Engine Exhaust Emissions

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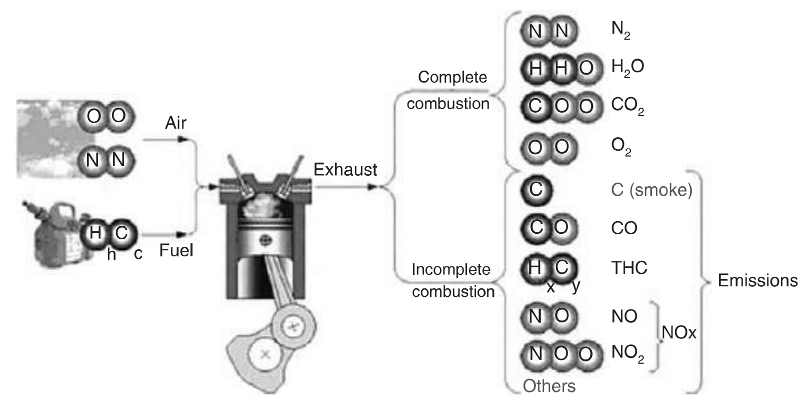
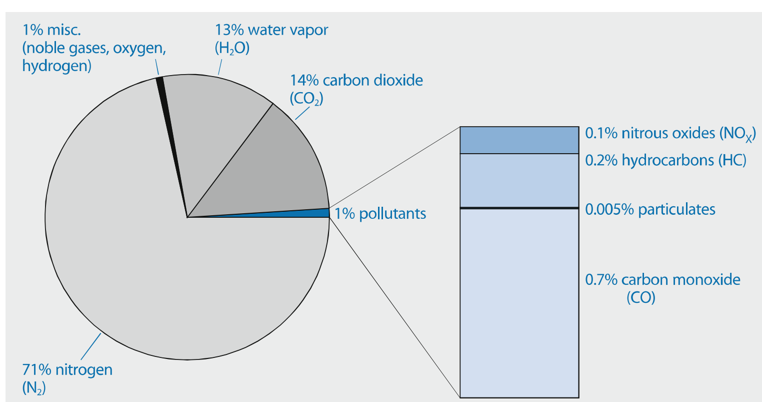
ME 401: Internal Combustion Engines

Gaseous Components of Combustion Processes



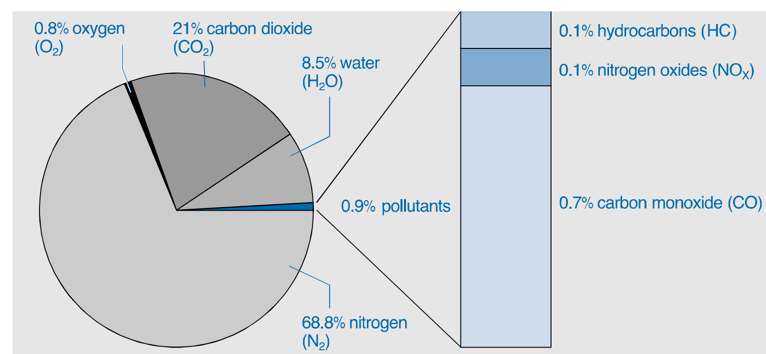
T562

Composition of Engine Exhaust (untreated)



T551

Exhaust gas composition (% volume): gasoline engine with $\phi = 1.0$



T552

Exhaust gas composition (% volume): diesel engine with $\phi = 1.0$

Main constituents of exhaust gases

- Water (H_2O)
- Carbon dioxide (CO_2)
- Nitrogen (N_2)

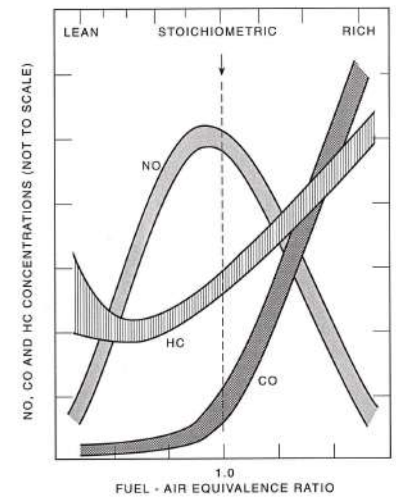
Pollutants: engine's untreated emissions is about 1% of the total exhaust-gas quantity. The most significant of these combustion are:

- Carbon monoxide (CO)
- Hydrocarbons (HC), and
- Nitrous oxides (NO_x)

Other important pollutants are:

