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## Emissions of unregulated pollutants from European gasoline and diesel passenger cars

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### Abstract:

Within the framework of the European Artemis project, the emissions of unregulated compounds were measured on new technology passenger cars. A sample of passenger cars was tested on a chassis dynamometer with constant volume sampling (CVS). The measurement of unregulated compounds comprised about 100 different VOC in the C<sub>2</sub>-C<sub>6</sub> and C<sub>7</sub>-C<sub>15</sub> range and carbonyl compounds. The sampling of these compounds was made using sorbent tubes followed by analysis with chromatography technology in liquid and gas phases. The influence of cold and warm starting conditions on the VOC composition was determined. The emission factors were determined and compared for either gasoline or diesel vehicles. The influence of the technology was evaluated and a first approach to understand the effect of recent technology on the ozone formation was developed.

**Keywords:** VOC, carbonyl compounds, speciated emissions, driving cycle, emission factor.

### 1. Introduction:

The transport sector is a major source of atmospheric pollutants. The Volatile Organic Compounds (VOC) result from incomplete combustion have a double influence on air quality. These molecules can act as primary toxic pollutants and play a role of precursor of the formation of photochemical-oxidant species.

Globally hydrocarbons emitted from vehicles are measured by THC analysers. In Europe few studies are carried out on the specified VOC (Schmitz. et al., 2000; Fontaine, 2000 ; Flandrin.,

2002) compared to the data concerning the regulated pollutants : See the state-of-the-art made some years ago in Europe (Hickman,1999).

The objective of this work is to improve the exhaust emission factors for the passenger cars by enlarging the emission factor database and by calculating emission factors according to the different purposes of the European Artemis project (Assessment and reliability of transport emission models and inventory systems). In the next future, in order to study the real impact of the automotive VOC emission, these improved emission factors will be used for atmospheric modelling, with the purpose to investigate its influence on the tropospheric ozone formation.

In this work, we describe the measurement of the speciated gas phase hydrocarbon and carbonyl emissions collected from recent technology passenger cars (ECE1504 to Euro 3) which represented the 2001 national French fleet. The vehicles used gasoline or diesel fuel, and measurements were made over the real-world test driving cycles and performed on a chassis dynamometer with constant volume sampling (CVS) at INRETS. The tailpipe emissions were sampled for light hydrocarbons (C<sub>2</sub>-C<sub>6</sub>), semi-volatile hydrocarbons (C<sub>7</sub>-C<sub>15</sub>) and aldehydes and ketones.

## **2. Experimental**

### **2.1 Vehicles and driving conditions**

The measuring program included 30 present passenger cars, i.e. 13 gasoline and 17 diesel fuelled cars. The vehicles conformed to emission standard ECE1504 to Euro 3. **Table 1** shows the distribution per fuel and standard of the sample. The emission measurements were performed on the chassis dynamometer. The sample of vehicles was tested using a set of 4 real-world driving cycles (see **Table 2**): an “Inrets urbain fluide court” cycle repeated 15 times (15xIUFC) (Joumard et al, 1999), started firstly cold, then secondly warm, and 2 cycles “VP faible/forte motorisation” for urban and motorway driving behaviour (André, 2004). The latter cycles consist in alternative cycles, specific to vehicles with low or high powers

respectively. The 2 15xIUFC cycles allow us to determine the excess emissions due to cold start. Both “VP” cycles show the emission for urban and motorway driving behaviour.

## **2.2 Sampling**

The exhaust gas from vehicle is diluted with filtered ambient air using a constant volume sampler (CVS) device (*Figure 1*). VOC are sampled in the dilution tunnel using sorbent tubes: Carbotrap B and C, Carbosieve III for “light” hydrocarbons (C<sub>2</sub>-C<sub>6</sub>) and Tenax for semi-volatile hydrocarbons (C<sub>7</sub> -C<sub>15</sub>). The sampling was optimized by the use of two cartridges in series. During the first tests, this experiment showed that 25 to 30% of light and 40 to 60% of semi-volatile hydrocarbons are sampled on the second cartridge. By decreasing the sampling flow rate (*Table 3*) we reduced the breakthrough rate respectively up to (18%) and (30%). Before each sampling of exhaust gas a background contribution of the air dilution was recorded. For the collection of the aldehydes and ketones the diluted exhaust gas is pulled through a DNPH coated silica cartridge. After sampling, the cartridges are transported to the analysis laboratory in a temperature controlled container at 0°C and are stored at – 10°C before analysis.

## **2.3 Analysis**

### **Regulated pollutants measurement**

The measurement of the regulated pollutants was achieved at INRETS by means of usual analytical techniques (non-dispersed infrared for CO and CO<sub>2</sub>, chemiluminescence for NO<sub>x</sub> and flame ionisation detection for total hydrocarbons ).

