2.2.3 VOC-Split of gasoline and diesel passenger cars

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2.2.3.1 Introduction

The **V**olatile **O**rganic **C**ompounds (VOC) in the atmosphere comprise many different species with various properties. Some of these compounds directly influence human health due to their toxicity. VOC are also important precursors of photochemically formed secondary pollutants like ozone. Since the individual VOC react with different rates and different mechanisms, they also differ in their contribution to photochemical ozone formation. For the development of efficient abatement strategies to lower the VOC emissions in order to improve air quality in urban areas with regard to direct toxic effects or photochemical air pollution, reliable data of VOC are required.

The emission factors of the total VOC from road traffic are known (Hassel et al. 1994; De Vlieger 1996; Lenaers 1996), but for typical European in-use passenger cars there are only few data concerning the VOC composition on the basis of measurements of individual cars (Bailey et al. 1990; Hoekman 1992; Jemma et al. 1995; Rijkeboer and Hendriksen 1993; Siegl et al. 1999). Another approach to obtain emission data from road traffic is to perform measurements at roadsides or in street tunnels (Pierson et al. 1996; Staehelin et al. 1998). The main issue of these studies was the evaluation of existing emission factor models for specific traffic situations rather then the extension of those models by emission factors of individual VOC.

In recent years new methods based on chassis dynamometer studies for determining emission data of motor vehicles have been developed (Hassel et al. 1994). From these data the dependence of the emissions of VOC, CO and NO_x on the driving behaviour is known. In a recent study (Schmitz et al. 1999, 2000) the dependence of the VOC-composition on different driving situations was investigated. Also the influence of cold-/ warm-conditions was quantified. The principle results concerning VOC are presented here.

2.2.3.2 Experimental

Vehicles and driving conditions

The measuring program included 15 different passenger cars. Three engine types were investigated: petrol driven cars equipped with a fuel injection system and a closed-looped controlled three-way-catalyst (TWC), petrol driven cars without any catalyst and cars with diesel engines. Five cars of each engine type were measured. Three of the cars with diesel engines were equipped with oxidative catalytic converters, one with a direct fuel injection.

The emission measurements were performed on the chassis dynamometer of TÜV Rheinland. A detailed description of the test facility is given in Hassel et al. (1994). The measurements were carried out under the conditions of the United States Federal Test Procedure (US FTP-75) and the "Autobahn" test are presented in Fig. 2.4.

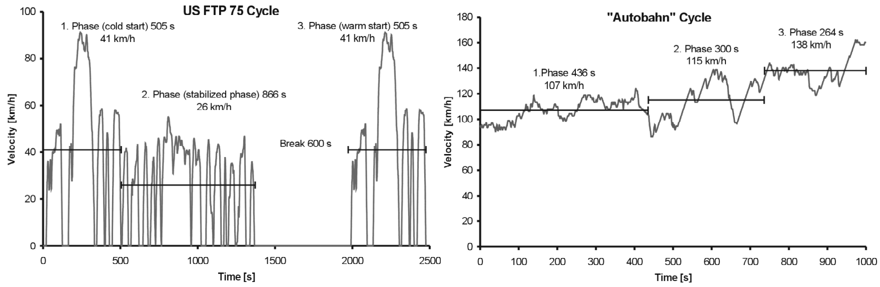

Fig. 2.4. Driving pattern of the US FTP-75 cycle and the "Autobahn"-cycle.

The FTP test is divided into three phases. The test begins with a cold start. Therefore, the cars are pre-conditioned at 20 °C over a period of 12 hours. In the first test phase an average speed of 41 km/h is driven. In the second test phase the average speed is only 26 km/h. After the second test phase the engine is shut off for 10 minutes and then the test continues with a warm start. The driving pattern of this third phase is identical with the driving pattern in the first phase. By comparing the emissions obtained in the first and in the third test phase, the effects caused by the cold start procedure can be derived from the data.

The "Autobahn"-cycle was developed by TÜV Rheinland. This cycle represents driving behaviour on German motorways. Again this cycle consists of three phases. From phase one to phase three the average velocity is increasing. In the third phase of the test cycle the cars have to accelerate from 127 km/h to the maximum speed of 162 km/h in 40 seconds. Under these conditions most of the cars tested in this program were running at their limits. The respective emissions represent high engine loads which are not covered in the US FTP-75.

