Appendix 1
Technologies available for measuring NO_X

Contents

This is a review of existing commercially available instruments for the measurement of oxides of nitrogen and the context within which they would operate for an in-service test for spark ignition petrol engined vehicles fitted with closed loop fuelling control and a three way catalyst. It is not a review of NO_X sensing per se.

1. Context of the measurement

One important parameter is the concentration of NO_X in the raw exhaust gas from petrol engines when the engines are run using various conditions.

The data in Table A1.1 are from the chassis dynamometer testing of five of the vehicles studied as recorded in Appendix 3 giving NO_X concentrations at two loaded steady states and the two idle conditions from the current in-service test.

Table A1.1 NO_X concentrations in the raw exhaust of petrol vehicles running under various conditions

	NO_X concentration in raw exhaust gas (in ppm)			
Vehicle, its engine and specification	Steady speed 50 kph (4th)	Steady speed 120 kph (4th)	normal idle	high idle
Make 1, 1800 cc, Euro II	4	60	0.6	1.2
Make 2, 1400 cc, Euro I	4	388	3.9	110
Make 3, 1500 cc, Euro I	310	1048	38.6	139
Make 4, 1800 cc, Euro I	128	326	0.8	36.9
Make 5, 1800 cc, Euro I	4	9	0.7	36.8

The data in Table A1.1 is, generally, for vehicles with a three way catalyst (TWC) that is working satisfactorily. The data in Table A1.2 is from a single vehicle, a 2.0 litre Euro I specification vehicle whose closed loop fuelling control was operating correctly. The data are of NO_X concentration when the vehicle is run at several steady speeds with a new catalyst, with a catalyst that had been fitted for 120,000 miles and when run with a silencer fitted in place of the TWC.

Table A1.2 NO_X concentrations in the raw exhaust of a vehicle fitted as a function of catalyst activity

	NO_X concentration in raw exhaust gas (in ppm)		
Speed	new catalyst	old catalyst	no catalyst
Idle	3	35	62
30 kph	3	49	154
70 kph	2	136	519
120 kph	50	83	2,644

It is noted that the Type 1 test limit values from Directive 98/29/EC Stage A are 0.15 g/km and for Stage B are 0.08 g/km. These values are approximately 50% and 26% of the limit values from 94/12/EC (Euro II), which are themselves 72% of the limit values from directive 91/41/EEC (Euro I). (Note that direct equivalence can't be calculated because both the test cycle, and the way the pollutant concentration levels are specified has changed between directives 94/12/EC and 98/69/EC.) Details of the Type 1 test limit values are given in the tables in Appendix 1 of the Phase 1 report. Notwithstanding, it is realistic to expect that the concentration of NO_X in the raw exhaust will fall by around a factor of 3 to 6 compared with the levels measured and reported in the two preceding tables. Consequently, it is anticipated that the typical concentrations that would need to be monitored by an in-service test are in the range 0 – 200 ppm for a well-maintained vehicle, and it anticipated up to 500 ppm for a faulty vehicle. It is also apparent that the concentrations that will be measured are drive cycle (load) dependent.

2 Issue of species

All combustion processes in air produce oxides of nitrogen though over a wide range of concentrations. Nitrogen dioxide (NO_2) and nitric oxide (NO) are both oxides of nitrogen and together (with N_2O which is present in even smaller concentrations) are referred to as NO_X. At the high temperatures involved in the combustion chambers of vehicles very little nitrogen dioxide is produced, rather it is its chemically moderately reactive parent nitrogen monoxide that is formed in significant quantities and emitted from the tail pipe. The rate of conversion of NO to NO_2 in the atmosphere is typically 50% in a few tens of minutes. Consequently, when determining the contribution of vehicles to air quality, whilst the combined emissions of both oxides, i.e. of NO_X, is important, measurement of NO alone from the tailpipe is a good approximation. This influences the measurement instrumentation that is suitable for measuring vehicle exhaust emissions.

The type approval regulations, Section 4.3.1.1 of Annex 3 to 70/220/EC, specify that the type of instrument that must be used for measuring NO_X for type approval of passenger cars and light-duty vans is either of the chemiluminescent (CLA) or of the non-dispensive ultraviolet resonance absorption (NDUVR) type, both in association with an NO_X - NO converter. The type approval regulations for heavy-duty engines, Section 3.3.5 of Appendix 4 to Annex 3 of directive 99/96/EC, are more restrictive. They specify that the only type of instrument that must be used for measuring NO_X is a (heated) chemiluminescent detector (CLD) in association with an NO_X - NO converter.