### **Unregulated pollutants measurement**

Carbotrap and Tenax samples were analysed by the thermal desorption preconcentration method, followed by quantification by high resolution gas chromatography with a flame ionisation detector (GC/FID) for compounds from C<sub>2</sub> to C<sub>6</sub> and with a mass spectrometer detector (GC/MS) for the compounds from C<sub>7</sub> to C<sub>15</sub>. For light hydrocarbons we used the thermal desorption system (Turbomatrix TD Perkin Elmers) using two stage desorption. In the first stage the analytes were desorbed with a nitrogen flow from sample tube then refocused

onto a narrow bore cold trap kept at  $-30^{\circ}\text{C}$  and filled with adsorbents, in the second one the trap was heated at  $300^{\circ}\text{C}$  to release materials into the chromatograph (**Figure 2**). In the case of hydrocarbons from  $\text{C}_7$  to  $\text{C}_{15}$ , the adsorbed substances are concentrated in a desorption chamber at  $220^{\circ}\text{C}$ , before to be inject onto the beginning of the cold column chromatograph. (Module Combi Injector/Desorber EM640 Brüker). The thermal desorption and chromatographic conditions used for speciation of emissions samples are summarized in **Table 4**. The multiple gradient column temperature conditions were selected as a compromise between maximum peak resolution and minimum analysis time. Materials used for compound identification and quantification were purchased from Scotty (hydrocarbon standard gases) and Sigma-Aldrich (hydrocarbon standard liquids). Gas standards were prepared by injection of gases from Scotty cans (or liquid for example: BTEX ) into a 10 litre dilution round bottom flask under vacuum ( $0-760$  mmHg at room temperature). These standards were diluted to the desired concentration, by filling the flask with nitrogen, then sampled on Tenax and Carbotrap cartridges by pumping (variation of the flow rate, variation of the sampling time to build the calibration curve). Hydrocarbons identifications were assigned by comparing retention times of chromatographic peaks from emissions samples with those from standard mixtures and by comparing mass spectra with those contained in NIST and/or WILEY libraries. The  $\text{C}_2$ - $\text{C}_{15}$  range of our identified compounds library contains 75 major species (26 alkanes, 9 alkenes/alkynes, 24 monoaromatics, 3 polyaromatics) (**Table 5 and 6**).

### **Carbonyl compounds measurement**

Carbonyl compounds collected in the DNPH cartridge were eluted with 2ml of HPLC grade acetonitrile and analysed by HPLC (Spectra Physics P4000) with UV detection at 365 nm ((Spectra Focus 3000). A  $4.6 \times 250$  mm C18 column (Alltima, Altech) was used and the gradient elution was describes as follows in **Table 7**. Identification and quantification were made based on matching the HPLC retention time with those of authentic standards purchased to Supelco (réf 476 72-U -13 hydrazones) and using a weighted amounts of the authentic

hydrazone standards. The 13 compounds identified are given in the *Table 8* and contains 11 aldehydes and 2 ketones.

The detection limits were estimated for all characterised compounds analysed by GC and HPLC. Curves of calibration were established for the quantification of each identified species and a minimum of concentration was defined for the detected compounds in order to be introduced into the database (*Table 8 and 9*). The determination of these minimum values is based on the sensitivity of the analytical methods used.

### **3. Results and Discussion**

The results of the exhaust gas speciation and the exhaust emission factor for each species and each vehicle category are reported below. The influence of the driving cycle and technology on the emissions are discussed too.

#### **3.1 Families compounds characterised in the exhaust gas**

The different family's compounds characterised by GC and HPLC analysis are alkanes, alkenes, alkynes, aromatics and carbonyls compounds. The major VOC group emitted by the different passenger cars are the aromatic compounds and the alkanes. The results of this study show that amongst the total gas phase non methane hydrocarbons emitted for a gasoline engine, 75-93 % were accounted for aromatics species, 6-18 % for linear and substituted alkanes, 1.2-4.3 % for alkenes and alkynes, and 0.1- 2 % for carbonyls compounds. And for a diesel engine 54-75 % of species analysed are aromatics, 18-31 % linear and substituted alkanes, 3-6 % alkenes and 2-6.4 % carbonyls compounds. The *Table 10* shows the emission factors (in mg km<sup>-1</sup>) of the different compounds for gasoline and diesel vehicles and for the different cycles. We observed an evolution of the species in the different families: For the carbonyl compounds, the major compounds detected are formaldehyde, acetaldehyde and ketone which account for approximately 73% of the total carbonyl emissions in the case of cold / warm starting. In the case of cars with diesel engines the proportion of these species is most important, it's relative to the fuel itself. The fractions of alkanes trapped on the cartridges include linear and substituted chains of carbons from C<sub>3</sub> to C<sub>16</sub> for the two types of

technology. Concerning the diesel cars, some compounds with a chain length higher to 16 carbons are clearly identified (nonadecane, octadecane, heptadecane) compounds which are not found in the emission of gasoline cars. Cis-2-butene and 1-pentene are majors' alkenes and alkynes emitted by the vehicles. For the aromatic family, the more abundant compounds are 2-, 3-, and 4- ethyltoluene and m-, p- xylene. Whatever the cycle is, the emission factor of gasoline cars are 10 times higher than the emission factor of diesel vehicles. In the case of diesel cars, some traces of polyaromatics species (PAH) are also qualitatively detected **as 1- and 2- methylnaphthalene**. But those species were not quantified in this part of the study, and are reported by (Paturel et al., 2004). Whatever the cycle is, the emission factor of gasoline cars is 10 times higher than the emission factor of diesel vehicles. Globally, a most important emission of VOC is observed with gasoline vehicles compared to the diesel ones, especially in the case of the cold 15xIUFC cycle. Generally, whatever vehicle technology and cycle are, aromatics compounds are the majority with a somewhat weaker part concerning the diesel compared to the gasoline cars. Saturated hydrocarbons comes second, according weaker percentages which are about 20 % for diesel cars and 12 % for gasoline cars. Concerning the carbonyl compounds, their own percentage is very low (0.5 % for gasoline and 10 % for diesel).

