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Trapping Efficiency for solid Particles ... and the Volatiles?

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Trapping Efficiency for Solid Particles ... and the Volatiles?

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Objective

The VERT[1] Project set the pragmatic task of finding, within 3 years, effective methods for curtailing diesel engine pollutant emissions. These methods must be feasible for immediate implementation at the work place and for off-road applications.

The prescribed MAK (maximum workplace concentration) limits, for pollutants in respiratory air, dictated the priorities. The following table compares the average emission values of off-road Diesel engines, according to the Swiss off-road inventory [1].

	Gases				Aerosols [5]	
mg/Nm^3	CO	NO	NO_2	SO_2	PM=EC + OC	H_2SO_4
Emissions [7]	1000	2700	300 [1]	100	250 [2]	25 [6]
Immission Limits MAK						
Switzerland	35	30	6	5	0.2 (TC) [3]	1
Germany					0.1 (EC) [4]	1
MSHA 1998					0.16 proposed	
MSHA 2003					0.05 proposed	
Dilution required	> 28	> 90	> 50	> 20	> 1000	> 25

1) fraction NO/NO_2 estimated
2) about 80% carbonaceous particle mass
3) Total Carbon (TC) = Elementary Carbon (EC) + Organic Carbon (OC)
4) Elementary Carbon as per TRGS 554, status 97
5) Size < 5 μm (settling velocity < 1.25 m/s)
6) SAE 1999-01-0116
7) According to Swiss off-road Inventory [1]

Table 1: Required dilution = Emission / Immission permissible

The table shows that the standard dilution (approx. 40) at workplaces can decrease the gaseous pollutants to a tolerable level. The sulfuric acid aerosol, which has its own MAK limit, also does not pose a problem. In contrast, the emission of combustion particles is too high. These must be diminished at the source by a factor 50 to 100. Only thus can the usual dilution attain respiratory air quality. Hence, a total curtailment of 1000 - 4000 is necessary, depending on the limits.

At the workplace, the Diesel combustion aerosol is very well defined. The Johannesburg convention specifies a 50% size limit of 5 μm. The composition is specified, depending on country, as either Total-Carbon TC or Elementary-Carbon EC.

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1 VERT project 1994-1999 for curtailing emissions from Diesel engines at tunnel sites. The promoters are the Swiss (Suva), German (TBG) and Austrian (AUVA) occupational health agencies, together with the Swiss environmental protection agency BUWAL,

Apparently the problem can only be solved with traps having a filtration efficiency of 98 to 99%, depending on the target limit [2]

Filtration efficiency of particle traps

Two urgent questions arose:

- How to define the filtration efficiency of such a trap?
- Which procedure to measure the performance and ultimately certify the available traps?

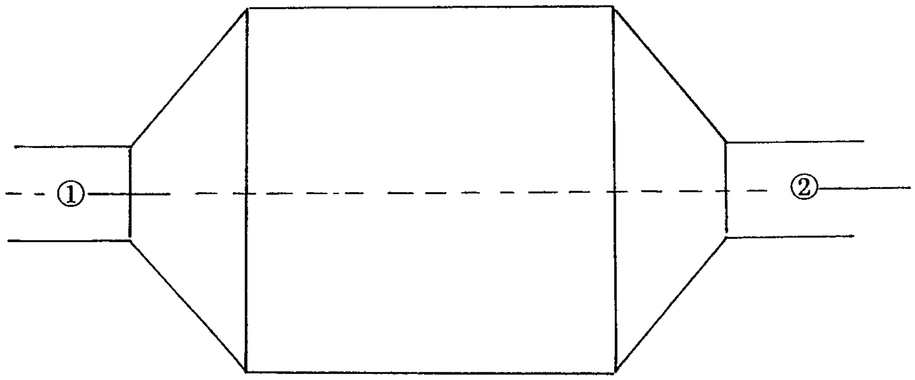


Fig. 1: Definition of the trap filtration rate

Traps can essentially only intercept particles that are not gaseous under flow conditions (temperatures of several hundred degrees C).

There are two possible definitions:

according to mass $$\eta_M = \frac{M_1 - M_2}{M_1}$$

or according to count $$\eta_N = \frac{N_1 - N_2}{N_1}$$

Both definitions are not completely satisfactory.

