

Identification of storage and release effects of SO_x artefacts on DPF systems after long-term use

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The VERT procedure for diesel particle filter systems (DPF) includes an inspection of filter efficiency of DPF after mandatory field tests over 2000 h (VFT3). For some DPF systems a significant release of nanoparticles in the lower size range (<100 nm) was observed especially after long term DPF use, resulting in a seemingly reduction of particle mass related filtration efficiency, especially at full load condition. The release of stored SO_x compounds from catalytic coatings of the DPF or the diesel oxidation catalyst (DOC) was proposed as possible reason. The given data clearly identify sulphur containing components as a major cause for the observed phenomenon, beside condensation effects which can explain about a third of the delta mass.

Introduction

Diesel engines are essential for transportation and other heavy duty industries but a major drawback is the emission of ultra fine soot particles which can cause serious respiratory and cardiovascular health problems. Appropriate technologies for efficient retaining of particulate emissions from diesel engines are particulate traps (DPF). The regeneration of closed DPF systems is mainly supported by metal additives or metallic coatings.

Beside high filter efficiency, the filter system is also a kind of reactor with relatively long residence time. Thus, secondary reaction products can be formed. The VERT procedure was especially developed to evaluate suitability and sustainability of the complete particle filter systems and includes not only tests for filter efficiency and reliability of new and aged filters but also an assessment of potential risks for the formation of toxic secondary

emission products^{[1][2]}. The abbreviation VERT indicates the initial goal of the project to improve occupational health at tunnel construction sites. VERT is a synonym for „Verminderung der Emissionen von Real-Dieselmotoren im Tunnelbau“, which means reduction of real diesel engine emissions at tunnel construction sites. A schematic of the VERT procedure is presented in figure 1. More details about VERT were described in previous publications.^{[1][2][3][4]} The Swiss Standardisation Institute has recently formed a committee to transfer the VERT procedure into a Swiss norm titled SNR 277205, which will be published in autumn 2007.

Some filter systems with catalytic coatings showed low or even negative filter efficiencies in VFT 3 test when gravimetric determinations based on filter masses were used. On the contrary, the particle number measurements resulted in filter efficiencies above 99 %. This study identifies a release of stored sulphuric artefacts and condensation effects as main causes for differences between particle number and mass determinations.