### **3.2 Influence of driving cycle**

In this part, we observe the influence of the driving cycle on the emission factor for the gasoline and diesel passenger vehicles. It should be noted that the emission factor for total VOC in the case of the cold 15xIUFC cycle of the gasoline cars is largely higher than in the case of diesel cars.

Hot pollutant emissions are higher in the “VP” urban cycle than in the “VP” motorway cycle the ratio emission factor is approximately 4 for the diesel and 4.5 for the gasoline cars. For the alkanes, the emission factors on the hot “VP” urban cycle are higher for the gasoline cars than for the diesel ones. On contrary, the variation of emissions from gasoline to diesel cars are weak, generally speaking, as far as the motorway cycle is concerned. Between urban and

motorway driving cycles, the emissions are generally, for the different VOC families, most important in the urban one (*Figure 3*). It's in relation with the characteristics of the cycle (mean speed, maximum speed, acceleration rate, etc) because in the case of motorway type, the speed profile is more regular.

### **3.3 Influence of cold and hot starts on the emissions**

The influence of cold or warm start conditions on the VOC composition was determined by the difference of the emission obtained during the cold 15xIUFC and hot 15xIUFC cycles. Globally, the emission is the most important for the cold 15xIUFC cycle as we can observed on the *Figure 4*. In the case of vehicles with gasoline engine the amount of aromatic compounds are 4.2 times more important in a cold start than a warm one, alkanes are twice more, alkenes 2.8, light substituted alkanes 3.1, and carbonyls compounds are emitted in the same proportion. For the diesel engine, the amount of aromatic compounds are in average 2.2 time more important in a cold start than a warm one, alkanes in average 1.5 more, alkene in average 1.6, and carbonyls compounds in average 1.18 time more important. Concerning the alkanes, the variation from cold to hot start is more important for the gasoline passenger cars than for the diesel ones. Hydrocarbons with more than sixteen carbons were identified and quantified on the hot 15xIUFC cycle for diesel engine, i.e. nonadecane ( $22.1 \text{ mg km}^{-1}$ ), octadecane ( $13.4 \text{ mg km}^{-1}$ ) and heptadecane ( $9.4 \text{ mg km}^{-1}$ ). Those compounds are not found in the emissions of gasoline passenger cars. During the cold start phase, the aromatic compounds and alkenes are emitted in high proportion compared to the warm start phase with gasoline and diesel cars. The total VOC emission factor for the cold start is higher for gasoline vehicles ( $7.2 \text{ g km}^{-1}$ ) compared to diesel ones ( $0.88 \text{ g km}^{-1}$ ).

### **3.4 Influence of the emission standard**

All the vehicles are characterised by an emission standard regulation. The regulation follows the European standard. The gasoline vehicles comply with Euro 1 to Euro 3 standard, the diesel ones with ECE1504 to Euro 3. In the case of gasoline engine, when we compared the different standards we noticed that the emission factors of aromatic compounds decreased



from Euro 1 to Euro 3 for “VP” urban and motorway driving cycles, which is the contrary of the cold start behaviour (*Figure 5*). In the case of diesel engines the emission factors for the same category of compounds are going up and down , i.e. for the cold 15xIUFC cycle the emission factor of aromatics compounds are for ECE1504, Euro 1, Euro 2 and Euro 3 resp. 0.75, 0.08, 2.25 and 0.75 g km<sup>-1</sup>. For all driving cycles the highest emission is generally observed in Euro 2 standard, this for all families of compounds detected. The *Figure 6* shows the evolution of the different compounds according to the European standard during the “VP” urban and motorway driving cycles. In the case of aldehydes, a decrease of the emission factors from ECE1504 to Euro 3 technology for gasoline and diesel fuel cars was observed. Alkanes have the same behaviour for the gasoline car but the emission increase with the standard for diesel cars and alkanes with a chain length up to 15 carbons increase too. For the others species, the evolution of emission factors with the regulation was not clearly defined, the figures were going up and down.

### **3.5 Perspective of the project**

After the evaluation of the different unregulated compounds, the result of the analysis will served to establish a database of representative emission factors for different European passenger car classes. This database could have a lot of application for the atmospheric pollution. Certain species are more polluting as much in terms of toxicity as in ozone formation potential.

In terms of toxicology, U.S EPA have established a list of Mobile Source Air transport compounds composed with the following species : acetaldehyde, acrolein, benzene, 1,3 butadiene, ethylbenzene, formaldehyde, n-hexane, toluene, xylene. The European data base will allow to improve the knowledge of these compounds, which were detected and measured in different driving cycles.

The impact of the different compounds on the ozone formation potential could be evaluated. and the data base could be used for atmospheric modelling. The ozone formation potential could be evaluated by a reactivity scale like the MIR (Maximum Incremental Reactivity)

(Carter, 1994). Applied under optimal California weather conditions which differ from the usual European climatic conditions, however, this potential can be used as an indicator for comparing the impact of the individual VOC emissions on the ozone formation for various types of vehicles. For the Artemis project, we can evaluate the major compounds by family able to produce ozone:

- Aldehyde: formaldehyde ( $< 0,035 \text{ g O}_3 / \text{g VOC}$ ), acrolein ( $0,015 \text{ g O}_3 / \text{g VOC}$ ) and acetaldehyde ( $0,04 \text{ g O}_3 / \text{g VOC}$ ).
- Alkene and Alkyne : cis -2- butene, 1-pentene and trans-2-butene
- Alkane: undecane, tetradecane, tridecane, nonane, dodecane, decane and isobutane.
- Aromatics : m- and p- xylene, 2-, 3-, 4- ethyltoluene, 1,3,5 trimethylbenzene and 1,2,4 trimethylbenzene.