Mass definition:

- The total mass of the solids?
- The total mass of all substances in the measurement?
- The mass of specific toxic substances?
- Considering the phase change, under what conditions to define the mass?

Similarly, for the particle count:

- The count of all particles?
- The count of measured solid particles?
- The count of toxic particles?
- Definition of the measurement procedure?

Influence of measurement procedure

The following mass-flow diagram illustrates the problem of the measurement procedure:

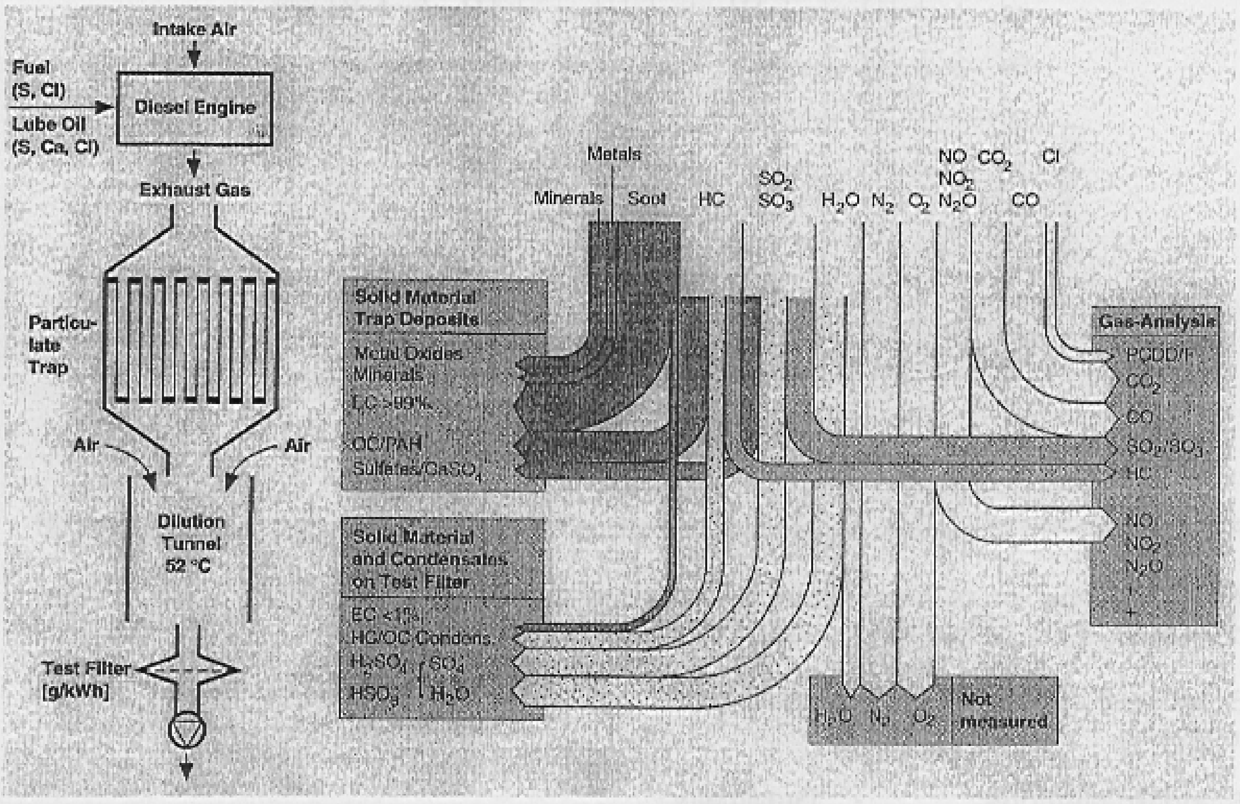


Fig. 2: Mass-flow diagram engine/trap and particle problematic

The trap has only a limited capability of adsorbing gaseous substances, up to a saturation value. Because of its catalytic and surface properties the trap can perhaps change other substances (Dioxin, Furane [3]). The trap mainly intercepts solid particles, i.e. the soot, metal oxides, minerals and sulfates. These solid particles, e.g. the soot, have a very large surface area that can bind other substances, e.g. polycyclic aromatic hydrocarbons. The trap substrate is designed to very efficiently filter and retain such solid particles. The trap could also intercept fluid droplets, however this capability is irrelevant at the high operating temperatures. Traps should only be evaluated for their ability to intercept and retain substances that are solid at the through-flow conditions.

