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Review of Measurement Requirements for Current Automobile Emissions Technologies

Produced for the National Measurement System Policy Unit, DTI as part of the Valid Analytical Measurement Programme

April 2004

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1. INTRODUCTION

While it may appear to the consumer that there has been a period of relative stability in automotive technological development in recent years, there are a number of factors exerting pressure on motor manufacturers to develop a new generation of vehicles producing lower emissions of species that have an adverse effect on health and the environment. The development of such vehicles for use in the UK and Europe is being driven by changing legislation that will require significant reductions in key emissions; in most cases the allowed emissions of such species will be approximately halved [see Section 2]. Motor manufacturers intend to meet these demands via a number of means including the optimisation of conventional combustion engines [improved injection, camless engine technology, etc.], improved exhaust aftertreatment technology [improved catalysts, particulate filters, etc.], the use of alternative fuels [biodiesel, LPG, etc.] and the introduction of electric motor assisted hybrid vehicles.

This report summarises the key emissions species, legislation affecting the allowed emissions of these species, alternative fuels and their effects on emissions and finally the analytical and sampling methods used to test and validate new spark ignition and compression ignition engines, and the associated measurement requirements which will need addressing.

2. EMISSIONS AND FUEL REGULATIONS

2.1 Vehicle Emissions

The pollutants from petrol, diesel, and alternative fuel combustion engines considered to be most harmful are principally carbon monoxide, oxides of nitrogen, unburnt hydrocarbons and fine/ultra-fine particles, and these pollutants are covered by legislation. These pollutants and their effects on health and the environment are described in more detail below:

- CO - In the presence of an adequate supply of oxygen most carbon monoxide produced during combustion is immediately oxidised to carbon dioxide. This is not the case in spark ignition engines in motor cars, especially under idling and deceleration conditions. Carbon monoxide binds to haemoglobin in preference to oxygen resulting in a reduction in the blood's oxygen carrying capacity and hence reduced availability of oxygen to key organs. Haemoglobin's affinity for carbon monoxide is 200-300 times more than that for oxygen. Extremely high levels of exposure can be fatal while lower concentrations can cause dizziness, headaches, and nausea and may pose a serious health risk to those suffering from heart disease.

- NO_x – the NO_x compounds [NO and NO_2] are formed when nitrogen present in the fuel-air mixture is oxidised at high temperature during the combustion process. Although the NO_x is emitted predominantly as NO [nitrogen monoxide], this reacts in the atmosphere to form nitrogen dioxide [NO_2] which can have adverse effects on health, particularly among people with respiratory illness. High levels of exposure have been linked with increased hospital admissions due to respiratory problems, while long term exposure may affect lung function and increase the response to allergens in sensitive people. NO_x also contributes to smog formation and acid rain, and contributes to ground level ozone formation.

- Particles - Fine particles can have an adverse effect on human health, particularly among those with existing respiratory and cardiovascular disorders. Particles have been associated with increased hospital admissions and bringing forward the deaths of those suffering from respiratory and cardiovascular illnesses. In the UK they are considered to be currently the most serious pollutant in terms of adverse health effects, though the specific harmful properties of the particles [size, composition or chemical properties, for example] are not yet established. Airborne particles are usually measured as PM_{10} – the mass concentration, in $\mu g/m^3$, of particles with an aerodynamic diameter less than 10 µm, which will pass through human airways into the lungs. There are indications that the health effects are more associated with the finer fraction termed $PM_{2.5}$ [less than 2.5 µm] or the ultra-fine particles [< 0.1 µm] than with this coarser fraction.

- HC - Hydrocarbons contribute to ground level ozone formation leading to risk of damage to the human respiratory system, crops and materials. In addition, certain hydrocarbons are carcinogenic while others are indirect greenhouse gases.

Of these pollutants, nitrogen dioxide and particulate matter are the ones most likely to exceed the limit values set by European legislation and UK regulations, and this will happen predominantly in urban environments where emissions from vehicles are the largest source.

The quantity of pollutants produced by combustion-engined vehicles in urban areas is a complex function of many factors, such as the variety in type, age and level of maintenance of the vehicles, traffic management schemes [such as congestion charging], and style of driving. The remainder of this section covers legislation relating to new car production, while the affect of different available fuels likely to be significant in the medium term is given in Section 3.

2.2 European Auto Oil Programme

Directive 70/220/EEC of 1970 was the first European directive to lay down emission limits, for passenger cars. Legislation for light commercial and heavy duty vehicles followed with subsequent amendments to this directive. The directive was again amended in 1994 when directive 94/12/EC was adopted. At this stage it was estimated that emissions of regulated pollutants would be reduced by over 90 percent by 1996/97, compared to levels produced in the early 1970's.