2.2.3.3 Sampling and analysis

The exhaust gas is diluted by a factor of 10 – 15 with filtered ambient air using a constant volume sampler (CVS) device and sampled in glass vessels. The use of Tedlar bags is unfavourable due to substantial blank values for some hydrocarbons (Schmitz et al. 2000). For the measurement of the C_2 – C_{10} hydrocarbons a GC-FID (HP 5890A) and a specially designed sampling device was used (Schmitz et al. 1997). The sampled air passes a cooling trap at –25 °C for removal of water before being sucked through a sample loop, which is kept at about –190 °C. When sampling is completed, the sample loop is heated up to 80°C and the hydrocarbons are injected on the capillary column (DB-1; 90 m x 0.32 mm x 3 µm). Temperature program: –50 °C / 2 min @ 5 °C/min → 200 °C / 15 min. A chromatogram taken from a car with TWC in the first phase of the US FTP-75 is shown in Fig. 2.5.

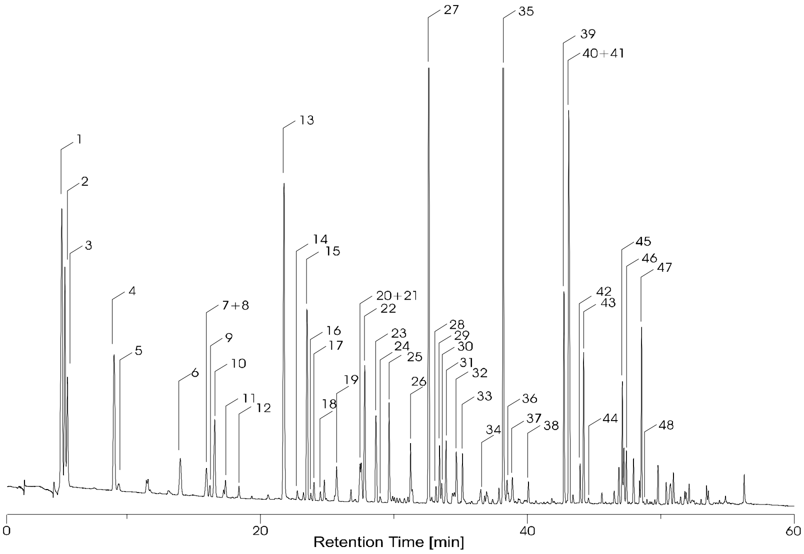

Fig. 2.5. Chromatogram taken from a TWC-vehicle: 1=ethene; 2=ethyne; 3=ethane; 4=propene; 5=propane; 6=i-butane; 7/8=i-/1-butene; 9=1,3-butadiene; 10=n-butane; 11=trans-2-butene; 12=cis-2-butene; 13=i-pentane (coelution with acetone); 14=1-pentene; 15=n-pentane; 16=isoprene; 17=trans-2-pentene; 18=cis-2-pentene;19=2,2-dimethylbutane; 20/21=cyclopentane/2,3-dimethybutane; 22=2-methylpentane; 23=3-methylpentane; 24=1-hexene; 25=n-hexane; 26=2,4-dimethylpentane; 27=benzene; 28=cyclohexane; 29=2-methylhexane; 30=2,3-dimethylpentane; 31=3-methylhexane; 32=i-octane; 33=n-heptane; 34=methylcyclohexane; 35=toluene; 36=2-methylheptane; 37=3-methylheptane; 38=n-octane; 39=ethylbenzene; 40/41=m-/p-xylene; 42=styrene; 43=o-xylene; 44=n-nonane; 45=n-propylbenzene; 46=1,3,5-trimethylbenzene; 47=1,2,4-trimethylbenzene; 48=n-decane.

2.2.3.4 Results

VOC-composition

The relative composition of the VOC measured for the different engine types is shown in Fig. 2.6. In order to get a better overview the single compounds were grouped into five substance classes.