With our measurements, the “VP” urban driving cycle and the cold urban start produced a lot of ozone. This study could be a preliminary step for atmospheric modelling, with the purpose to investigate its influence on the tropospheric ozone formation.

## **Conclusions**

The unregulated emissions of various vehicles representing the 2001 French passenger car fleet were measured on real-world driving cycles. Combining the three sets of speciation data provided a profile of the gas phase hydrocarbons emissions for gasoline and diesel fuel. The emission factors were determined for all the species and for the different driving cycles. The results show the influence of the specific conditions of each driving cycle and the impact of new technology on the global emission. Whatever the driving cycle is, the decrease of unit emissions from Euro 1 to Euro 3 standards is almost systematic for aromatic compounds; Diesel vehicles always appear less polluting than gasoline ones. The comparison between cold and hot starts was performed in order to study more precisely the impact of the automotive VOC emissions in an urban site. In the next future the database will be used for atmospheric modelling, with the purpose to see the influence on the ozone formation.

All these data are currently processed again but with all emission measurements of unregulated pollutants carried out or collected within the Artemis project, in order to derive the emission factors of these pollutants in the next European Artemis inventorying tool for the transport means, which should be available by Spring 2005.

### **Acknowledgements**

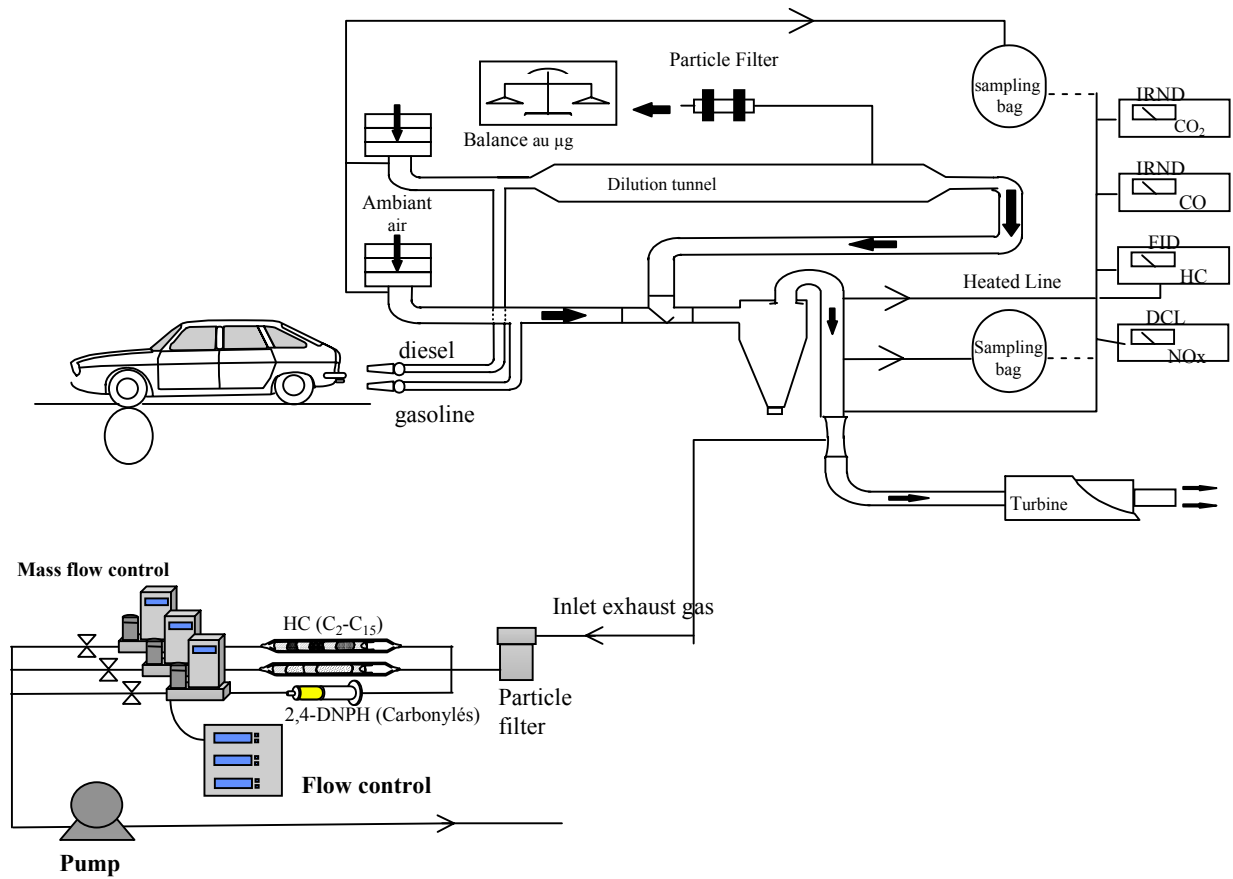
This study was carried out within the 5<sup>th</sup> framework programme of the European Community with the Artemis project concurrently supported by ADEME, the French environment agency.