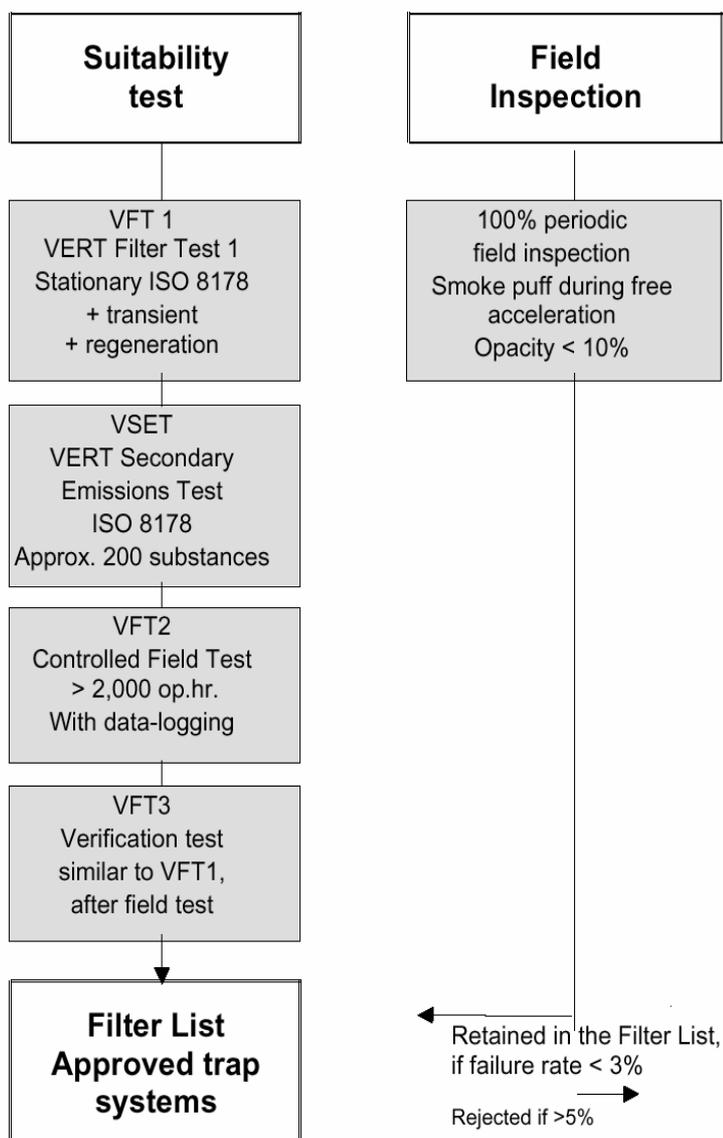
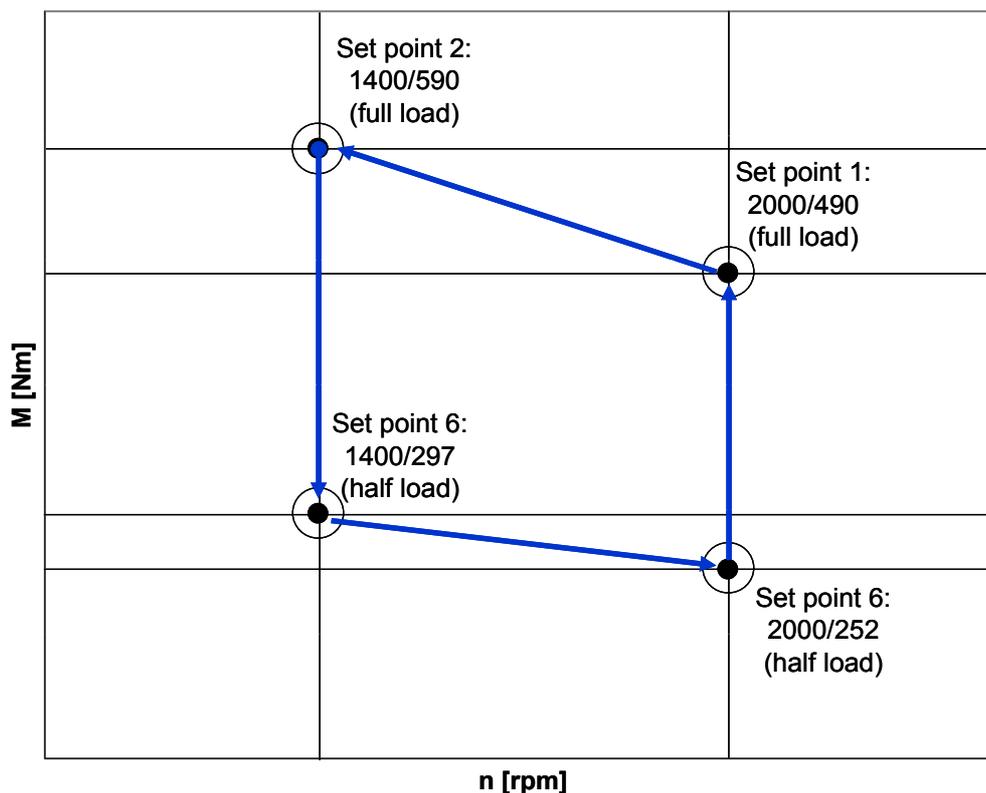


Figure 1: VERT suitability test procedure**Experimental and Results****Sampling**

VFT 3 of VERT procedure controls the filter efficiency after 2000 operating hours. After delivery the test for the aged filter is performed at an engine test stand. Figure 2 shows the four static set points. The VFT 3 test sequence is listed below (table 1).