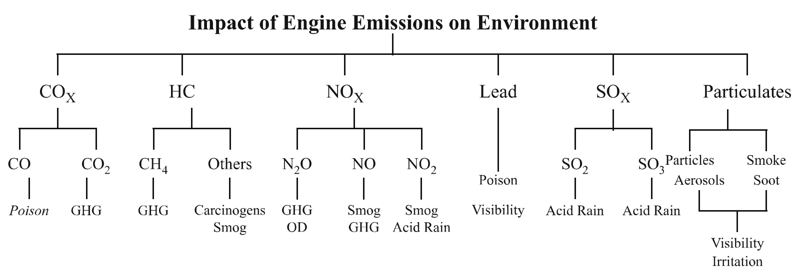
- Aldehyde (H − C − O compounds)
- Sulphur dioxide from diesel fuel (as diesel contains sulphur)
- Particulates including soot, especially with diesel engines.

▶ In engine technology, the nitrogen oxides NO & NO_2 are usually combined and are referred to as NO_x.



T547

SIE emission vs. ϕ



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GHG: Green House Gases, OD: Ozone Depletion

Toxicity & effects of pollutants on mankind

The maximum workplace concentration (MAK value) of a pollutant is indicated e.g. in ppm or mg/m^3.

- **Carbon monoxide:** A colorless and odourless gas. Its adherence to haemoglobin is far stronger (factor 240) than that of oxygen. Even low CO concentrations may therefore be sufficient to cause suffocation. The MAK value is 33 mg/m^3.
- **Unburned hydrocarbons:** Depending on their composition, they have a more or less narcotic effect and irritate man's mucous membranes. Certain components have a carcinogenic effect (aromates, e.g. 3,4 benzapyrene, benzene).
- **Aldehydes:** Components with a sharp smell and narcotic effect. Some of these compounds are considered to cause cancer. The MAK value, e.g. of formaldehyde, is 0.6 mg/m^3.

- **Nitrogen dioxide:** A gas with a sharp smell and red-brown color. Low concentrations are sufficient to cause lung irritation, tissue damage and irritation of mucous membranes. A risk of acid formation is present. The MAK value is 9 mg/m^3.
- **Nitrogen monoxide:** An odourless gas that affects lungs function & irritates mucous membranes. Risk of nitric acid formation. It is unstable under ambient conditions and changes into $N0_2$, the MAK value also is 9 mg/m^3.
- **Sulphur dioxide:** An odourless gas with a sharp smell, causing irritation of mucous membranes. Produces sulphuric acid under the action with water. The MAK value is 2 ml/m^3.
- **Particulates:** Diesel engines generate particulate emissions (carcinogenic potential) and sulphur dioxide emissions that contribute to environmental damage known as "tree death". Part of the particulates can enter the lungs and are dangerous since they deposit substances that constitute a health hazard.

Generation of NO_x

There are **four** major chemical mechanisms that produce NO.

1. Thermal or Zeldovich mechanism,
2. Prompt or Fenimore mechanism,
3. N_2O route,
4. Combustion of Fuel Bound Nitrogen (FBN).

1. Thermal or Zeldovich Mechanism: Three major steps:

$$N_2 + O \rightarrow NO + N \quad k_1 = 1.8 \times 10^{14} \exp(-38370/T) \tag{1}$$

$$N + O_2 \rightarrow NO + O \quad k_2 = 1.8 \times 10^{10} \exp(-4680/T) \tag{2}$$

$$N + OH \rightarrow NO + H \quad k_3 = 7.1 \times 10^{13} \exp(-450/T) \tag{3}$$

- First reaction is the rate limiting step due to very high activation temperature. Once N is formed, it is consumed by Eq. 2. Eq. 3 is important in rich parts of the flame.
- Little NO is formed when temperature is below 1800 K. Its production rate increases more than fourfold when temperature increases by 100 K.