Because of the presence of NO_2 and because only NO can be detected directly by some techniques, analysers often incorporate an NO_2 to NO converter. This is typically a heated tube containing carbon. Part of the conversion occurs because of thermal decomposition:

$$2NO_2 + \text{Heat} \rightarrow 2\,NO + O_2$$

and the remainder of the conversion is carried out by the residual NO_2 reacting with the carbon

$$2NO_2 + C \rightarrow 2\,NO + CO_2.$$

Interestingly, this is exactly the same reaction that is promoted by an oxy-cat on a diesel engined vehicle.

The result is that when a mixture of NO and NO_2 passes through the converter and then into an NO detector, the sum of NO and NO_2 (i.e. NO_X) is detected.

The type approval regulations, Section 4.3.1.1 of Annex 3 to 70/220/EC, in addition to stipulating that a NO_X - NO converter should be used with the analysis instrument, also direct that the efficiency of the NO_X converter must be checked and be within prescribed limits.

3. Techniques used for measuring NO_X

3.1 NDIR

3.1.1 Principles of operation

Many molecules absorb infra-red electro-magnetic radiation. This occurs at discrete wavelengths/energies dependent on the molecular species involved, i.e. it can be viewed as a fingerprint for the molecules. The energy of principal absorption bands for some key species of interest in automotive emissions are:

Species	Absorption energy (cm^{-1})
CO	2143
CO_2	2349
NO	1876
NO_2	1617
water vapour	1595, 3750
hydrocarbons	2950

Without going into great detail, it can been seen that 4 of the 6 species listed above have, within the species considered, unique absorption energies. The exceptions are NO_2 and water vapour which both have absorbances around 1600 cm^{-1}.

Given this general background, it can be seen why IR absorbance generally is a possible technique for the detection of CO, CO_2, NO and hydrocarbons.

Versatile laboratory equipment tends to use a monochromator to disperse (split up) the light into its component wavelengths. This enables the spectrum of any sample to be recorded. In less versatile analysers, designed for the analysis of specific species, the monochromator unit is replaced with a filter that only transmits selected wavelengths which the target species will absorb. This variant of infra-red instruments is most commonly known as non-dispersive infra-red (NDIR) measurement.

3.1.2 Species measured, typical specification and other details

It has been seen how the NDIR absorption technique can measure NO, but not NO_2 because of interference from water vapour (a species inevitably present in automotive exhausts).

Information from suppliers gives typical operating ranges of 0 – 500 ppm. In terms of robustness, size and suitability for in-service testing, it should be noted that NDIR is the technique used to measure CO, CO_2 and hydrocarbons in the majority of garage vehicle exhaust 4-gas analysers.

3.2 FTIR

3.2.1 Principles of operation

Fourier transform infra-red spectroscopy is a variant of infra-red absorption spectroscopy. Rather than measuring the absorption of each narrow band of wavelengths consecutively to generate an absorption spectrum, the amount of light from a broad band source transmitted through a scanning interferometer is measured as a function of interferometer optical pathlength. The Fourier transform of this is the absorption spectrum. With increasing computational power, and improved interferometers, the improved signal to noise prospects afforded by Fourier transform spectroscopy have led to it being increasingly widely used in place of conventional absorption spectroscopy within laboratories.

However, despite the advantages of FTIR spectroscopy it remains a form of infra-red spectroscopy and the fundamental interference of NO_2 measurement by water vapour remains. Further, whilst an FTIR spectrometer can replace a versatile laboratory absorption spectrometer, FTIR spectrometers are significantly more complex than NDIR instruments.

3.2.2 Species measured, typical specification and other details

As for NDIR absorption spectroscopy, FTIR can measure NO, but not NO_2 because of interference from water vapour.

Information from suppliers gives typical operating ranges of 0 – 500 ppm and of course the ability to simultaneously measure CO, CO_2 and hydrocarbons. Prices vary from £10k - £25k (the latter being a typical figure for a research instrument).