**Figure 2:** Set points for VFT1 and VFT3 test of the VERT procedure**Table 1:** Test sequence of VFT 1 and VFT 3 test of the VERT procedure

- ⇒ **Test directly after delivery:**
Set points: 2 → 6 → 5 → 1 → 2 (repetition) each for 9 minutes
- ⇒ **Loading phase:**
4 hours at low load ($t_{5\text{ max}} \leq 270\text{ °C}$)
- ⇒ **Test after loading phase:**
Set points: 6 → 9 each for 9 minutes
- ⇒ **Regeneration phase:**
1.1 hour at high load ($t_{5\text{ max}} \approx 465\text{ °C}$)
- ⇒ **Test after regeneration phase:**
Set points: 2 → 6 → 5 → 1 → 2 (repetition) each for 9 minutes

Gravimetric Analysis

At each set point, emissions on two filters have been sampled one after another and gravimetrically determined. The filter weights were determined before and after sampling. Before each weighing, the filters were conditioning at 50 % humidity. A visual control showed no black soot at the sampled filters. The colour of the filters appeared white to light yellow directly after sampling (figure 3). The yellow discolouring disappeared after longer storage.

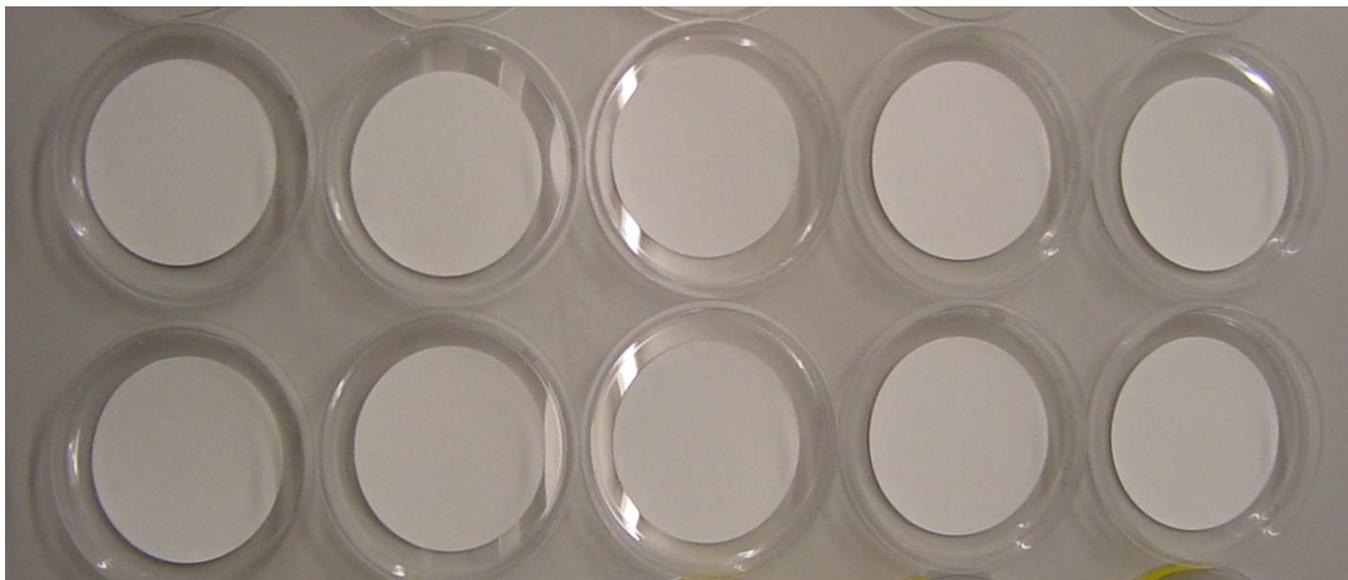


Figure 3: Sampling filters of VFT3 for DPF7

Gravimetric results of the first two set points of VFT3 test for five different DPF systems are combined in Table 2. The temperatures before and after DPF are also included. The DPF systems 3 and 7 showed high filter masses after sampling, resulting in low or negative filter efficiency whereas the other DPF systems showed no conspicuous differences in filtration efficiencies based on particle mass or particle number.

Remarkable is the fact, that set point 2 shows higher delta mass (Δm) than set point 6, which leads to the assumption that higher delta masses correlate with higher temperature. Concluding from these results, it was supposed that condensation effects or a release of stored sulphuric artefacts from the catalytic coating material might cause the high masses for DPF 3 and 7.