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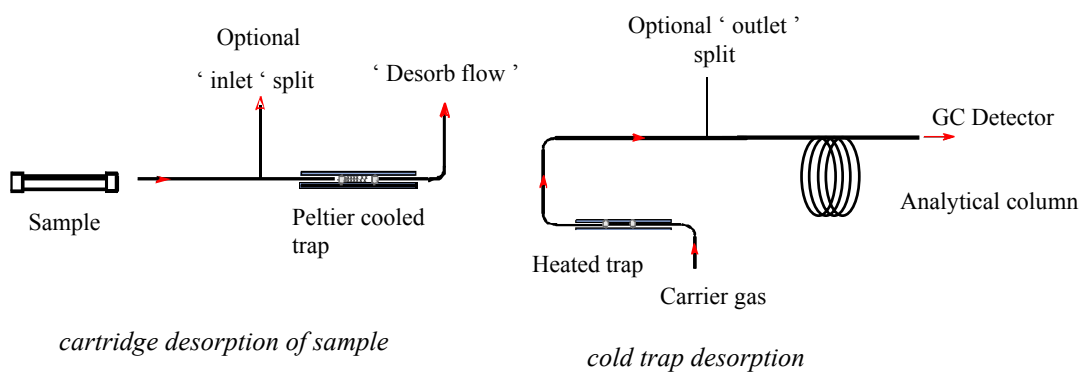
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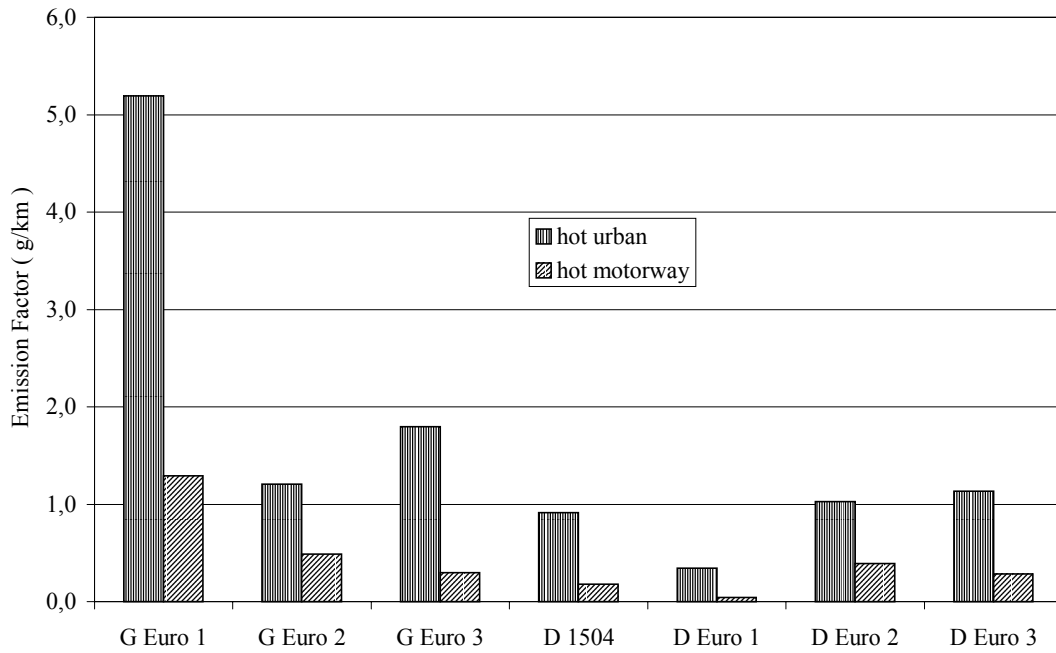
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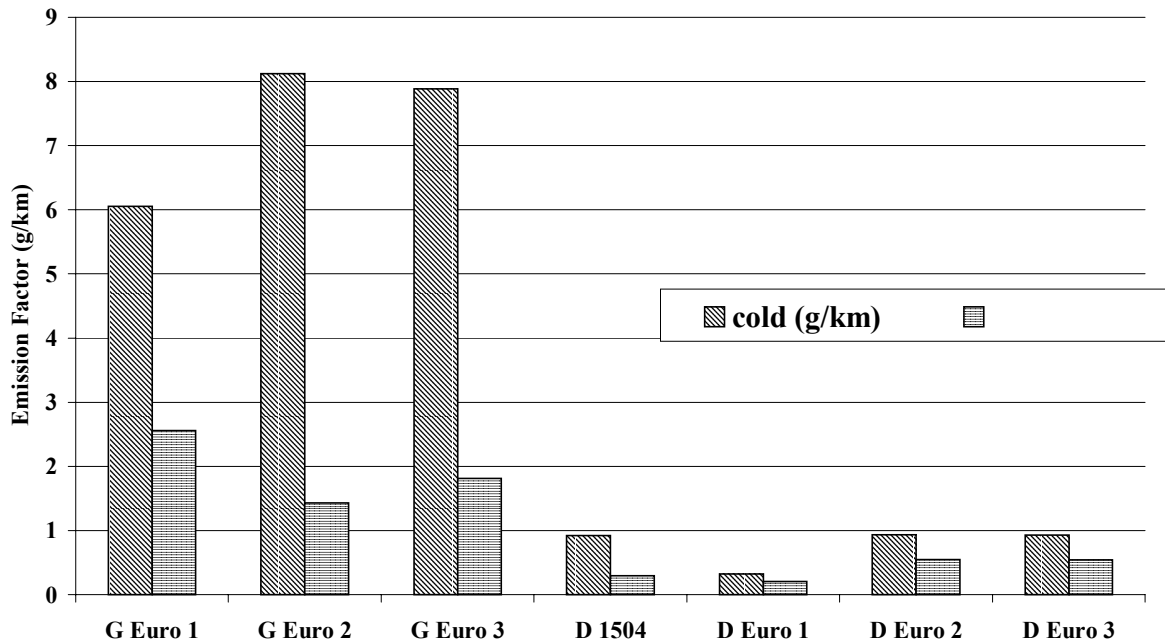
**Figure 1. Chassis dynamometer with Constant Volume Sampling (CVS) with the scheme of the analysis for unregulated compounds.**