Whilst there is a general feeling that FTIR is not yet sufficiently robust for routine garage use, new products are in the market and are also being developed. For example, GASMET™ have a portable FTIR instrument using what they describe as the most reliable interferometer in the market place, made by Temet Instruments[1]. It is designed to run of mains or 12V DC for portable use and the application notes include information for vehicle exhaust analysis. The price for a one off instrument is in the region £25k - £30k depending on the options required.

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[1] see for example on their web site http://www.gasmet.fi

3.3 CHEMILUMINESCENCE

3.3.1 Principles of operation

Nitric oxide reacts with ozone, a chemical form of oxygen, to give nitrogen dioxide in a reaction that generates light:

$$NO + O_3 \rightarrow NO_2 + O_2 + \text{light emission.}$$

The intensity of the light emitted is proportional to the mass flow-rate of nitric oxide into the reaction chamber and can be measured with high sensitivity using a photomultiplier tube. This, therefore, represents the basis for a sensitive, quantitative analysis of gaseous NO.

The light generating reaction requires ozone. This is usually made by a silent electric discharge (at several tens of kV) through a stream of externally provided oxygen and is generated in the ozoniser, which is usually an integral part of the analyser.

The type approval regulations, 70/220 Section 4.3.1.1 of Annex 3, specifies that the type of instrument that must be used for measuring NO_X for type approval is *either of the chemiluminescent (CLA) or of the non-dispensive ultraviolet resonance absorption (NDUVR) type, both with an* NO_X *- NO converter*. It also stipulates (in Appendix 6) that the instruments must be calibrated. This includes (in Section 3 of the directive) checking the efficiency of the NO_X converter.

3.3.2 Species measured, typical specification and other details

It has been seen how the chemiluminescence technique can measure NO, but not NO_2.

Information from suppliers gives typical operating ranges of 0 – 500 ppm.

It does consume a gas, either O_2 or compressed air, as a feed gas to the ozoniser, although an internal pump to use ambient air can be used. Both the meter and the converter’s efficiency require periodic calibration.

Chemiluminescence tends to be the measurement technique preferred by automotive test houses. It is one of the 2 techniques specified in the type approval regulations. It also has the reputation of not being portable. However, this may be because of instrument manufacturers’ knowledge and perceptions of demand rather than anything more fundamental. For example, Horiba are marketing what they describe as the first advanced gas analyser in a portable case (although the unit’s weight is approximately 17 kg). Interestingly, the five-gas analyser version (PG-250) uses chemiluminescence NO_X detection. The price for a one off instrument was quoted as £13.6k. In the context of a future need to replace the current gas analysers, this would be a contender .

3.4 ELECTROCHEMICAL CELL

3.4.1 Principles of operation

Just as nitric oxide reacts with ozone to give nitrogen dioxide, the basis of chemiluminescence detection of NO, so too it can be oxidised in an electrochemical cell. Instead of the reaction generating light (as for chemiluminescence), in this form the reaction generates a small electric current which can be detected. The magnitude of the current is proportional to the mass flow-rate of nitric oxide into the reaction chamber and can be measured with high sensitivity using relatively standard electronics.

The electrochemical cell requires an electrolyte that could be a liquid or, ideally, a solid.

Some key advantages of this approach to measuring NO are that it is cheap, simple and robust. However, it is fair to say that this technology is not as mature as either chemiluminescence detection or NDIR and durability might be an issue.

3.4.2 Species measured, typical specification and other details

It has been seen how electrochemical cells can measure NO, but not NO_2.

Information from suppliers gives typical operating ranges of 0 – 500 ppm, going up to 5000 ppm. It should also be noted that whilst Britain and many other countries do not require the measurement of NO_X during an annual in-service test, there are countries that do. In the US, where testing regimes are decided on a state by state basis, 5-gas analysers are moderately common sensing CO, CO_2, HC and O_2 (as in the 4-gas analysers used in Britain) plus NO_X. A number of these 5-gas analysers, which are designed for garage use, are based on electrochemical sensors (for example the meters made by SPX Inc, SPTC and Sensors Inc).

Other manufacturers of 5-gas analysers, or upgrades to give a 4-gas analyser NO_X measurement capability (e.g. Richard Oliver and Bosch) have also confirmed that they measure NO (NO_X) using an electrochemical cell

This serves to illustrate that, worldwide, electrochemical detection of NO_X for in-service testing is becoming increasingly a preferred option.