Table 2: Results from VFT3 test for 5 different catalytic DPF Systems at the first 2 set points for the test directly after delivery

	Operation conditions		t_5	t_6	Sample 1	Sample 2
	operating point	n / M [rpm / Nm]	[°C]	[°C]		
DPF3	2	1400/600	488	370	6.8	6.4
DPF4	2	1400/605	433	265	0.3	0.6
DPF5	2	1400/605	440	286	0.1	0.2
DPF6	2	1400/590	462	405	0.7	0.7
DPF7	2	1400/605	491	417	32	30
DPF3	6	1400/297	319	283	0.2	0.1
DPF4	6	1400/299	312	284	0.1	0.1
DPF5	6	1400/299	310	273	0.1	0.1
DPF6	6	1400/297	312	295	0.2	0.1
DPF7	6	1400/297	321	289	0.2	0.4
DPF3	2 (repetition)	1400/600	490	388	3.7	3.6
DPF4	2 (repetition)	1400/605	452	309	0.7	0.9
DPF5	2 (repetition)	1400/605	451	443	0.2	0.2
DPF6	2 (repetition)	1400/587	470	431	0.0	0.0
DPF7	2 (repetition)	1400/600	501	418	20	18

t_5 = temperature before after DPF / t_6 = temperature after DPF

The following figure (figure 4) presents possible oxidation reactions for sulphur dioxide to sulphuric acid. A release of sulphur components at higher temperature was supposed to cause the high mass at the gravimetric filters especially at set point 2.

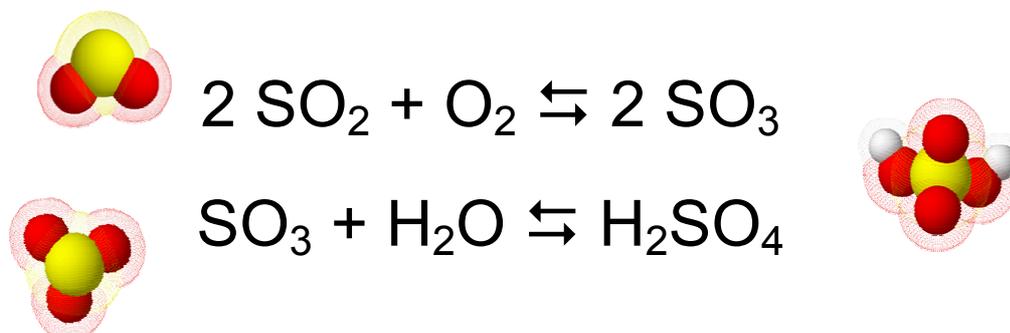


Figure 4: Possible reactions for different sulphur species

Chemical Analysis

A chemical investigation of the filters from VFT 3 test for the DPF 7 were chosen for further investigations on condensation effects and release of anionic artefacts such as sulphate. The filters were dried at 100 °C till weight constancy and weight. Blank filters were handled similarly. The amount of the condensation was calculated as difference between new and dried filter.

Filter segments with a diameter of 2 cm were punched for chemical characterization. For identification of anionic artefact species such as sulphate, the filter segments were extracted in a Soxhlet extraction set up using a 50:50 mixture of isopropyl alcohol and ultra-pure water (figure 5). Three blank filters were similarly extracted. The analyses were performed by ionic chromatography (IC) (figure 6). The ion chromatography system is composed of a chemically suppressed modular system (Metrohm, Switzerland) with IC pump 709, VA detector 791, IC detector 732, IC separation centre 733, pump unit 752, IC interface 762, and IC sample processor 766.