The Auto Oil Programme was initiated in 1992 after extensive discussions involving the European Commission and European automobile and oil industries. The aim of this technical work programme was to provide a solid foundation upon which to base future European legislative proposals. In addition to reductions in emissions through technological advancements in conventional vehicles, the programme also assessed the potential of other approaches to reducing emissions including:

- Traffic management
- Enhanced urban public transport
- New propulsion techniques
- Alternative fuels

The European Commission published its Auto Oil Programme report in 1996. In June 1996, as a result of the Auto Oil Programme, the Commission adopted a future strategy for the control and reduction of emissions from road vehicles together with several proposals for directives. Included in these were proposals related to the quality standards for petrol and diesel fuels, and passenger car emissions. These were followed by proposals for tighter emissions standards for light commercial and heavy-duty vehicles, and improved procedures for inspection and maintenance.

The Auto Oil Programme II was established at the beginning of 1997 and was designed to provide the technical input for the European Commission's work on future vehicle emission limit values, fuel quality standards and other related measures. The objective was to provide an updated cost-effective strategy designed to meet requirements of the European Union air quality standards and related objectives by 2010. The final proposal resulting from the Auto Oil Programme II was to contain mandatory emission limit values to be applied from 1st January, 2005. The strategy was also to be consistent with the objectives laid down in the European Union's strategy to reduce CO_2 emissions from passenger cars and improve fuel quality. The directives adopted in October 1998 by the Council and European Parliament, containing the package of measures on fuels and passenger car and light commercial vehicles as well as the final Auto Oil Programme II mandate, specified many, although not all, of the 2005 requirements.

Table 1 summarises mandatory vehicle emission standards [covering CO, unburnt hydrocarbons, NO_x, and particulates for diesels] resulting from both Auto Oil Programmes.

Standard	Directive	Type of vehicle	Date
Euro I	91/444/EEC 93/59/EEC 91/542/EEC	Passenger cars Light commercial Heavy diesel	31/12/92 01/10/94 01/10/93
Euro II	94/12/EC 96/69/EC 91/542/EEC	Passenger cars Light commercial Heavy diesel	01/01/97 01/10/97 01/10/96
Euro III	98/69/EC Common position	Passenger cars and light commercial Heavy diesel	01/01/01 01/01/01
Euro IV	98/69/EC Common position	Passenger cars and light commercial Heavy diesel	01/01/06 01/01/06

Table 1 Mandatory vehicle emission standards [covering CO, unburnt hydrocarbons, NO_x, and particulates for diesels].

Directive 98/69/EC applies to all petrol and diesel light vehicles built after 1st January 2000 and to diesel light vehicles sold after 1st January 2001. Standards are set for exhaust emissions for CO, hydrocarbons, NO_x, and particulates. In addition to limits for exhaust emissions at normal and low ambient temperature, European Directive 98/69/EC also covers evaporative emissions, crankcase gas emissions, the durability of anti-pollution devices and a requirement for on-board diagnostic systems [OBD]. The tests are most often performed by vehicle manufacturers under national inspection. The test types for petrol engines as defined in Directive 98/69/EC are as follows:

Type I* verify average exhaust emissions after cold start.

Type II carbon monoxide emissions at idling.

Type III emissions of crankcase gases.

Type IV evaporation emissions.

Type V* durability of anti-pollution control devices.

Type VI verifying the average low temperature carbon monoxide and hydrocarbon exhaust emissions after cold start.

* For compression engines [i.e. diesel] only Type I and Type V apply.

The test cycle and test procedure, used to ensure that vehicles meet the standards in the Directive, uses a dynamometer [or rolling road].

Table 2 summarises the European Union emissions regulations for passenger cars. These data show that in most cases the allowed emissions of most species will be approximately halved.

Pollutant	1997 – EURO II		2000 – EURO III		2005 – EURO IV	
[g/km]	Petrol	Diesel	Petrol	Diesel	Petrol	Diesel
HC	-	-	0.20	-	0.10	-
NO_x	-	-	0.15	0.50	0.08	0.25
HC+NO_x	0.50	0.70*	-	0.56	-	0.30
CO	2.20	1.00	2.30	0.64	1.00	0.50
PM	-	0.88+	-	0.05	-	0.025

* Limit was 0.90 for direct injection diesels until 30th September 1999.
+ Limit was 0.10 for direct injection diesels until 30th September 1999.
HC [hydrocarbons]; NO_x [oxides of nitrogen]; CO [carbon monoxide]; PM [particulate matter].

Table 2 European Union passenger car emissions regulations.

CO_2 is covered by a voluntary agreement made in July 1998. "CO2perate" is a joint R&D action by the European Automotive Manufacturers and their suppliers to focus research and development on the issue of reducing CO2 emissions from vehicles. The programme originates from the concern of greenhouse environmental effects. This issue was highlighted at the Kyoto Conference on Climate Change in December 1997 where nearly all developed countries agreed to legally binding targets to reduce their greenhouse gas [including CO_2] emissions. The voluntary agreement supports the development to reach an average CO_2 emission level of 140 g/km for new cars sold by the year 2008, about 25% less than in 1995 - a target agreed between the European Automotive Manufacturers and the European Union. Beyond that the programme aims to contribute to further CO2 reduction towards 120 g/km by year 2012. Further information on the "CO2perate" CO_2 reduction initiative can be found on the ACEA and EUCAR websites [see Section 6 "Relevant UK and European companies and organisations"]. EU Directive 1999/94/EC requires that new car fuel consumption and CO_2 emissions data are to be made freely available to consumers. Car dealers will be required to display a label on each car showing the fuel consumption and CO_2 emissions of that particular model; in addition to this the same data must be present in all printed documentation referring to the vehicle in question.