The conventional measurement procedure is inconsistent with the above facts. Instead, the exhaust gases are cooled in the so-called dilution tunnel. Consequently, several substances, e.g. sulfuric and sulfurous acids, hydrocarbons, water vapor, etc. are cooled below their dew point. The resulting condensates are trapped in the downstream measurement filter together with the solid particles. The conventional measurement procedure does not differentiate the substance character.

The sulfur content, of fuel and lubricant, is a particular challenge in evaluating the so-called Diesel particles. This sulfur is oxidized during combustion to SO_2 and, depending on process conditions, further to SO_3. SO_3 strongly influences the exhaust gas dew-point, even at very low concentrations, as shown in the following figure [4].

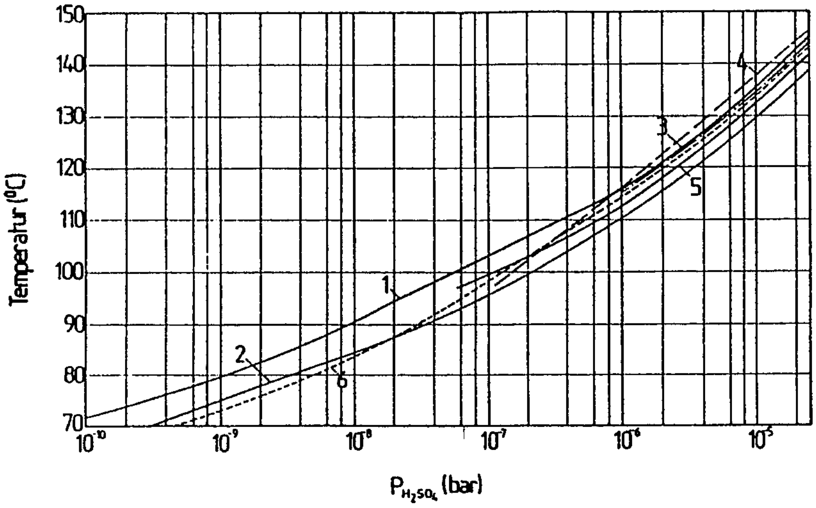


Fig. 3: Dew point of water in exhaust gas influenced by sulfur content and SO_3 formation [4]

A significant portion of the water, plentiful in the exhaust gas, condenses as droplets. These deposit as highly diluted sulfuric acid on the measurement filter.

Because of uncertainties in the measurement procedure, the VERT project used all methods in parallel.

Standard Methods:
- Gravimetry
- Opacimetry
- Black Carbon Reflection (Bosch)

Particle Sizing
- SMPS: TSI
- SMPS: Hauke
- Impactor: Anderson
- Low Pressure Impactor: Berner

Online Methods:
- Aethalometry (Black Carbon)
- Photo Emission PAS)
- Diffusion Charging DC
- Epiphaniometry (Surface)

Filter Cake Analysis:
- Coulometry: EC + OC (Suva)
- Separation EC, OC, Sulfates, Water
- Trace Metal Analysis: ICP-OES, X-Ray, Fluorescence Spectroscopy, Atom Ads. Spectr., X-Ray Diffraction, TGA Infrared Spectrometry (EMPA)
- PAK-Analysis: GC + MS (EMPA)
- Dioxins and Furanes: GC + MS (EMPA)

The above methods were employed to investigate many (about 30) traps on engine test rigs under steady state (ISO 8178) and transient (free acceleration) conditions. Both utility vehicular and automobile engines were used as test engines.

VERT field test

A selection of filter systems were subject to a two-year field test on construction site machines:

Engine	Filter	Regeneration	Symbol
Liebherr			
D904T	SHW(HJS)	Additive Eolys (Ce)	LIB1
D904T	BUCK	Catalytic coating	LIB2
D914TI	ECS	Additive Lubrizol (Cu)	LIB3
D916T	DEUTZ	Full flow Diesel burner	LIB4
Caterpillar			
3306TA	SHW	Additive satacen (Fe)	CAT1
3306T	DEUTZ	Full flow Diesel burner	CAT2
3116T	BUCK	Additive satacen (Fe)	CAT3
3118	UNIKAT	Periodic electric	CAT4
3406T	UNIKAT	Periodic electric	CAT5
3116T	HUG	Catalytic coating	CAT6

Table 2: Particle traps in the VERT field test

Filtration efficiency according to mass or particle counts?