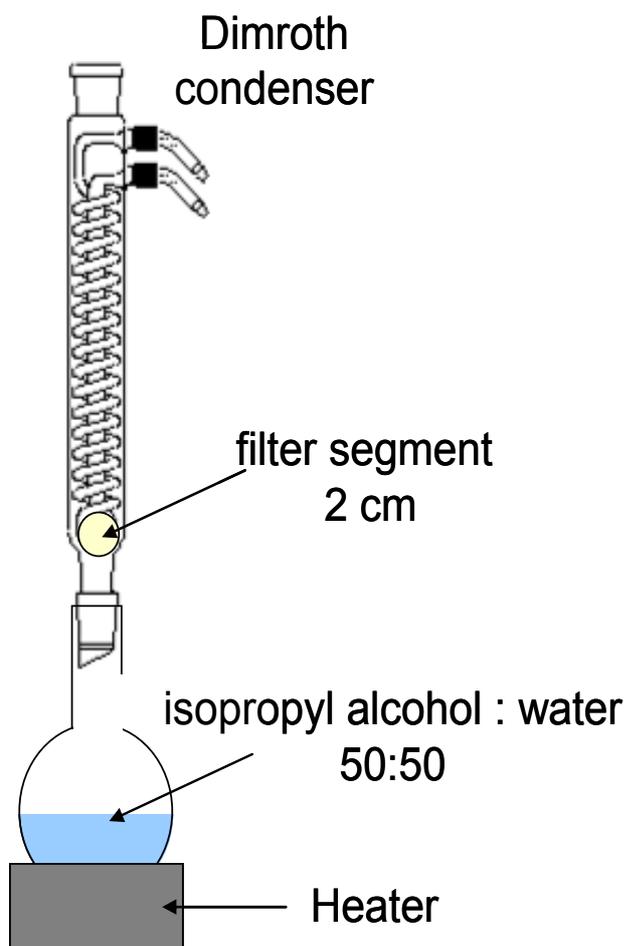


Figure 5 SOXHLET set-up for filter extraction for ionic chromatography analysis

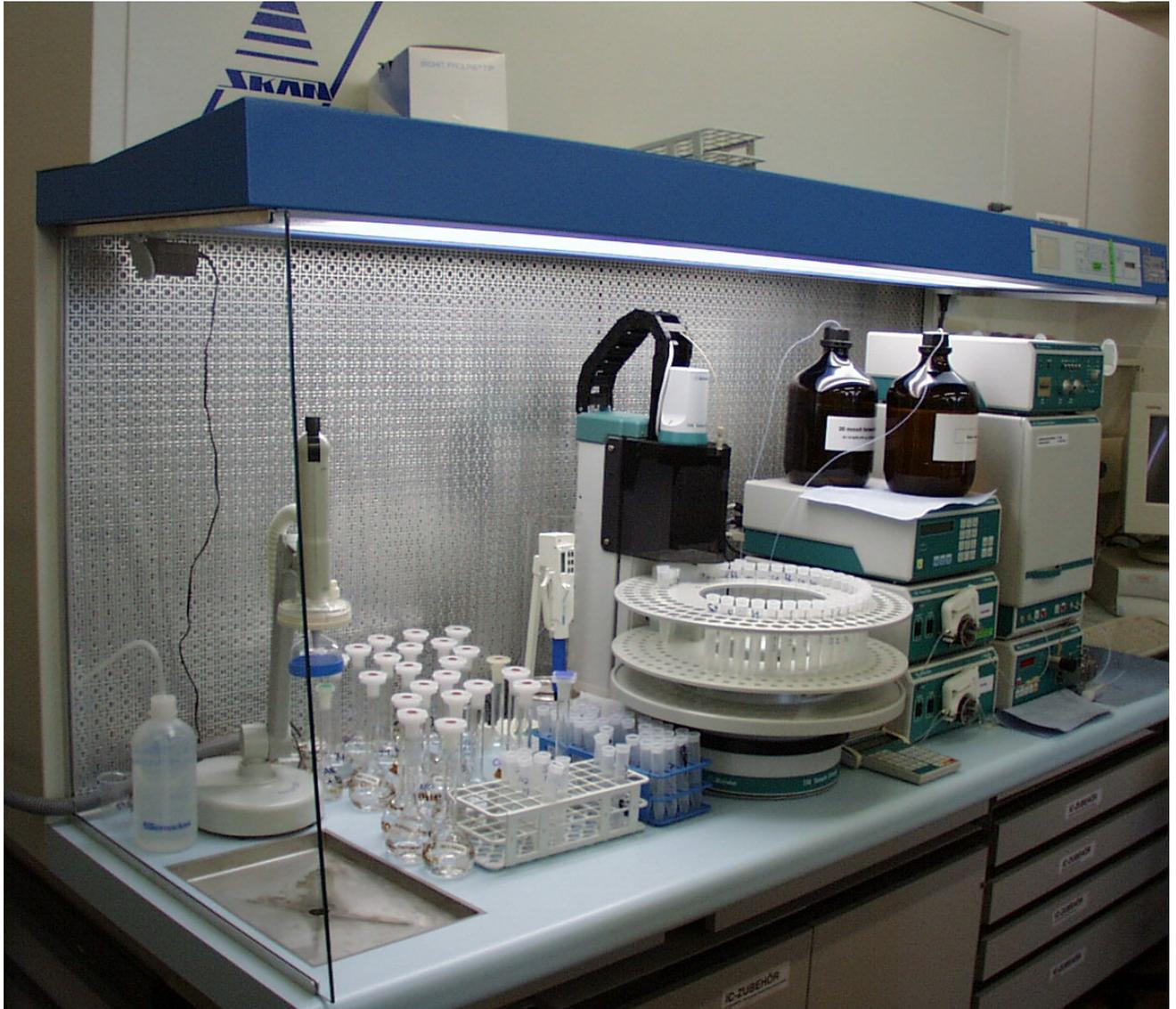


Figure 6 *Modular ionic chromatography system*

Chlorine Cl^- , nitrite NO_2^- , nitrate NO_3^- , phosphate PO_4^{3-} and sulphate SO_4^{2-} were selected as potential inorganic anionic artefact species. The results for the extracted filter segments were calculated to the original filter size. Table 3 presents the results of the gravimetric sampling filters achieved from a VFT3 for DPF 7 as well as the corresponding IC analysis for the anionic species chlorine Cl^- , nitrite NO_2^- , nitrate NO_3^- , phosphate PO_4^{3-} and sulphate SO_4^{2-} . All data are given in mg/filter. Additionally, engine operating conditions and temperatures before and after DPF are included.

Table 3 Results of analysis for gravimetric sampling filters achieved from a VFT3 for DPF 7 for the test directly after delivery

Sample ID	Set point	n / M	Δm	t_5	t_6	Amount of water loss	Cl	NO ₂	NO ₃	PO ₄	SO ₄
		[min ⁻¹ / Nm]	[mg]	[°C]	[°C]		mg/filter				