Tighter fuel specifications designed to reduce greenhouse gases and other pollutants were also delivered by the European Commission through the Auto Oil programme. Fuel specifications agreed for 2000 were agreed under the Auto Oil I programme [directive 98/70/EC]. This directive was transposed into UK law by the Motor Fuel [Composition and Content] Regulations 1999 [SI. 1999/3107]. The main specifications were:

- Petrol

  - Maximum 150 ppm sulphur.
  - 42 % volume max for aromatics.

- Diesel

  - Maximum 350 ppm sulphur.
  - 845 kg/m^3 maximum density.

Directive 98/70/EC also agreed a number of specifications for 2005 including:

- Petrol

  - Maximum 50 ppm sulphur.
  - 35 % volume max for aromatics

- Diesel

  - Maximum 50 ppm sulphur.

Four main types of fuel are available at forecourts in the UK. These are:

- 95 octane unleaded petrol;
- 97 octane unleaded petrol;
- lead replacement petrol [LRP]
- diesel [DERV]

The technical requirements of these fuels, including chemical composition, are covered by the European Directive 98/70/EC, implemented into UK law by the Motor Fuel [Composition and Content] Regulations 1999. These fuels also meet the requirements of the following British Standards:

- 95 octane unleaded – BS EN 228:2000;
- 97 octane unleaded – BS 7800:2000;
- DERV – BS EN 590:2000.

Ultra-low sulphur fuels are required to meet the following additional requirements:

- Petrol - for those grades listed above, a maximum sulphur content of 50 parts per million (ppm) as opposed to 150 ppm allowed in 98/70/EC, and a maximum aromatics content of 35 per cent volume as opposed to 42 per cent in 98/70/EC;

- DERV - maximum sulfur content of 50 ppm as opposed to 350 ppm allowed in 98/70/EC, and a maximum density of 835 kg/m^3 as opposed to 845 kg/m^3.

3. FUELS

3.1 Petrol

Petrol contains mainly C_5 to C_{13} alkanes along with a mixture of other compounds including cyclohexane and its derivatives, a range of alkenes, benzene, toluene, xylene, and higher aromatics. The chemical composition for unleaded petrol is defined in the European Directive 98/70/EC [see section entitled “Emissions and Fuels Regulations”]. In a petrol combustion engine, petrol vapour is mixed with air in the cylinder and then ignited by an electric spark. Emissions from petrol engines include carbon monoxide, oxides of nitrogen, hydrocarbons, and particulates. While the origins of the first three species are well researched and the control methods associated with these pollutants are now mandatory, research into the origins and control of particulate emissions from petrol engines has not received sufficient attention. In contrast, the problem of particulate emissions from diesel engines is now well understood and technical solutions are now available. Petrol engines do not emit significant amounts of particulates large enough to form the visible soot normally associated with diesel engines. Petrol engines do however produce significant emissions of ultra-fine particles [diameter less than or equal to 0.1 μm]. In some cases petrol engines may produce larger amounts of ultra-fine particles than diesel engines. In diesel engines the ultra-fine particles make up a small fraction of the total mass of particulate emissions, however it is possible that they are disproportionately more toxic than the larger particles. This is significant in relation to legislation relating to particulates, as current engine particulate emission standards are based solely on mass. As the total mass of particulate matter emitted by petrol engines is relatively low compared to diesel engines there has been little emphasis on reducing particulate emissions from petrol engines. This may change in the face of harder evidence relating ultra-fine particulate emissions to adverse effects on health.

3.2 Diesel

Diesel consists mainly of C_{13} to C_{25} compounds and boils in the range 220°C to 350°C. A modern diesel engine draws in air, compresses it and then injects fuel into the compressed air. The heat of the compressed air ignites the fuel spontaneously. A petrol engine compresses at a ratio of 8:1 to 12:1, while a diesel engine compresses at a ratio of 14:1 to as high as 25:1. The higher compression ratio of the diesel engine leads to better fuel efficiency. Since carbon dioxide emissions are directly proportional to fuel consumption, and as diesel cars use 30 to 40% less fuel, they emit 30 to 40% less carbon dioxide than petrol cars. Diesel engines also produce considerably less carbon monoxide than petrol engines. This occurs because diesel engines use an excess of air in the fuel mixture whereas petrol engines often use a stoichiometric fuel/air mixture that can result in increased carbon monoxide emissions due to incomplete combustion. Diesel engines are effectively “lean-burn” across the full power/speed range. Diesel engines may also, in some circumstances, emit less NO_x than a petrol engine, however when a car with a petrol engine is fitted with a three-way catalytic converter [“three-way" referring to the three regulated emissions it helps to reduce: carbon monoxide, hydrocarbons and NOx molecules] the opposite is true. Hydrocarbon emissions from diesel engines are also lower than those produced by petrol engines.