The relative VOC pattern obtained from the TWC cars shows strong variations depending on the different test phases. Under cold start conditions, the VOC pattern is dominated by aromatic compounds followed by the alkanes and the alkenes. In the corresponding warm phase (US FTP-75 phase 3) the VOC pattern is changing completely. The more reactive alkenes and aromatic compounds are reduced more efficiently. Therefore, the main fraction of the VOC is given by the alkanes, a fact which also is reported in an Australian study (Duffy et al. 1999). At higher average velocity, the fraction of alkenes and aromatics is increasing continuously. In the last phase of the "Autobahn" cycle the aromatic fraction nearly reaches 60% of the VOC pattern. This again is due to the effect of rich air/fuel mixtures which are injected under high load conditions existing in the "Autobahn" cycle. Therefore, conversion efficiency of the catalyst for the hydrocarbons is diminished as described above. This effect leads to an overall increase in total hydrocarbon emission (Schmitz et. al. 2000)) and to a change in the VOC pattern especially in the third phase of the test cycle.

The VOC-patterns of cars without exhaust treatment undergo only minor changes. The pattern measured in the cold start phase is nearly identical to that obtained in the warm phase. Only at higher average speed a slight increase of the alkenes and hence a slight decrease of the alkane compounds is observed.

Alkenes are by far the largest fraction of hydrocarbons emitted from cars with diesel engines, although it has to be mentioned that diesel engines also emit considerable amounts of carbonyl compounds (Schmitz et al. 2000). A similar VOC fraction in the exhaust gas of in-use light-duty diesel vehicles was also found in other studies (Rijkeboer and Hendriksen 1993; Siegl et al. 1999). Diesel cars have the only engine type where alkynes play an important role; here their fraction is even larger than the fraction of alkanes.

The measured mass emissions in mg/km of the VOC grouped in different substance classes and the mean confidence levels (95% significance) calculated for the small number of vehicles (5 cars of each engine type) are given in Table 2.3 and Table 2.4. Detailed results for the individual compounds are given in Schmitz et al. (1999).

The mean values of the individually measured VOC show large confidence levels of about 80%. In the US FTP-75 the confidence levels are smaller than that calculated for the "Autobahn" cycle. The confidence intervals which were found for the mean values of the TWC cars and cars with diesel engines are significantly higher than that for cars without exhaust gas treatment. The large scatter is due to the small number of cars of each engine type and due to differences in the mass emissions because of vehicle age, standard of maintenance and type of manufacture.

Table 2.3. Emission rates of VOC measured in the different phases of the US FTP-75.

Substance	US FTP-75 phase 1		US FTP-75 phase 2		US FTP-75 phase 3	
	Mean emission [mg/km]	95% Confidence level [%]	Mean emission [mg/km]	95% Confidence level [%]	Mean emission [mg/km]	95% Confidence level [%]
Gasoline cars with TWC						
Alkanes	130.2	58	5.5	72	18.8	41
Alkenes	62.6	70	0.4	85	1.9	74
Alkynes	21.0	81	0.0	72	0.1	84
Aromatics	250.8	63	2.9	64	10.2	68
Gasoline cars without TWC						
Alkanes	662	29	651	51	568	49
Alkenes	344	33	341	38	292	40
Alkynes	139	30	101	34	77	24
Aromatics	1267	28	1138	35	976	34
Diesel Cars						
Alkanes	8.2	65	7.9	74	5.2	63
Alkenes	44.4	47	35.4	52	20.2	63
Alkynes	8.8	61	5.9	70	4.2	73
Aromatics	9.1	49	7.5	46	4.6	48

Table 2.4. Emission rates of VOC measured in the different phases of the Autobahn cycle.