The following table contains the measured filtration efficiency of these filters after completing the field tests:

	PMAG (mass criterion)		PZAG (count criterion)	
	Standard Diesel	Fe additive	Standard Diesel	Fe additive
LIB2	76.52	81.00	95.38	97.80
LIB4	70.46	76.08	86.65	91.63
CAT1	77.54	87.64	97.79	98.80
CAT3	64.20	76.74	91.03	96.78
CAT4	54.76	76.54	98.98	99.60
LIB1	3.2	22.2	96.3	97.1
LIB3	12.4	43.0	99.9	ca. 99

Table 3: Filter efficiency of different systems after the VERT field test (Filter deployment 1500 - 7000 operating hours)

The reported data are differentiated according to the definition:

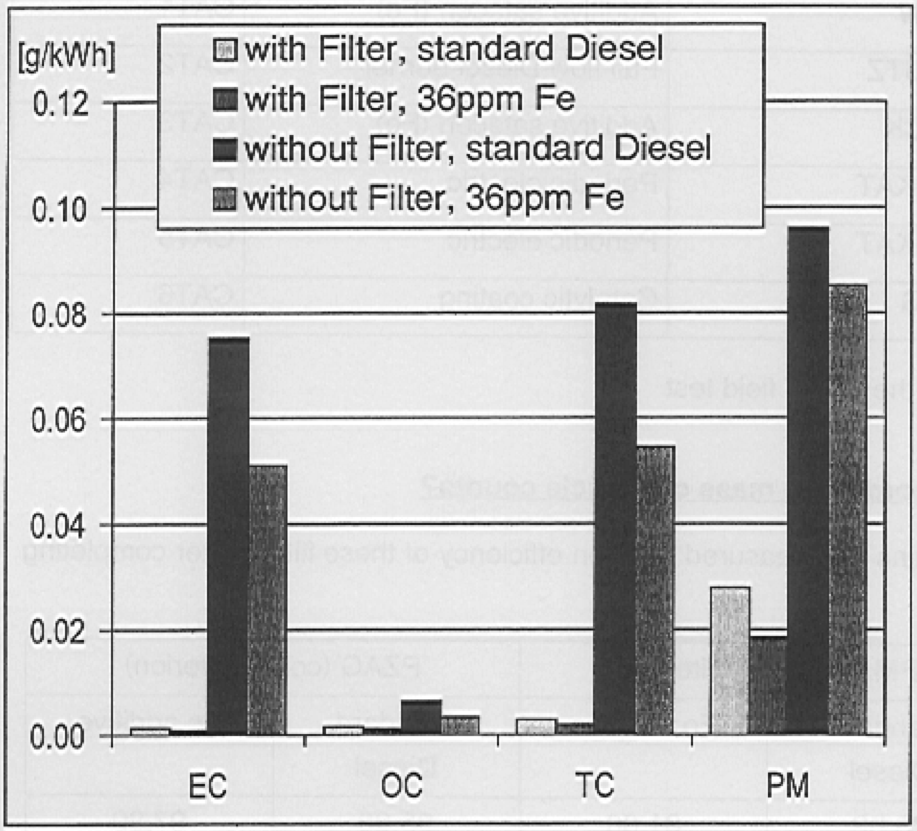
- PMAG: Mass filtration efficiency, compliant with legislated procedure
- PZAG: Filtration efficiency according to the count of solid particles

The two columns "Standard-Diesel" and "Additive" distinguish between the burdened and the trap regenerated with additives.

The data are the average value of 4 representative points in the ISO 8178 test cycle.

All traps display good to excellent values according to the particle count criterion. In contrast, the mass criterion indicates substantially lower and sometimes vanishing small filtration efficiencies.

Further investigations were done using coulometry. The following figure confirms that the particle count criterion correlates well with the definition of the elementary carbon content.