The major drawback associated with diesel engines is the level of particulate emissions. Over 90% of the particles emitted from diesel engines are smaller than 1 μm. These particles consist mainly of aggregates of spherical elemental carbon particles coated with organic and inorganic substances. The particles have a porous surface and a large surface area. Lowvolatility compounds such as aliphatic hydrocarbons and polycyclic aromatic hydrocarbons [PAH] condense on the surface of these particles. Many of these condensed compounds are suspected carcinogens and the ability of fine and ultra-fine particles to penetrate deep into the lungs is of particular concern. The adverse effects of particulate matter from diesel exhaust emissions on the respiratory system is well documented and it remains one of the most significant air pollutants, particularly in urban environments. Technological advances in particulate traps [often combined with deNO$_x$ catalysts] for diesel exhaust will reduce this problem significantly. Systems containing this technology are already employed in a limited number of commercial vehicles such as heavy-goods vehicles and buses.

Since it is now mandatory for petrol cars to be fitted with three-way catalytic converters, in practice vehicles with diesel engines can only offer improved CO_2 and hydrocarbon emissions over vehicles with petrol engines.

3.3 Compressed Natural Gas [CNG] and Liquefied Natural Gas [LNG]

Natural gas is composed of a mixture of hydrocarbons, primarily methane. The interest in natural gas as an alternative fuel stems mainly from its clean burning qualities, its domestic resource base, and its commercial availability to end-users. Because of the gaseous nature of this fuel, it must be stored onboard a vehicle in either a compressed gaseous state [CNG] or in a liquefied state [LNG]. It is produced either from gas wells or in conjunction with crude oil production. When natural gas is cooled to approximately –165 ^{o}C at atmospheric pressure it condenses to a liquid. It is stored in a double-walled, insulated storage vessel; the pressure in the vessel is typically between 30 and 50 psi. In contrast, CNG is stored as a gas at pressures of up to 200 bar and the weight of a CNG storage vessel is therefore significantly higher than that of a LNG cylinder for a comparable volume of fuel. As can be seen below CNG and LNG compare favourably with petrol in relation to emissions performance.

- 90–97% lower CO.
- 25% lower CO_2.
- 35-60% lower NO.
- 50-75% lower NMHC.
- Storage method results in zero evaporative emissions.
- Higher octane rating – higher power output in dedicated engine.

3.4 Liquefied Petroleum Gas [LPG]

Liquefied petroleum gas [LPG] consists mainly of propane, propene, butane, and butene in various mixtures. Automotive LPG sold in the UK consists primarily of propane. Around 60% of the world supply of LPG comes from the separation of natural gas products with the remaining 40% coming as a by product of the refinery operations. The components of LPG are gases at normal temperatures and pressures; it is therefore stored onboard the vehicle as a liquid under pressure. The pressure required to liquefy the gas is approximately 7 bar. This is considerably lower than the pressure required to store CNG [up to 200 bar]. The strength, and consequently weight and cost, of the tank required to store LPG is therefore considerably less than that of a CNG tank. The UK now has an effective infrastructure for the distribution of automotive LPG [over 1200 refuelling stations] and with the added cost-savings over petrol [consumers are charged approximately half the price of petrol for an equivalent quantity of LPG] LPG is now a popular alternative fuel. LPG also has benefits over petrol and diesel when it comes to emissions:

Compared to petrol

- 12% lower CO.
- 30% lower NO_X, HC, CO.

Compared to diesel

- 90% lower NO_x.
- 1/50th particulates.
- 1/500th ultra-fine particles.
- 50% quieter.

The specification for commercial butane and commercial propane is laid out in the British Standard BS 4250:1997 while the requirements and test methods for automotive LPG are defined in BS EN 589:2000. The latter standard does not define the composition of LPG in terms of ratios of components but rather as having a minimum motor octane number [MON]. The ratio of component gases can vary over a wide range and still meet the required MON. The method for calculating the MON is also described in BS EN 589:2000. In addition to meeting the required MON there are four grades of LPG defined in terms of seasonal vapour pressure limits; these are calculated with EN ISO 8973. Typically, LPG contains more propane in winter to keep the vapour pressure high for easy starting, and less propane in summer.

3.5 Biodiesel

Biodiesel is made from natural, renewable sources such as new and used vegetable oils and animal fats. The fats and oils are reacted with an alcohol [most often methanol] to produce a fuel consisting of fatty acid alkyl esters; glycerol is produced as a co-product. Blends of up to 20 % biodiesel [mixed with standard diesel] can be used in most standard diesel engines. A 5 % blend is now available on the retail market in the UK and some lorry fleets are converting to 100 % biodiesel fuelling. The use of pure biodiesel may require certain engine modifications but can still be used in some engines with little or no modification.

When used in a conventional diesel engine, biodiesel substantially reduces emissions of unburned hydrocarbons, carbon monoxide, sulphates, polycyclic aromatic hydrocarbons [PAH], nitrated PAH, and particulate matter. The reductions achieved increase as the proportion of biodiesel blended into diesel fuel increases. The highest reduction is achieved using pure biodiesel.