**Figure 2 : Thermodesorption of cartridge follow by GC/FID analysis.**



**Figure 3: Average emission factors of the sum of VOC for hot “VP” urban vs motorway driving cycles (g km<sup>-1</sup>).**



**Figure 4: Average emission factors of the sum of VOC for cold vs hot 15xIUFC driving cycles (in g km<sup>-1</sup>).**

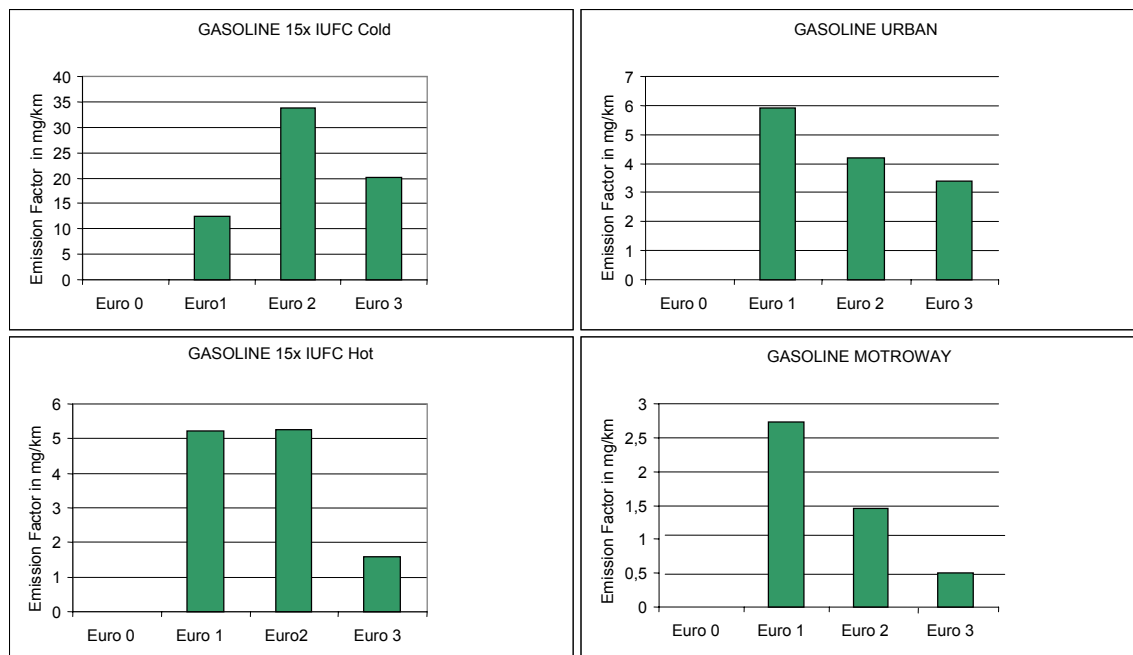


Figure 5: Emission factors of the aromatic compounds according to the European emission standard and the driving cycle for gasoline cars.