2. Prompt or Fenimore Mechanism: Oxides of nitrogen can be produced promptly at the flame front by the presence of CH radicals, an intermediate species produced only at the flame front at relatively low temperature (around 1000 K).

$$CH + N_2 \rightarrow HCN + N \tag{4}$$

$$HCN + N \rightarrow^{O_2} \cdots \rightarrow NO \tag{5}$$

3. N_2O Route: Under high pressures, the following 3-body recombination reaction can produce N_2O through:

$$N_2 + O + M \rightarrow N_2O + M \tag{6}$$

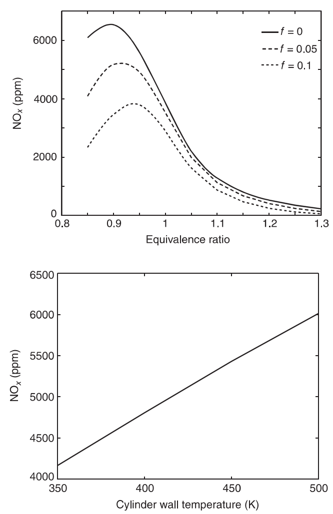
Once N_2O is formed, it reacts with O to form NO via

$$N_2O + O \rightarrow NO + NO \tag{7}$$

▶ NO can be formed at low temperatures of around 1200 K.

4. Combustion of Fuel Bound Nitrogen (FBN):

- NO_x can be formed directly from fuels, such as coal, containing nitrogen compounds such as NH_3 or pyridine (C_5NH_5).
- FBN is also significant in the combustion of biologically-derived fuels since they typically contain more nitrogen than their petroleum-based counterparts.



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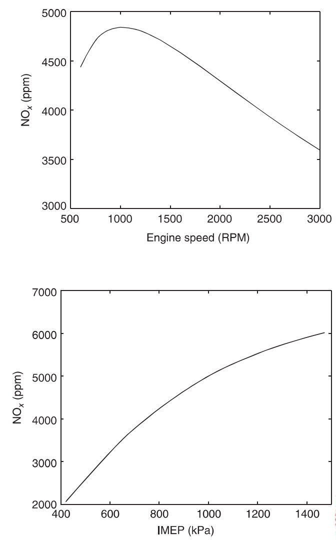

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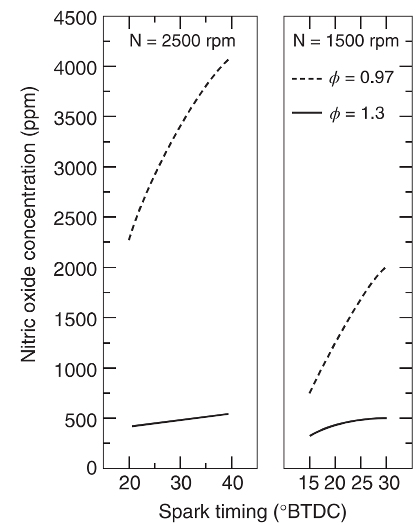

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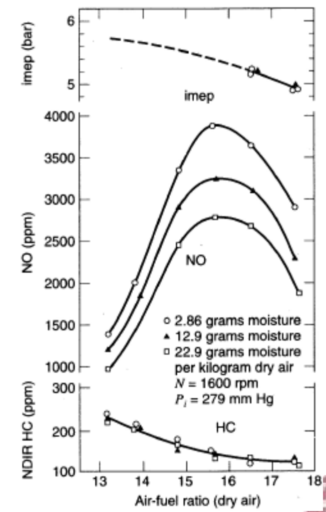


T559

Generation of CO

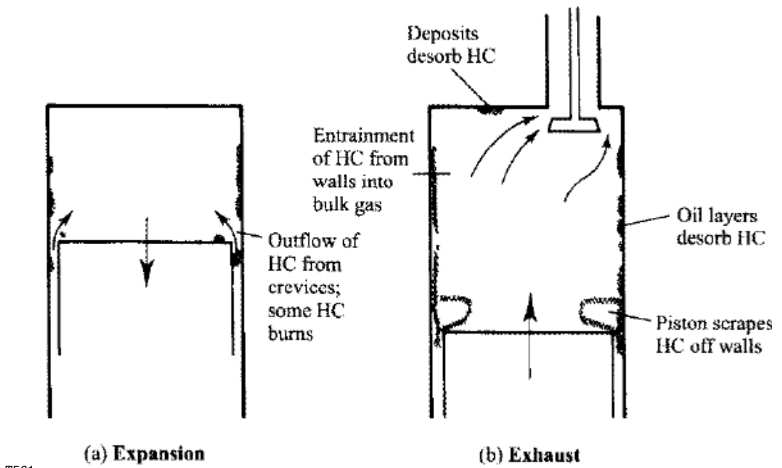
- Carbon monoxide results from incomplete combustion of rich air/fuel mixtures due to an air deficiency. In such conditions, CO formation is described by 'water gas shift equation':

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

- Although CO is also produced during operation with excess air, the concentrations are minimal. The presence of CO may be traced to a local lack of homogeneity of the air-fuel mixture and to reaction processes that occur near the wall or to freezing of reactions as an increasing amount of air becomes available.
- Fuel droplets that fail to vaporize form pockets of rich mixture that do not burn completely.