The use of biodiesel decreases the solid carbon fraction of particulate matter [this results from more complete combustion to CO_2 due to oxygen in biodiesel] and reduces the sulphate fraction [biodiesel contains less than 24 ppm sulphur], while the soluble, or hydrocarbon, fraction stays the same or increases. Therefore, biodiesel works well with new technologies such as catalysts [which reduce the soluble fraction of diesel particulate but not the solid carbon fraction], particulate traps, and exhaust gas recirculation.

On the negative side, emissions of nitrogen oxides increase as the proportion of biodiesel blended into diesel fuel increases.

3.6 Ethanol

Ethanol is an alcohol-based alternative fuel produced by fermenting and distilling starch crops that have been converted into simple sugars. Feedstocks for this fuel include corn, barley and wheat. Ethanol can also be produced from "cellulosic biomass" such as trees and grasses; this is called bioethanol. Ethanol can be used to increase octane and improve the emissions quality of petrol.

- 10 % ethanol blends reduce carbon monoxide better than any other reformulated petrol blend, by more than 25%.

- Ethanol is low in reactivity and high in oxygen content, making it an effective tool in reducing ozone pollution.

- Ethanol is a safe replacement for toxic octane enhancers in petrol such as benzene, toluene and xylene.

A 10 % ethanol and 90 % petrol blend can be used in conventional petrol engines while 85 % pure ethanol can be used in a modified dual fuel engine that can also use conventional petrol. Both of these fuels are now commonplace in the United States and their potential for use in the UK was highlighted in the recent Energy White Paper.

3.7 Methanol

Methanol has been used as an alternative fuel in the United States. It was used in flexible fuel vehicles that run on a blend of 85 % methanol and 15 % petrol, however its use has declined as vehicle manufacturers no longer supply suitable vehicles. If methanol is used as an alternative fuel in the UK it will most likely be as a source for hydrogen for use in fuel cell vehicles.

3.8 Hydrogen

Hydrogen can be used as fuel in a suitable combustion engine. The major by-product of the combustion of hydrogen is water; all other emissions associated with the combustion of carbon-based fuels, apart from nitrogen oxides, are zero. Although hydrogen can be used to fuel combustion engines its real potential is as the fuel for fuel cell vehicles.

4. ANALYTICAL TECHNIQUES FOR EMISSION MEASUREMENTS

4.1 Introduction

Table 3 summarises the typical analytical techniques used to measure the non-particulate exhaust emission species. These analytical techniques are well established and it is clear that the automotive industry intends to use current analytical instrumentation, combined with improved sampling techniques [see Section 5], to meet the challenge of measuring the lower auto emissions from vehicles capable of meeting EURO IV emissions standards.

Component	Method
Total hydrocarbons [THC]	Heated flame ionisation detector [FID}
Carbon monoxide [CO]	Non-Dispersive Infrared [NDIR]
Oxides of nitrogen [NO/NO_x]	Vacuum chemiluminescence detector [CLD]
Methane [CH_4]	Gas chromatograph with flame ionisation detector [GC-FID]
Carbon dioxide [CO_2]	Non-Dispersive Infrared [NDIR]

Table 3 Analytical techniques used to measure exhaust gas emission species.

The analytical techniques described below all require the use of certified calibration gases in order to ensure consistent and accurate emission measurement results. Instruments are calibrated in accordance with manufacturers instructions and the calibration gases used should be traceable to an appropriate national institute's Primary Reference Material [PRM]. The British Technical Council of the Motor and Petroleum Industries [BTC] have published a document outlining the correct procedures for the preparation, certification and use of calibration and span gases. The relevant sub-committees of the BTC have also published standard specifications for zero, service gases and span/calibration gases relating to exhaust emissions measurements. Table 4 summarises the range of calibration gases used by the vehicle emissions measurement industry.

Species	Typical concentration range
Carbon monoxide	1ppm – 10 %
Carbon dioxide	1 ppm – 30 %
Nitric oxide	1 ppm – 5 %
Propane	900 ppb – 1 %
Methane	1 – 999 ppm
Sulphur dioxide	1 – 1000 ppm
Hydrogen sulphide	1 – 99ppm

Table 4 Composition of calibration gases used by the automotive industry. Mixtures containing more than one of the components listed in Table 4 are also used routinely by automotive testing laboratories.

4.2 Gas Chromatograph with Flame Ionisation Detector

A flame ionisation detector [FID] is used to measure the concentration of hydrocarbon species in a sample gas. Hydrocarbons are detected by burning the sample gas in a hydrogen-air flame. The hydrogen used contains a negligible amount of hydrocarbons and hence only trace amounts of ionisation occur in the hydrogen-air flame. When a sample gas containing hydrocarbons is burnt in this flame a complex ionisation process occurs creating a large number of ions. A high polarising voltage is applied between two electrodes located around the burner nozzle. Negative ions migrate to the positive electrode and positive ions migrate to the negative electrode. The resulting ionisation current is closely related to the concentration of hydrocarbons in the sample gas. The sample gas can be fed directly into the FID resulting in a measurement of the total hydrocarbon concentration, or species can be separated within a gas chromatography column, allowing the measurement of individual hydrocarbon concentrations.