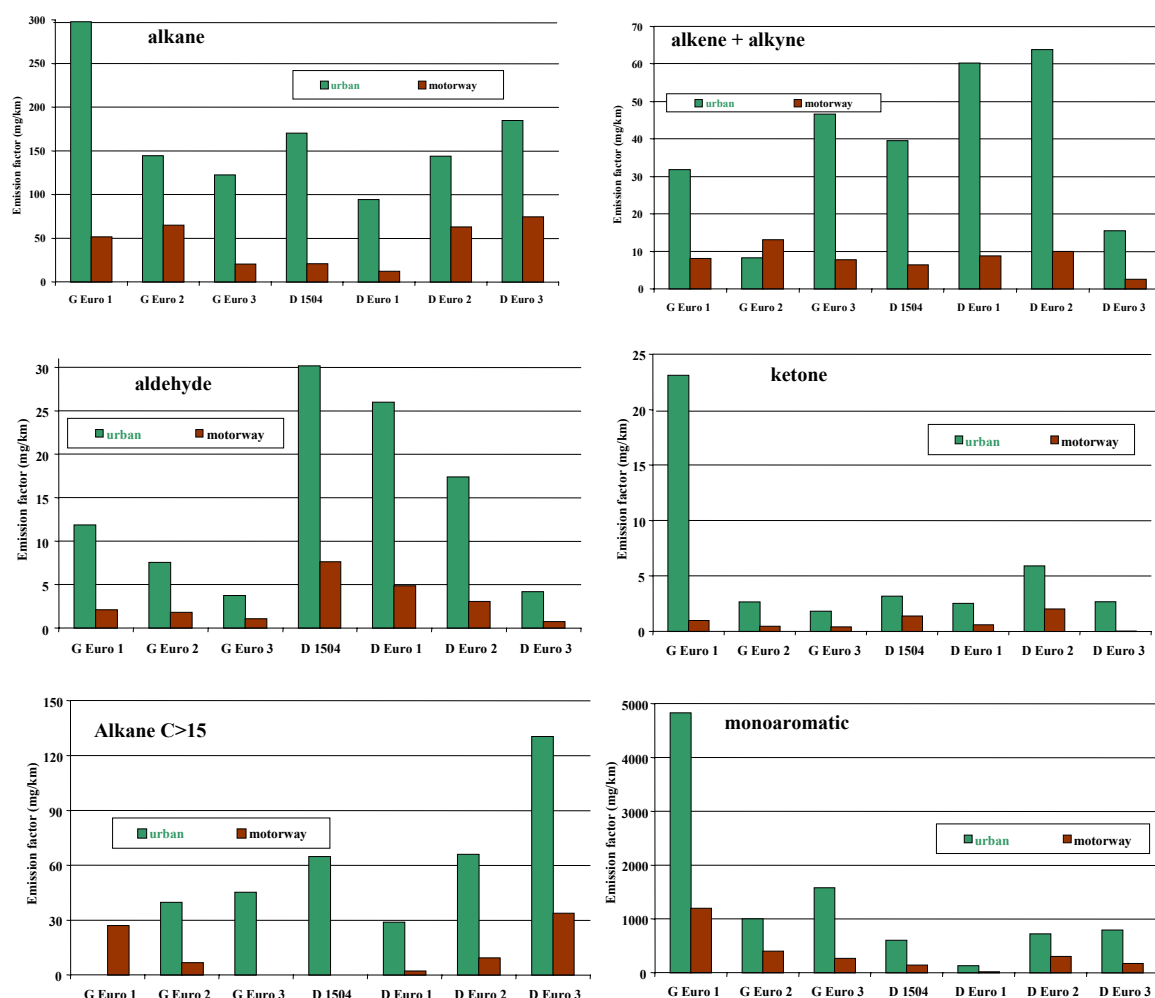


Figure 6: Evolution of the emission for the different compound families during "VP" urban and motorway driving cycles.

**Table:****Table 1: Distribution per fuel and emission standard of the sample of vehicles.**

Sample		Number of vehicles
Gasoline	Euro 1	3
	Euro 2	6
	Euro 3	4
	<b>Total</b>	<b>13</b>
Diesel	ECE 1504	2
	Euro1	3
	Euro 2	10
	Euro 3	2
	<b>Total</b>	<b>17</b>

**Table 2. The features of the driving cycles.**

Driving cycle	Duration (sec)	Length (m)	Mean speed (km h <sup>-1</sup> )	Max. speed (km h <sup>-1</sup> )	Condition
15xIUFC	2835	14 985	19.037	44	Cold, urban
15xIUFC	2835	14 985	19.037	44	Hot, urban
VP low / high mot. urban	945 / 918	4 799 / 4 924	18.3 / 19.3	55.7 / 57.6	Hot, urban
VP low / high mot. motorway	729 / 750	24 090 / 25 377	119.0 / 121.8	150.7 / 157.1	Hot, motorway

**Table 3: Flow rate sampling on the cartridges:**

Type of Cartridge	Tenax	Carbotrap	Carbotrap	2,4 DNPH	2,4 DNPH
Driving Cycle	All types of cycles	15xIUFC	VP	15xIUFC	VP
Flow rate ml min <sup>-1</sup>	From 300 to 75	From 100 to 25	100	From 1200 to 600	1200



**Table 4 : Conditions for speciated analysis of hydrocarbon emissions**

Desorption conditions	TurbomatrixTD	Combi Injector / desorberEM640Brüker
Cartridge temperature	250°C	220°C
Desorption time	7.5min	5min
Cold trap temperature	-30°C to 300°C (hold 1min)	
Transfer line temperature	200°C	

GC conditions	Autosystem Perkin Elmer	EM640 Brüker
Column type	RT Alumina Restek	DB5
Column dimensions	(50m x 0.53 x 1µm)	(25m x 0.32 x 0.25µm)
Carrier gas type	Nitrogen	nitrogen
Column head pressure	8 psi	0,3bar
Detector type	FID	Mass (40-300 u.m.a.)
Detector temperature	250°C	200°C
Transfer line temperature	200°C	
Injector temperature		200°C
Connector temperature		200°C

Column oven temperature program :

Initial temperature of	35°C (hold 5min)	35°C (hold 5min)
Increase	5°C min <sup>-1</sup> to 110°C	5°C min <sup>-1</sup> to 220°C
(hold 20 min)		
Increase	10°C min <sup>-1</sup> to 200°C (hold 40 min)	

**Table 5 : Compounds identified by GC/FID in the exhaust gas**

1-butene	cis-1,2 dimethylcyclohexane	hexane
1-pentene	trans-1,2 dimethylcyclohexane	isobutene
cis-2-butene	cis-1,4 dimethylcyclohexane	isopentane
ethene	trans-1,4 dimethylcyclohexane	n-butane
ethane	2,2- dimethylpropane	n- heptane
hexene	2-methylpentane	n-pentane
propene	2-methylpropane	propane
trans-2-butene	3-methylpentane	2,2 -dimethylbutane
acetylene	cyclohexane	

**Table 6: Compounds identified by GC/MS in the exhaust gas**

1,2,3,5 tetramethylbenzene	tridecane	pentadecane
1,2,4,5 tetramethylbenzene	1-methyl-3-propylbenzene	tetradecane
1,2,4 trimethylbenzene	n-undecane	n-octane
1,2,5 trimethylbenzene	2-ethyltoluene	benzene
1,3 diethylbenzene	3-ethyltoluene	ethylbenzene
1,3 –dimethyl-4-ethylbenzene	4-ethyltoluene	isobutylbenzene
1,4 diethylbenzene	n-decane	propylbenzene
1,4 –dimethyl-2-ethylbenzene	n-dodecane	tert-butylbenzene