Generation of HC

- HC emissions are caused by incomplete combustion where there is an oxygen deficiency. New hydrocarbon compounds, not initially present in the original fuel, are also produced.
- Two general classifications that are widely used are total hydrocarbons (THC) and non-methane organic gases (NMOG).
- In SIEs, six principal mechanisms are responsible: (1) crevices, (2) oil layers, (3) carbon deposits, (4) liquid fuel, (5) cylinder wall flame quenching, and (6) exhaust valve leakage. The crevice mechanism is responsible for about 38% of HC emissions.
- In CIEs, HC come primarily from
  (1) Fuel trapped in the injector at the end of injection that later diffuses out, (2) fuel mixed into air surrounding the spray so lean that it cannot burn, (3) fuel trapped along the walls by crevices, deposits, or oil due to impingement by the spray.



T561

Generation of Particulates

- A high concentration of particulate matter (PM) is manifested as visible smoke or soot in the exhaust gases. Particulates are a major emissions problem for diesel engines, as their performance is smoke limited.
- Uncombusted and partly combusted hydrocarbons form deposits on the soot, where they are joined by aldehyde, with their overpowering odour.
- Aerosol components (minutely dispersed solids or fluids in gases) and sulphates bond to the soot. The sulphates result from the sulphur content in the fuel.
- The problem of solids (particulates) in exhaust gas is primarily associated with diesel engines. Levels of particulate emissions from gasoline engines are negligible.

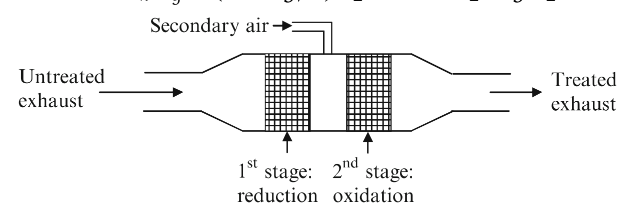
Particulates, when they appear to the human observer, are called **smoke**. Smoke colors are indicative of the dominant source of particulate:

- **Black**: soot or more accurately carbon, which typically makes up some 95% of diesel smoke either in elemental, the majority, or organic form.
- **Blue**: hydrocarbons, typically due to lubricating oil burning due to an engine fault.
- **White**: water vapour, typically from condensation in a cold engine or coolant leaking into the combustion chambers. White smoke is not detected by conventional tail-pipe smoke meters.
- **Brown**: NO_2, maybe detected in exhaust of heavy fuel engines.

SIE: Three-Way Catalyst

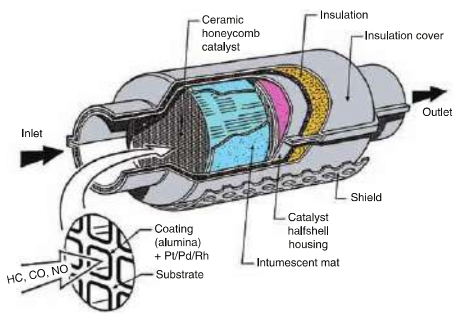
A 3-way catalytic converter simultaneously performs three tasks:

1. Reduction of nitrogen oxides to nitrogen and oxygen:
$$2NO_x \rightarrow xO_2 + N_2$$
2. Oxidation of carbon monoxide to carbon dioxide:
$$2CO + O_2 \rightarrow 2CO_2$$
3. Oxidation of unburned hydrocarbons (HC) to CO_2 and water:
$$2C_xH_y + (2x + y/2)O_2 \rightarrow 2xCO_2 + yH_2O$$



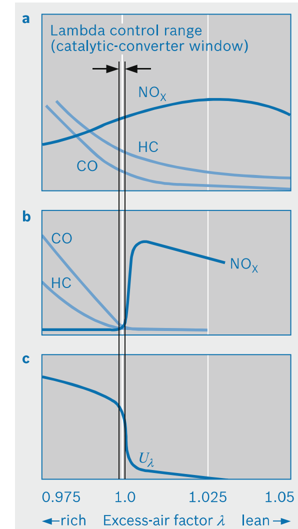
T566

- Catalysts used: a platinum/rhodium blend for reducing reactions & a platinum/palladium blend for oxidizing reactions.
- The catalytic reactions occur on the surface of the catalyst so the metals are often coated onto either a ceramic honeycomb or ceramic beads to increase the available catalyst surface area.
- 3-way catalytic converter must reach a minimum temperature of roughly 300°C (**light-off**) before pollutants can be converted.