η_N = 99.98%

$\eta_{M coulometry, EC}$ = 99%

$\eta_{M total}$ = 69% (54 - 76)

Fig. 4: Coulometric analysis of the CAT4 filter

This analysis was done at full load and partial engine speed. The columns show the test cases with and without filter, both for standard Diesel and for additive fuel, i.e. regenerated trap.

The coulometric analysis convincingly confirms the evaluation according to the particle count criterion. In contrast, the particle mass criterion yields much worse results (54 - 76%, depending on operating point).

Artifacts through condensation of sulfur products

The two exceptional test cases LIB1 and LIB3 were selected for clarification through deeper analyses.

	PMAG (mass criterion)		PZAG (count criterion)	
	Standard Diesel	Fe additive	Standard Diesel	Fe additive
LIB1				
Full load	**-182.0**	**-67.8**	93.7	97.1
Part load	87.2	89.7	97.6	98.0
LIB3				
Full load	**-80.0**	**-64.0**	91.8	ca. 98
Part load	93.0	90.1	99.7	ca. 99

Table 4: Filtration rate as per particle mass and count at 2 load points LIB1 and LIB3

The displayed results are not the aggregate value of all ISO 8178 test points. Instead, these are the individual values at two particularly exceptional test points, i.e. at a full load and a part load point. There are dramatic discrepancies at the full load point. Whereas the count evaluation indicates very high filtration rates, the mass criterion yields negative numbers, i.e. trap deployment results in higher mass measurement on the tested filter compared to raw gas without particle filter.

The following figure explains using the analysis of the filter residues:

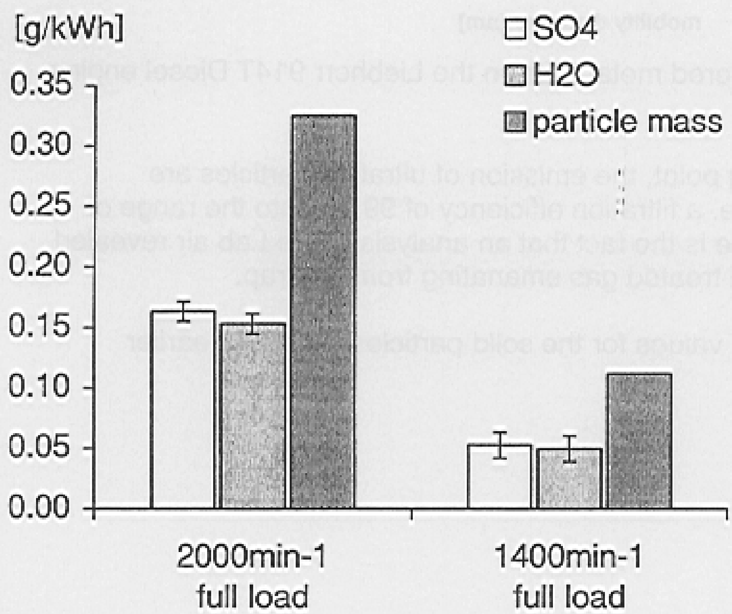


Fig. 5: Filter cake analysis LIB1, full load

The analysis reveals that the evaluated particle mass consists almost exclusively of water and sulfate ions. Carbon from soot is practically absent. This phenomenon can be explained for the two cases as follows. A copper additive was used with LIB3 and promoted the catalytic $SO_2 \rightarrow SO_3$ conversion. Catalytic effects cannot be excluded for LIB1, a sintered metal filter. Moreover, this trap had retained many particles. Consequently, the exhaust-gas temperature increased and hence SO_2 to SO_3 conversion already occurred within the engine.

Performance of good particle traps

Many vendors are offering particle traps having very high efficiencies. A typical example is the sintered metal filter illustrated.