<b>1-methyl-2-isopropylbenzene</b>	<b>n-hexadecane</b>	<b>toluene</b>
<b>1-methyl-4-isopropylbenzene</b>	<b>isopropylbenzene</b>	<b>1-methylnaphtalene</b>
<b>1-methyl-2-propylbenzene</b>	<b>m-xylene + p-xylene</b>	<b>2-methylnaphtalene</b>
<b>n-nonane</b>	<b>o-xylene</b>	<b>naphtalene</b>

**Table 7: Conditions for speciated analysis of carbonyls compounds**

<b>Solvents</b>	<b>Water</b>	<b>Acetonitrile</b>	<b>Tetrahydrofuran</b>	<b>Time</b>
<b>Initial gradient elution</b>	<b>44</b>	<b>35</b>	<b>21</b>	<b>Hold 17 min</b>
<b>Lineary increase</b>	<b>24</b>	<b>55</b>	<b>21</b>	<b>Over 2min</b>
<b>Lineary increase</b>	<b>44</b>	<b>35</b>	<b>21</b>	<b>Over 1min</b>
<b>Final gradient elution</b>	<b>44</b>	<b>35</b>	<b>21</b>	<b>Hold 5 min</b>

**Table 8: Carbonyl compounds identified by HPLC in the exhaust gas with their minimum concentration**

<b>Compounds</b>	<b>Limit of detection (ng cartridge<sup>-1</sup>)</b>
<b>Formaldehyde</b>	<b>5</b>
<b>Acetaldehyde</b>	<b>6</b>
<b>Acetone</b>	<b>8</b>
<b>Acrolein</b>	<b>6</b>
<b>Propionaldehyde</b>	<b>8</b>
<b>crotonaldehyde</b>	<b>9</b>
<b>2-Butanone</b>	<b>11</b>
<b>Methacrolein</b>	<b>8</b>
<b>Butyraldehyde</b>	<b>10</b>
<b>Benzaldehyde</b>	<b>13</b>
<b>Valeraldehyde</b>	<b>12</b>
<b>p-tolualdehyde</b>	<b>14</b>
<b>Hexaldehyde</b>	<b>9</b>

**Tableau 9: Minimum concentration for VOC**

<b>Compounds</b>	<b>Limit of detection ng cartridge<sup>-1</sup></b>	<b>Methods</b>
<b>Ethane to n-pentane</b>	<b>5 to 15</b>	<b>GC /FID</b>
<b>1 pentene to 1,4-dimethylcyclohexane cis</b>	<b>10</b>	<b>GC /FID</b>
<b>Aromatics</b>	<b>3 to 12</b>	<b>GC /MS</b>
<b>Alkanes from C<sub>7</sub> to C<sub>15</sub></b>	<b>25</b>	<b>GC /MS</b>

**Tableau 10: Distribution of the different compounds for gasoline and diesel vehicles:  
Emission factor in mg km<sup>-1</sup>**

	15xIUFC	15xIUFC	VP urban	VP mway	15xIUFC	15xIUFC	VP urban	VP mway
	cold	hot	hot	hot	cold	hot	hot	hot
	13 gasoline vehicles				17 diesel vehicles			
aldehyde	6,7	5,2	1,2	0,3	19,6	17,3	2,1	0,4
ketone	1,7	2,5	6,4	0,1	3,7	3,1	8,0	0,7
alkene alkyne	93,1	33,4	10,8	3,1	34,7	16,5	0,0	1,2
alkane	447,0	213,4	16,3	5,3	135,9	108,0	7,6	2,5
alkane C>15	8,4	2,7	20,8	8,1	27,9	44,9	17,8	4,1
monoaromatic	6643,6	1574,8	273,2	55,9	664,5	325,6	43,7	13,5
polyaromatic	0,0	0,0	0,0	0,1	1,9	1,2	1,7	0,0
<b>TOTAL VOC</b>	<b>7200,5</b>	<b>1832</b>	<b>328,7</b>	<b>72,9</b>	<b>888,2</b>	<b>516,6</b>	<b>80,9</b>	<b>22,4</b>

### Figures Captions:

Figure 1. Chassis dynamometer with Constant Volume Sampling (CVS) with the scheme of the analysis for unregulated compounds

Figure 2 : Thermodesorption of cartridge follow by GC/FID analysis.

Figure 3 : Average emission factors of the sum of VOC for hot “VP” urban vs motorway driving cycles ( $\text{g km}^{-1}$ ).

Figure 4 : Average emission factors of the sum of VOC for cold vs hot 15xIUFC driving cycles (in  $\text{g km}^{-1}$ )

Figure 5: Emission factors of the aromatic compounds according to the European emission standard and the driving cycle for gasoline cars.

Figure 6. : Evolution of the emission for the different compound families during “VP” urban and motorway driving cycles.

### Tables:

Table 1: Distribution per fuel and emission standard of the sample of vehicles.

Table 2. The features of the driving cycles

Table 3: Flow rate sampling on the cartridges

Table 4 : Conditions for speciated analysis of hydrocarbon emissions

Table 5 : Compounds identified by GC/FID in the exhaust gas

Table 6: Compounds identified by GC/MS in the exhaust gas

Table 7: Conditions for speciated analysis of carbonyls compounds

Table 8 : Carbonyl compounds identified by HPLC in the exhaust gas with their minimum concentration

Tableau 9: Minimum concentration for VOC

Tableau 10: Distribution of the different compounds for gasoline and diesel vehicles: Emission factor in  $\text{mg km}^{-1}$