T573

- At $\lambda = 1$, a state of balance arises between the oxidation and reduction reactions, and results in highest possible conversion rate for all three pollutant components.
- For lean condition ($\lambda > 1$): HCs and CO are oxidized by the oxygen present in the exhaust gas. The raw NO_x emissions are released untreated.
- For rich condition ($\lambda < 1$): the NO_x reduction reactions takes place with HCs and CO as the reducing agents. Excess hydrocarbons and carbon monoxide which cannot be converted for lack of oxygen are released untreated.



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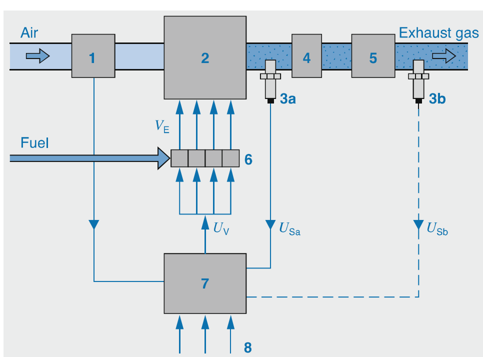
Lambda Control Loop

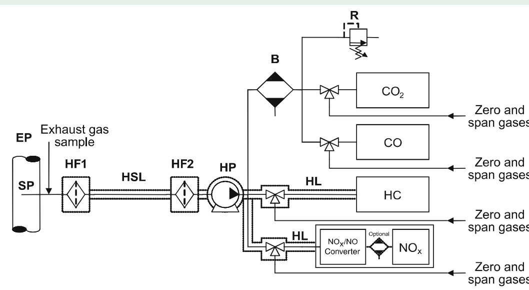


T569

1. Air-mass sensor, 2. Engine, 3a. Lambda sensor upstream of primary catalyst, 3b. Two-step lambda sensor downstream of main catalyst, 4. Primary catalyst (three-way catalyst), 5. Main catalyst, 6. Fuel injectors, 7. Engine ECU, 8. Input signals.

U_S *Sensor voltage,* U_V *Valve control voltage,* V_E *Injected fuel quantity*

Exhaust Emission Measurement System (ISO 16183)

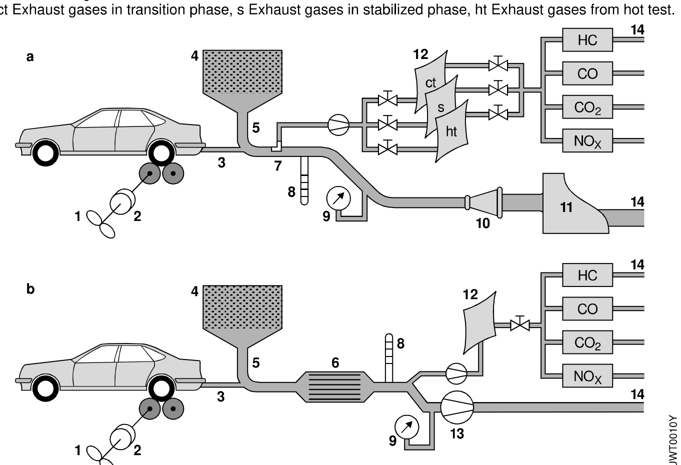


EP	Exhaust pipe	HP	Heated Pump	CO	CO Analyzer
SP	Sample Probe	R	Back pressure Regulator	HC	THC Analyzer
HF1	Heated Prefilter	B	Dryer (Cooling Bath)	NO_x	NO_x Analyzer
HSL	Heated Sample Line	HL	Heated Sample Line	NO_x/NO	NO_2 to NO Converter
HF2	Heated Filter	CO_2	CO_2 Analyzer		