4.3 Non-Dispersive Infrared Analysers

In non-dispersive infrared analysis, the absorption of infrared radiation at a particular wavelength is monitored. The analyte of interest should absorb infrared radiation at this wavelength while the matrix gas and other potentially interfering gases should not. Optical filters are used to select the wavelength at which absorbance is to be monitored. Two modes of analysis can then be used for measuring the intensity of incident light and transmitted light:

1. **Single Beam** – alternatively pass two similar wavelengths of light through the sample; the first wavelength at which the analyte absorbs light and the second wavelength at which the analyte does not absorb light.

2. **Double beam** – alternatively pass the same wavelength [that is absorbed by the analyte] through the sample cell and a reference cell that contains the same matrix as the sample but without the analyte species present.

4.4 Chemiluminescence

Chemiluminescence uses quantitative measurements of the optical emission from excited chemical species to determine the analyte concentration. The measurement of NO and NO_x is based on the chemiluminescent gas phase reaction between ozone and nitrogen monoxide:

$$NO + O_3 \rightarrow NO_2 + O_2$$

Approximately 10% of the nitrogen dioxide produced as a result of this reaction is in an electrically excited state. The transition from this excited state to normal results in the emission of a photon as the molecule loses energy, varying in wavelength between 0.6 and 0.3 μm:

$$NO + O_3 \rightarrow NO_2 + O_2 + \text{photon}$$

The intensity of the emission is proportional to the concentration of NO in the sample gas. The emission is measured using a photomultiplier and associated electronics.

In order to measure the concentrations of NO and NO_2 present in a gas sample a two-stage analysis is required. In the first stage the sample gas is introduced directly into the analysis chamber. The resulting measurement indicates the concentration of NO in the sample. In the second stage the sample gas is passed over a catalyst where any NO_2 present in the sample is converted to NO. This sample is then analysed to give the total NO_x concentration. The difference between the result from the second stage and the result from the first stage is the NO_2 concentration.

5. EXHAUST GAS SAMPLING

5.1 Introduction

The exhaust gases produced by motor vehicles consist of a complex mixture of combustion products [a large proportion of which is water], unburned fuel and air. This mixture exits the exhaust at high temperature. In simulated driving conditions on the dynamometer, the conditions of which are governed by European Union Legislation, the volume of exhaust gases produced by the vehicle changes depending the rate of acceleration/deceleration and speed. In order to make a quantitative determination of the emission rates of a particular vehicle [in g/km] a constant volume sampling system is required that provides a constant total flow rate of vehicle exhaust gases plus dilution air; samples of which can be taken for analysis.

5.2 Critical Flow Venturi – Constant Volume Sampler

Up until now the dilution of a constant volume of exhaust gases for analysis has been achieved using the Critical Flow Venturi – Constant Volume Sampler [CFV-CVS] system; a system originally developed for automotive testing in the early 1970's. Figure 1 shows a simplified schematic of the CFV-CVS system.

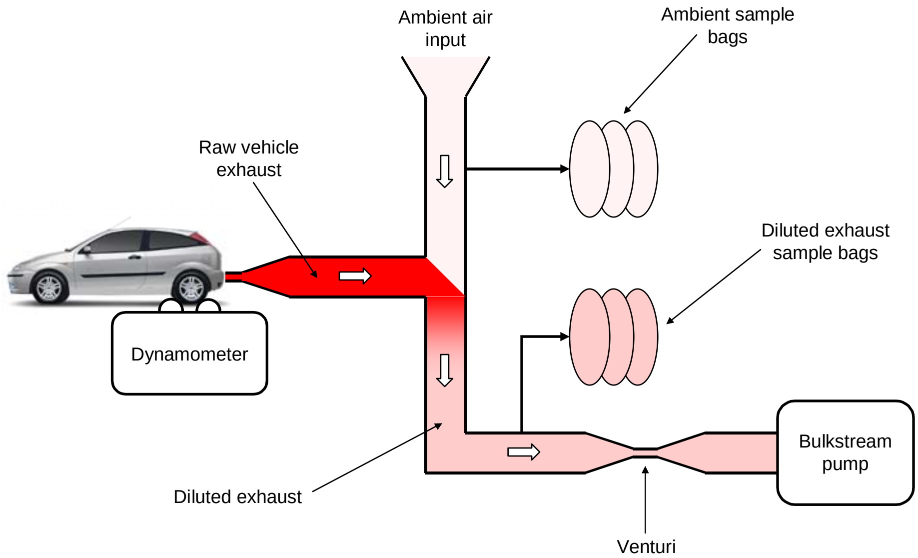

Figure 1 Critical Flow Venturi – Constant Volume Sampler [CFV-CVS] system for dilution of exhaust gases.