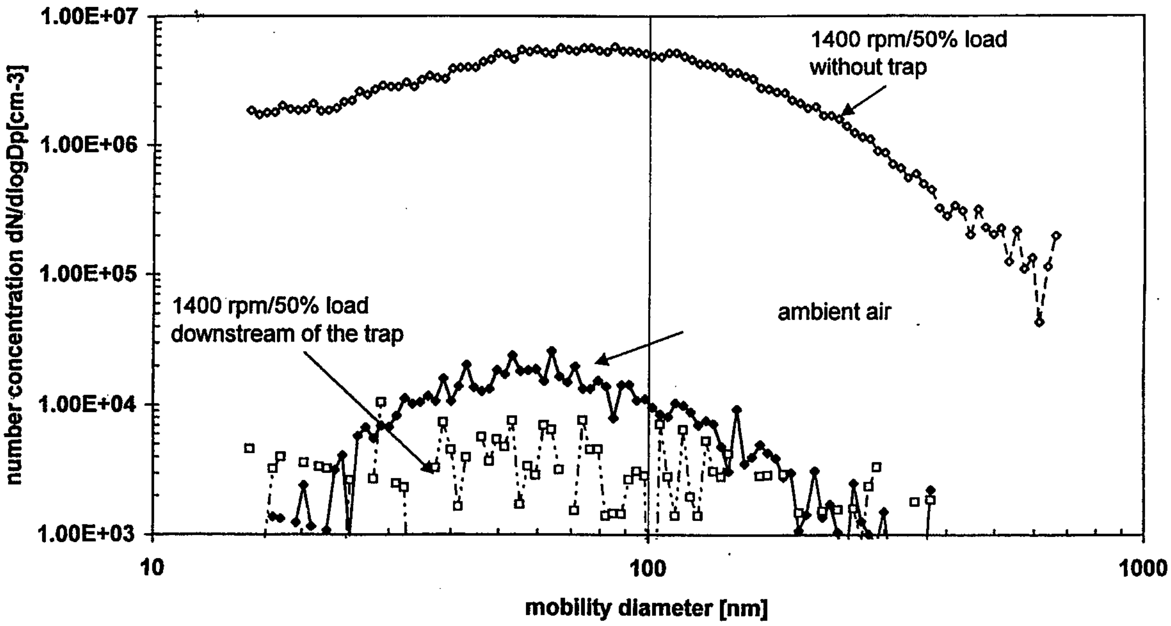


Fig. 6: Filtration characteristics of a sintered metal filter on the Liebherr 914T Diesel engine

At the 50% load and part rpm operating point, the emission of ultrafine particles are diminished by 3 orders of magnitude, i.e. a filtration efficiency of 99.9% into the range of primary particles. Particularly impressive is the fact that an analysis of the Lab air revealed higher particle pollution than the diluted treated gas emanating from the trap.

Many traps nowadays attain such good values for the solid particles. See also earlier publications [2] and [5].

Strategies for curtailing exhaust gas emissions

The experience gained leads to the following proposals for curtailing exhaust gas emissions:

1. Traps must be employed to counter occupational health problems stemming from the carcinogenic polycyclic hydrocarbons transported on the solid particles. Good traps are extremely effective in curtailing emissions from all engine types. The general future expectation is efficiencies of 99.9%. The special attractiveness of this technology is the immediate deployment for all engines, both existing and new. Thus, the problem of ultrafine particle emissions can be remedied at a stroke.

2. Sulfuric acid aerosols are rather unlikely to be injurious. Nevertheless, if they are identified as a health hazard, then the only remedy is to remove sulfur from fuel and lubricant. This is technically feasible and can be immediately implemented. The deployment of oxidation catalytic converters should be avoided. These promote SO_3 formation without conferring benefits.

3. Another occupational health hazard might be the emission of hydrocarbon condensates, to the extent that they are not bound on the particles. The hydrocarbons can be catalytically eliminated. The particle trap can be coated for catalytic oxidation of the hydrocarbons in their gaseous phase. The trap can also be combined with an oxidation catalytic converter. Sulfur-free fuel is, of course, a prerequisite.

Conclusions

The results of the VERT project should be implemented at the workplace. The priority is clearly the deployment of highly efficient traps. Sulfur-free fuel is a recommended auxiliary counter-measure.

The evaluation and certification of particle traps must be based on a measurement procedure that fundamentally evaluates the filtration characteristics for solid particles. It is advantageous to perform the evaluation on the engine and thus consider the specific properties of combustion particles.

By controlling the functional boundary conditions (maximum through-flow, exhaust-gas temperature), the trap can be simply characterized with a single index, i.e. the filtration efficiency depending on the particle size. This opens the attractive possibility of only certifying the trap on a typical engine test platform, without measuring all combinations of traps and combustion engines as part of the certification process.

The emission from any engine is sufficiently accurately obtained from the engine's raw emission of solid particles multiplied by the trap's filtration efficiency.

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