LOD							0.03	0.03	0.03	0.03	0.03
V21	2	1400/605	32.1	491	417	11.2	<DL	<DL	<DL	<DL	6.0
V22	2	1400/605	30.3	491	417	10.1	<DL	<DL	<DL	<DL	5.2
V23	6	1400/297	0.2	321	289	0	0.03	<DL	0.08	<DL	0.03
V24	6	1400/297	0.4	321	289	0	0.03	<DL	0.05	<DL	0.2
V25	5	2000/252	0.2	334	309	0	0.05	<DL	0.11	<DL	0.05
V26	5	2000/252	0.4	334	309	0	<DL	<DL	0.03	<DL	0.25
V28	1	2000/530	5.4	481	430	0.8	<DL	<DL	<DL	<DL	1.9
V29	1	2000/530	6.1	481	430	0.9	<DL	<DL	<DL	<DL	2.2
V27	2 (Rep)	1400/600	19.9	501	418	5.9	<DL	<DL	<DL	<DL	4.9
V30	2 (Rep)	1400/600	18.4	501	418	5.3	<DL	<DL	<DL	<DL	4.1

Discussion

Condensation contributes about one third to the total delta mass. High sulphate SO_4^{2-} concentrations were determined for the gravimetric filters with high delta mass (figure 7). The other chosen anionic species showed no significant concentrations in the filter extractions. The amount of sulphur was determined to contribute between 20 to 36 % to the total delta mass. An amount of about 30 to 50 % is so far not identified but supposed to be SO_3 or other sulphur components. Further species selective investigations are planned.