T565

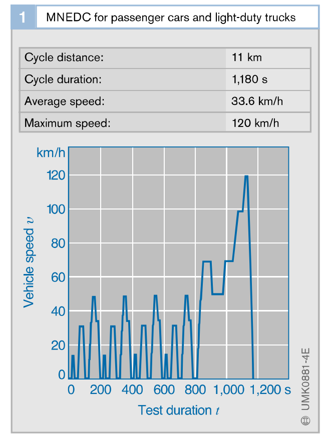
Test layouts

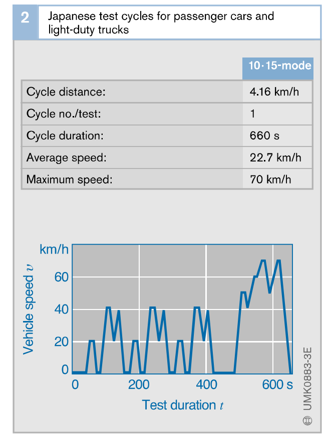
a For US Federal Test (shown here with venturi system), **b** For European test (shown here with rotary-piston compressor).
1 Brake, **2** Rotating mass, **3** Exhaust gas, **4** Air filter, **5** Dilution air, **6** Cooler, **7** Test-sample venturi nozzle, **8** Gas temperature, **9** Pressure, **10** Venturi nozzle, **11** Fan, **12** Sample bag, **13** Rotary-piston blower, **14** To discharge.
ct Exhaust gases in transition phase, s Exhaust gases in stabilized phase, ht Exhaust gases from hot test.



T570

Emission testing is based on standardized driving phases in which gear-shifts, braking, idle phases & standstill periods are defied to provided a high level correspondence to normal traffic.

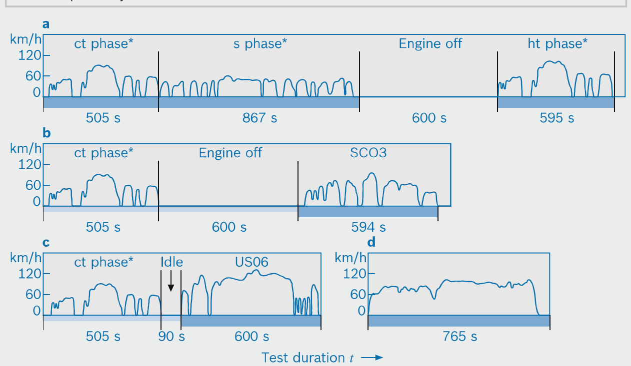




T572

Modified New European Driving Cycle (MNEDC) & Japanese test cycle

Test cycle	a FTP 75	b SC03	c US06	d Highway
Cycle distance:	17.87 km	5.76 km	12.87 km	16.44 km
Cycle duration:	1877 s + 600 s pause	594 s	600 s	765 s
Average speed in cycle:	34.1 km/h	34.9 km/h	77.3 km/h	77.4 km/h
Maximum speed in cycle:	91.2 km/h	88.2 km/h	129.2 km/h	94.4 km/h



T571

US test cycles for passenger cars and light-duty trucks/vans

Emission Test Methods

Component	Procedure
CO, CO_2	Non-dispersive Infra-red analyser (NDIR)
NO_x	Chemiluminescence detector (CLD)
HC	Flame-ionization detector (FID)
CH_4	Combination of gas-chromatography & FID (GC-FID)
Particulates	Weighing of filters before & after the test drive

European Emission Limits for Gasoline Passenger Cars

Stage	Date	CO (g/km)	HC (g/km)	HC + NO_x (g/km)	NO_x (g/km)	PM (g/km)	PN (#/km)
Euro 1	07-1992	2.72	—	0.97	—	—	—
Euro 2	01-1996	2.20	—	0.5	—	—	—
Euro 3	01-2000	2.30	0.20	—	0.15	—	—
Euro 4	01-2005	1.0	0.10	—	0.08	—	—
Euro 5	09-2009	1.0	0.10 (0.068)	—	0.06	0.005* (0.0045)	—
Euro 6	09-2014	1.0	0.10 (0.068)	—	0.06	0.005* (0.0045)	6×10^{12} (applies to DI engines only)

T563

European Emission Limits for Diesel Passenger Cars

Stage	Date	CO (g/km)	HC (g/km)	HC + NO_x (g/km)	NO_x (g/km)	PM (g/km)	PN (#/km)
Euro 1	07-1992	2.72	—	0.97	—	0.14	—
Euro 2, IDI	01-1996	1.0	—	0.70	—	0.08	—
Euro 2, DI	01-1996	1.0	—	0.90	—	0.10	—
Euro 3	01-2000	0.64	—	0.56	0.50	0.05	—
Euro 4	01-2005	0.50	—	0.30	0.25	0.025	—
Euro 5a	09-2009	0.50	—	0.23	0.18	0.005* (0.0045)	—
Euro 5b	09-2011	0.50	—	0.23	0.18	0.005* (0.0045)	6×10^{11}
Euro 6	09-2014	0.05	—	0.17	0.08	0.005* (0.0045)	6×10^{11}

T564