Substance	Autobahn phase 1		Autobahn phase 2		Autobahn phase 3	
	Mean emission [mg/km]	95% Confidence level [%]	Mean emission [mg/km]	95% Confidence level [%]	Mean emis-sion [mg/km]	95% Confidence level [%]
Gasoline cars with TWC						
Alkanes	18.0	79	11.8	63	28.8	70
Alkenes	4.2	83	7.5	83	60.7	96
Alkynes	0.1	70	0.2	119	0.9	103
Aromatics	16.7	74	18.8	81	129.5	71
Gasoline cars without TWC						
Alkanes	215	40	259	38	225	52
Alkenes	293	50	367	67	503	70
Alkynes	86	32	119	36	176	34
Aromatics	580	43	724	51	847	70
Diesel Cars						
Alkanes	1.6	77	1.5	82	1.2	103
Alkenes	6.5	103	8.1	93	9.4	104
Alkynes	1.7	109	2.3	105	4.3	110
Aromatics	1.9	73	2.2	79	3.0	116

It was found that the sum of the identified VOC and the corresponding THC measurements agree better than 20% (Schmitz et. al. 1999). Therefore, a normalisation of the VOC composition to the measured THC was performed resulting in smaller confidence intervals than for the mass emissions. In principle, the normalized VOC patterns can be adapted to existing emission factors of THC which are available for a large number of driving situations. However, it has to be carefully studied to which extend the driving patterns of the investigated test phases are representative for real word driving.

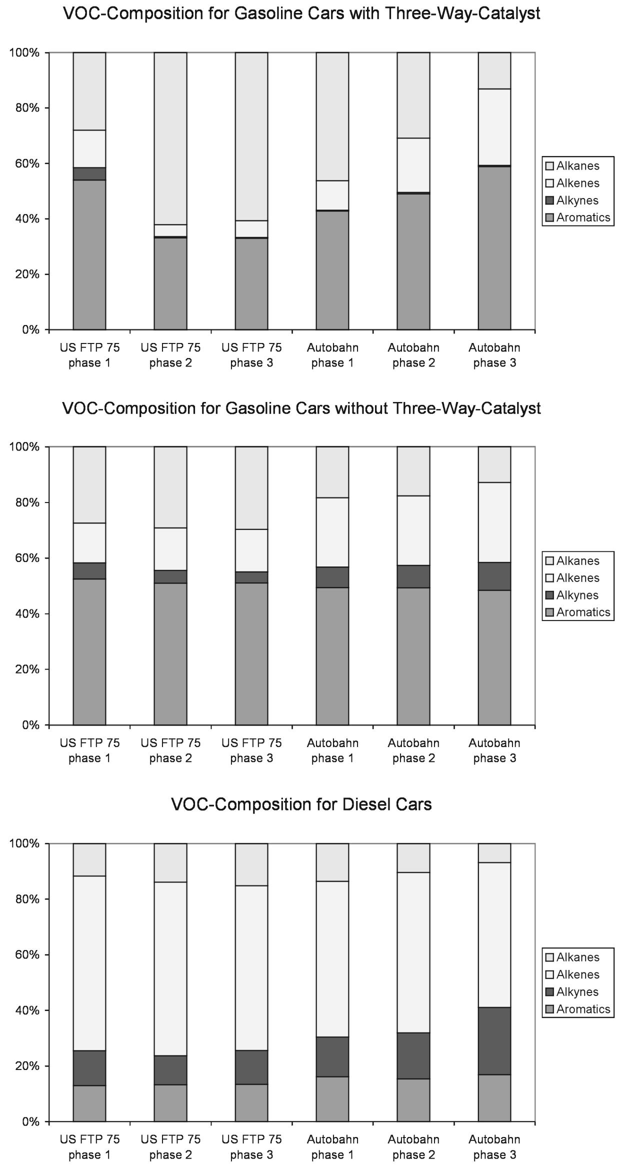

Fig. 2.6. VOC pattern obtained for the three vehicle categories for all phases of both cycles.

Ozone Formation Potential (OFP)

In order to assess the measured VOC emissions concerning the photochemical ozone production, the **O**zone **F**ormation **P**otential (OFP) using the method by Carter (1994) was calculated for the different engine types. This method is based on a model scenario in which ozone formation is calculated under optimum conditions: i.e. high solar fluxes and a base scenario with VOC/NO_x-ratios which yield a maximum ozone formation. For single hydrocarbons a **M**aximum **I**ncremental **R**eactivity (MIR) can be determined in terms of grams ozone formed per gram hydrocarbon added to the scenario. The OFP of a certain VOC mixture is calculated by summing up the products of measured VOC concentrations and corresponding MIR factors:

$$OFP = \sum_i VOC_i \cdot MIR_i \tag{2.2}$$

It is important to note that these conditions represent typical California conditions and are significantly different from typical summertime conditions in Central Europe. Nevertheless, for just a mere ranking of VOC mixtures with regard to ozone production these MIR-factors are very useful.