The results also indicate an influence of temperature on storage and release of sulphur components. Only at set points with temperatures above $350\text{ }^\circ\text{C}$, a significant delta mass increase and a significant sulphate concentration were observed (figure 8). Moreover, the hypothesis of a temperature effect on storage and release is also supported by the fact that only the two DPF systems (DPF 3 and DPF 7) showed high delta masses which were mainly operated at low load conditions (city traffic) during 2000 hour operation on real diesel vehicles. Low load conditions result in low temperature at the filter, probably mainly below $300\text{ }^\circ\text{C}$. Therefore, it can be concluded, that platinum catalytic coated DPF systems show storage effects for sulphur artefacts at low load operation conditions and a release of these artefacts at temperatures above $350\text{ }^\circ\text{C}$. A condensation of released SO_x components in the dilution tunnel during VFT 3 sampling is likely.

Since gravimetric filters for the different set points (table 3) were sampled one after another, it can be assumed, that release processes for sulphur artefacts require a certain time. It can be estimated to more than 40 minutes for the here investigated two DPF systems. DPF 7 was larger in dimension than DPF 3 which might explain the difference in delta mass. The storage and release time is probably dependent on the DPF dimension and the available catalytic coating as well as on the operating conditions before VERT VFT 3 test.

Platinum catalytic coated DPF systems operated at low engine load conditions tend to storage of sulphur artefacts. In such cases, gravimetric determinations based on particle mass (PM) result in negative filter efficiency whereas the number based filter efficiencies for solid nanoparticles (particle number) is $>99\%$. Therefore, particle number determinations are preferable, while particle mass determinations lead to wrong results for filter efficiency for soot particles.

