of safe sampling volume of 600 mg Carbosieve S-III:

- 2/3 of 50 litre, or 33 litre for moderate conditions of temperature and relative humidity.
- 1/10 of 33 litre, or 3.3 litre for high relative humidity
- ½ of 3.3 litre, or 1.7 litre for high relative humidity and temperature.

n-BUTANE

Butane used: 60 ppm in dry air (approximately 143 mg/m^3).
Amount of sorbent in thermal desorption tube: 600 mg.

Test result for flow rate of approximately 100 ml/min.: no breakthrough after passing 200 litre through the test tube. Test stopped due to limited supply of test gas.

Calculation of safe sampling volume of 600 mg Carbosieve S-III:

- 70% of 200 litre, or 140 litre for moderate conditions of temperature and relative humidity.
- 1/10 of 140 litre, or 14 litre for high relative humidity
- ½ of 14 litre, or 7 litre for high relative humidity and temperature.

APPENDIX 3 GAS CHROMATOGRAM OF GASOLINE VAPOUR ON OV 1701 COLUMN

Figure A3.1 Full chromatogram Chromosorb 106

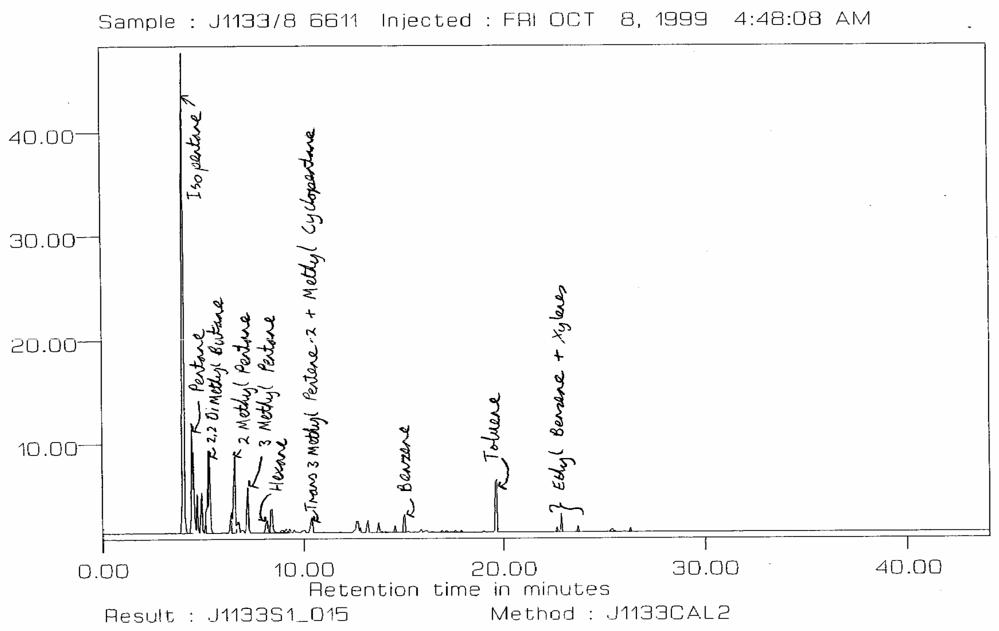

Figure A3.2 Chromatogram Chromosorb 106 (0-10 minutes)

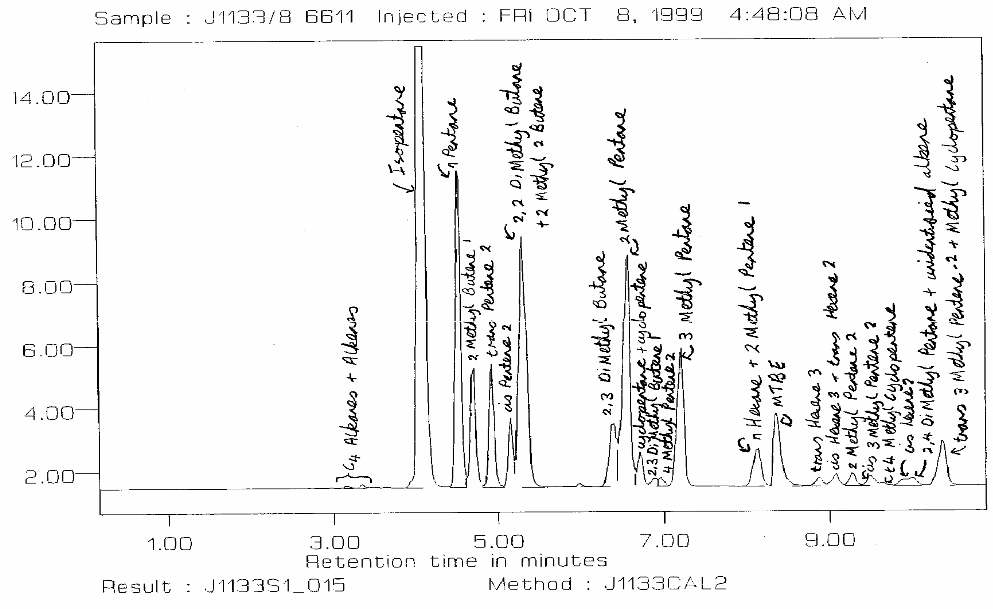

Figure A3.3 Chromatogram Chromosorb 106 (10-20 minutes)

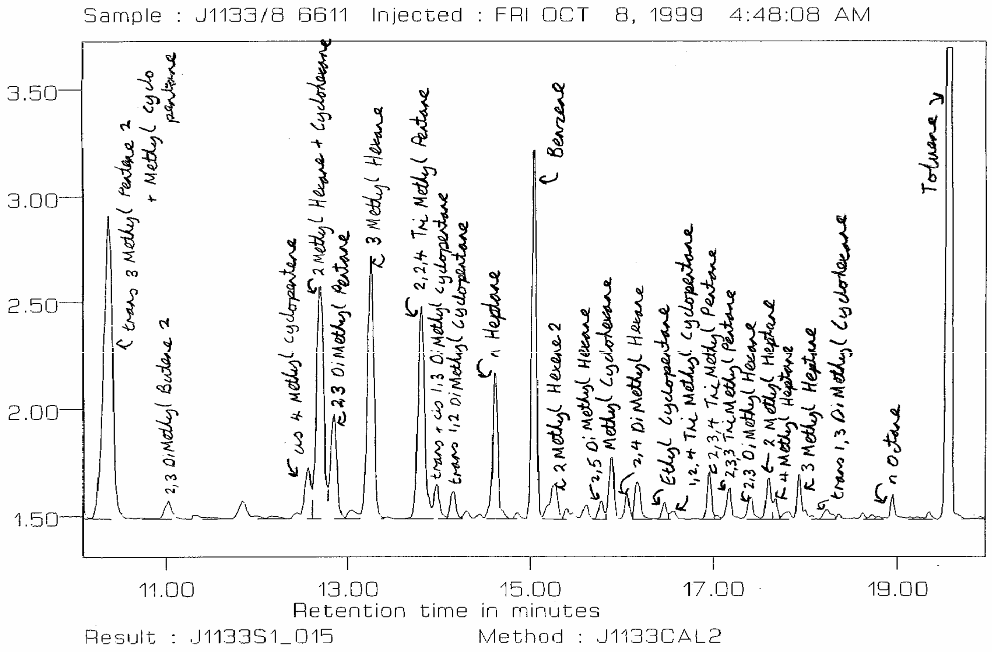

Figure A3.4 Chromatogram Chromosorb 106 (20-30 minutes)