When calculating the ozone forming potential for the 5 phases with warmed-up engines, a speed dependency can be derived (see Fig. 2.7). As expected, the highest ozone formation potential is observed for cars without catalyst due to the highest mass emission of THC in connection with a high share of reactive substances like alkenes and aromatics.

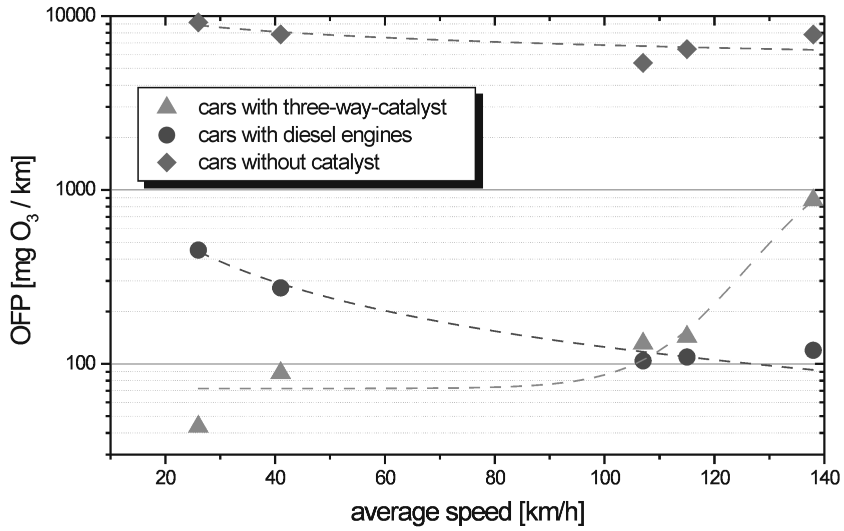

Fig. 2.7. Ozone formation potential as function of mean speed in different test phases. Note the logarithmic scale. The fitted lines only show trends between OFP and mean velocity.

The ozone formation potential for the TWC cars is found to be up to two orders of magnitude lower than for cars without catalyst and is increasing with increasing speed. The low values in the ozone formation potential at moderate speeds are caused by the high efficiency of the catalysts resulting in low mass emissions of THC and low emissions of reactive hydrocarbons. The efficiency of the catalyst decreases with higher average velocities. At an average speed of 140 km/h there is an increase of the ozone formation potential of a factor of 200 compared to the OFP values calculated for low average speed.

In contrast, the OFP of the diesel cars decreases with increasing speed. Highest OFP values are observed at moderate speed, whereas lowest OFP values are found in the Autobahn cycle. This dependency is caused by the fact that the mass emissions of diesel cars are continuously decreasing with increasing mean speed (Schmitz et al. 2000) without major changes in the reactivity of the VOC composition.

2.2.3.5 Summary and conclusions

The VOC compositions of three different engine types were measured under conditions of the US FTP-75 and the „Autobahn"-test cycle. The variations of the VOC compositions in the different phases observed for gasoline cars without catalysts and diesel cars are moderate. For the cars with three-way-catalyst there is a strong dependency of the VOC composition on the operating conditions of the engine and the temperature of the catalyst. There is a large change in the VOC-pattern from cold start phase to the phases with warmed-up engine. A significant change can be observed at high engine loads and high speeds compared to moderate driving conditions with warmed-up engines.

The resulting OFP of the VOC emissions shows a dependency with respect to the average speed. Especially for cars with three-way-catalysts the speed dependency of the OFP has to be taken into account. In this context it should be stressed that there is a lack of information with regard to traffic situations like stop and go or other relevant parameters like road inclination.

Using the emission results of this study it should be mentioned that the measurements are based on mean market fuels in Germany of the reference year 1997. It is known that VOC composition and therefore OFP will change (Decker et al. 1996) when fuel composition is significantly modified.

2.2.3.6 Acknowledgement

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