This sampling system dilutes the entire vehicle exhaust stream with sufficient ambient air to prevent water condensation in the diluted exhaust mixture; typically the average dilution ratio is 15:1. A large sample pump [bulkstream pump] is used to draw ambient air into the system in order to dilute the exhaust gas. The quantity of diluted exhaust gas being pumped is measured via the use of a critical flow venturi [typically 350 SCFM]. A small quantity of the diluted exhaust gas is then diverted into a Tedlar sample bag. At the same time a sample of ambient air is diverted into a second sample bag. A number of bags can be connected and samples taken at different stages of the regulation drive cycle. Once the test procedure has been completed the pairs of sample bags [diluted exhaust sample and ambient air sample] are analysed for concentrations of the exhaust gas pollution species e.g. HC, CH_4, CO, CO_2 and NO_x. The mass of emissions from the vehicle of each species is given by the mass of the species in the diluted exhaust gas sample minus the mass of the species in the ambient sample. Knowing the measured concentrations of each species and the volume of diluted exhaust gas it is possible to determine the mass of each species in the original, undiluted exhaust gas and hence the mass of each species produced over a set distance that the vehicle has travelled on the dynamometer. These figures can then be compared to regulation figures to determine if the vehicle meets emissions requirements.

The CFV-CVS system has been used successfully for many years. However, the system has several intrinsic problems, some of which will have to addressed if emissions laboratories intend to use current analytical equipment to measure emissions from vehicles which are designed to meet new, lower emissions standards. These problems are as follows:

- Dilution ratios achieved using current technology will be too low for the testing of alternatively fuelled vehicles using ethanol or CNG [due to increased water content in exhaust];

- Dilution ratios achieved using current technology will be too high for future low emissions measurements;

- There is no control of ambient hydrocarbon emissions. These emissions will cause significant interference at the new lower standards;

- Sampling and measurement of ambient hydrocarbon concentrations may not be representative of the true diluent;

- The conventional CFV-CVS system relies on a number of assumptions regarding the chemistry of the exhaust gases to give an accurate measurement of the mass emissions. These assumptions may not hold well enough for future vehicle technologies and testing requirements.

A number of modifications to the conventional CFV-CVS system have been proposed in order to address the shortcomings of the system just described. Lower CFV-CVS dilution ratios can be achieved by heating the lines, components and analysers in the system to temperatures above the predicted diluted exhaust dewpoint, but this has a number of drawbacks:

- An increase in maintenance problems;

- Not all analysers function correctly at elevated temperatures;

- Difficult to achieve uniform heating throughout the system. Cold spots can occur leading to condensation of water;

- Outgassing of hydrocarbon contaminants from sample bags increases as the temperature increases.

A second method is to optimise the dilution ratio for the specific test cycle conditions. This can be achieved by replacing the single CFV with a multi-venturi CFV system that allows adjustment of the diluted exhaust flowrate to match vehicle, fuel and test schedule requirements. While this appears to be a useful approach, the dilution ratio cannot be optimised to the theoretical minimum due to varying vehicle exhaust volume flowrates. The diluted flowrate has to be sized to accommodate the maximum vehicle exhaust emission flowrate in order to eliminate water condensation. Ambient air contamination also remains an issue.

Ambient air purification technologies capable of refining air at flowrates up to 2000 SCFM are available, but the size and cost requirements of such systems are prohibitive to most emissions testing laboratories.

5.3 Bag Mini-Diluter

While there have been many modifications made to the conventional CFV-CVS system described above, problems with this approach remain. In the USA, an alternative sampling method has been developed in order to test vehicles designed to meet new, tighter emissions standards relevant nationally or in the state of California: Ultra Low Emission Vehicle [ULEV] and Super Ultra Low Emission Vehicle [SULEV] standards. This alternative system is the Bag Mini-Diluter [BMD]. Figure 2 shows a schematic of a generic BMD system.

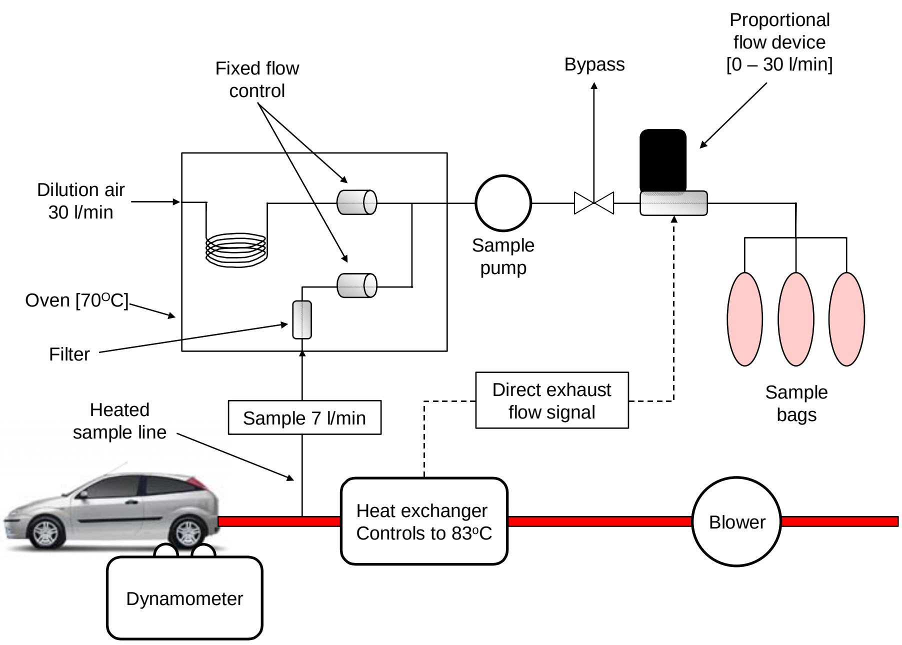

Figure 2 Generic Bag Mini-Diluter system.

Initially, the raw exhaust flow is measured using a direct vehicle exhaust [DVE] measuring instrument [e.g. ultrasonic flow meter]. Metering of the exhaust gas flow allows the bag fill mass flow controller [MFC] to adjust the bag fill rate of diluted sample proportional to the vehicle exhaust flow. Metering of the exhaust gas flow also provides the total exhaust volume per test phase allowing the mass emissions to be calculated.

The second system function of the BMD is to dilute a representative sample of the exhaust gas with zero air. This zero air is either supplied in cylinders or produced from ambient air that is purified at the point-of-use. Zero air supplied in cylinders is allowed to contain up to 1 ppm of the key contaminants while purified ambient air can be produced containing less than 0.05 ppb hydrocarbons. In the system depicted in Figure 2 the dilution of the raw exhaust gas sample with zero air is achieved using two fixed flow control devices; these can be either MFCs or CFVs. One of the flow control devices controls the input of raw exhaust sample flow while the second controls the input of zero air.

Condensation problems associated with conventional CFV-CVS systems are eliminated in the BMD system by heating the vehicle exhaust up to and including the DVE volume system. The sample probe, lines and the dilution point are also heated, as is the zero air. Downstream of the dilution oven the dewpoint temperature of the diluted exhaust gas is sufficiently low to avoid condensation in the pipework.

The ratio between the zero air flowrate and the raw exhaust flowrate is set at a minimum such that water condensation is avoided. Typically the flowrate of raw exhaust gas within the oven is 6-7 l/min while the flowrate of zero air is typically 30-35 l/min. The flowrates are dependent on the size of sample bags used.

The dilution ratio remains constant throughout the vehicle test. For petrol fuels, a minimum dilution ratio of 6:1 is required [compare this to the average dilution ratio of 15:1 used in the conventional CFV-CVS system]. The dilution ratio must be set such that the sample bags can be maintained at ambient temperature without condensation. The dilution ratio is independent of engine displacement [i.e. raw exhaust flowrate] and drive cycle - it is only influenced by the composition of the test fuel.

The final function of the BMD is to fill the sample bags with diluted exhaust gas. This is achieved using a MFC, the flow rate of which is controlled proportionally with the vehicle’s exhaust volume flowrate. The control signal is provided by the DVE volume instrument. The excess flow resulting from varying flowrate through the final MFC [and the fixed diluted exhaust gas flow] is bypassed and vented.

The BMD system eliminates the problems associated with the conventional CFV-CVS system listed earlier:

- The dilution ratio is programmable or fixed by design to eliminate water condensation;

- The dilution ratio is optimised to the lowest value such that the concentrations of contaminant species in the diluted exhaust gas are maximised for subsequent measurement;

- Dilution air [purified ambient air or zero air in cylinders] contains reduced levels of contaminants as untreated ambient air is no longer used as the diluent.

- Ambient bag measurements are eliminated;

- Knowledge of the chemical composition of the exhaust gas is no longer required.

6. FUTURE REQUIREMENTS FOR MEASUREMENT INFRASTRUCTURE

In the short to medium term, the measurement requirements of the more stringent emissions legislation coming into force are being addressed primarily by changes to exhaust gas sampling equipment design. These will tend to involve less dilution of the exhaust gas, and hence less reduction in the concentration of the calibration gas for the analyser than would otherwise be expected.

The more stringent legislation will, however, require a much more thorough evaluation of all of the factors involved in the production of emissions data – not just the gas concentrations at the analysers, but the increased numbers of flow and temperature control devices preceding this measurement.

The first sets of new test equipment are due to be installed in UK commercial test houses from 2003, and the details of how they are to be implemented are not yet decided. There is therefore a very good opportunity for the National Measurement System to provide active help in optimising new test procedures, using established mechanisms such as BTC.

Apart from the calibration of components of emissions measuring systems, there is scope for "whole system" checks covering both the sampling and analytical parts, using exhaust gas simulators - higher concentration calibration gas at elevated temperature and water content – delivering test gas at the point normally occupied by the car exhaust pipe. This is likely to become increasingly important as test laboratories start to use significantly different sampling methods and analytical equipment to generate their results.

In the longer term, the automotive industry is likely to be heading towards a hydrogen fuel cell powered future. Before then, new engine technologies such as combustion / electric hybrids, combined with alternative fuels, are likely to become more common. There may well be specialised measurement requirements for other pollutants, or measurements which take account of the electrical contribution of a hybrid engine. In all these cases, with close participation with the industries involved, NMS work will be able to make important contributions to developments with pervasive and far-reaching consequences.