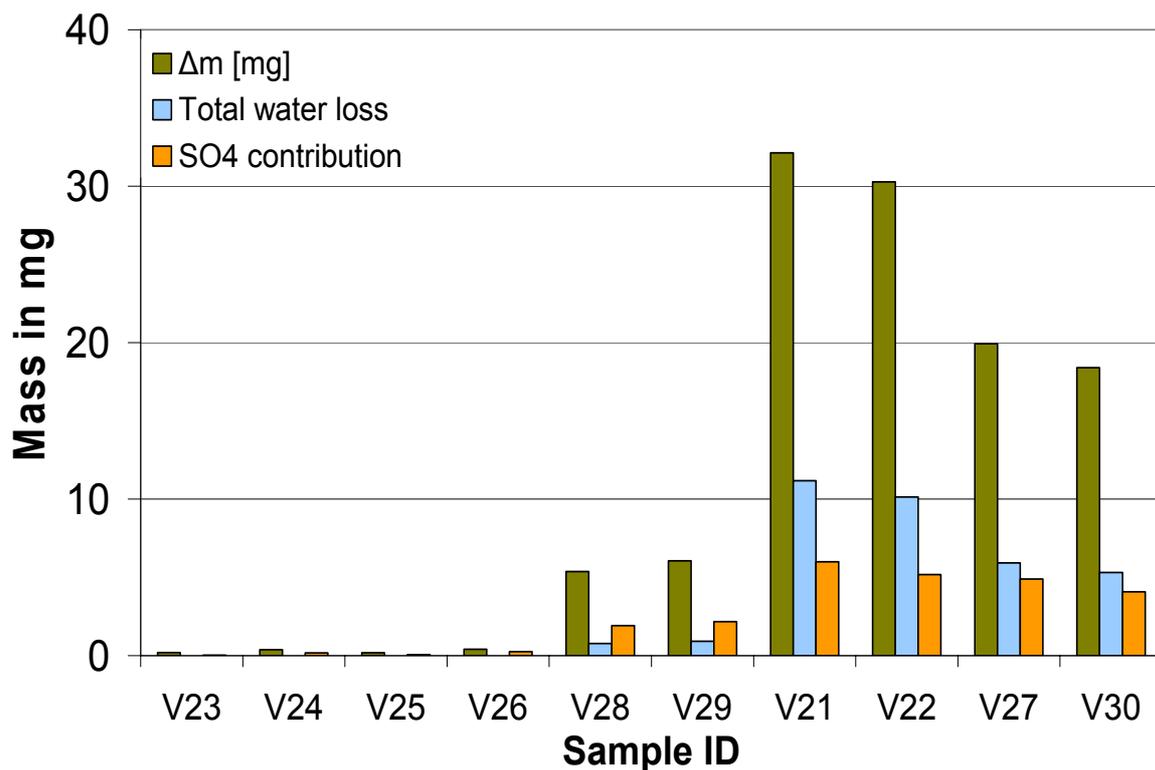


Figure 7 Determined amount of water and SO₄ on Δm

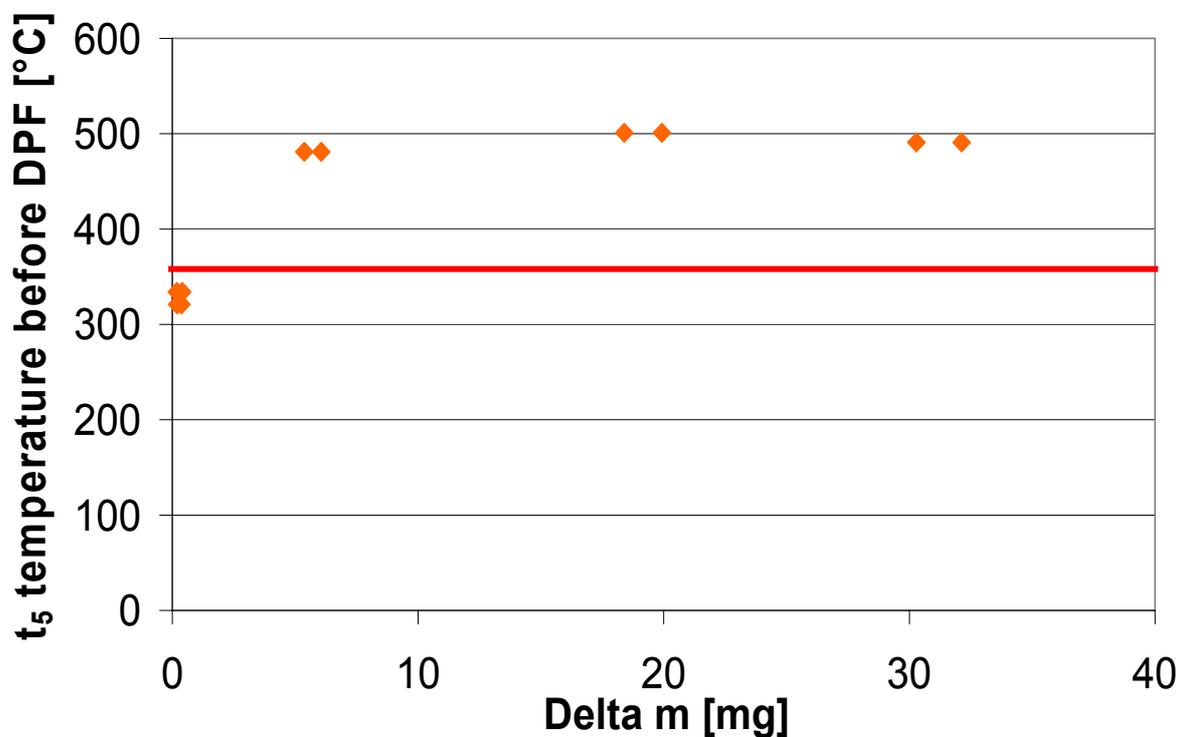


Figure 8 Δm dependent on operation temperature

Storage and Release Effects of DOCs

In a previous Empa study^[5], similar release effects were observed for platinum coated diesel oxidation catalysts (DOC). Emissions of a EURO-2 light-duty diesel vehicle (LDV) with oxidation catalysts were online investigated in the transient **Common Artemis Driving Cycle (CADC)** at Empa vehicle dynamometer. Mass spectrometric analysis of SO₂ at m/z 64 from undiluted exhaust gas were achieved for the LDV operated with low-sulphur (<10 ppm) and high-sulphur (190 ppm) diesel.

Driving cycle conditions and CO₂ progress are given in figure 9a. As expected the high-sulphur fuel showed larger SO₂ emissions (figure 9b) than the low-sulphur fuel (figure 9c and 9d). However, a spontaneous increase of SO₂ emission at higher speed was observed for the first peak at 120 km/h in the test represented in figure 9c which might indicate a temporarily release of sulphur components from the Pt coated DOC at higher temperature. The subsequent repetition (figure 9d) shows SO₂ emission on the expected levels.

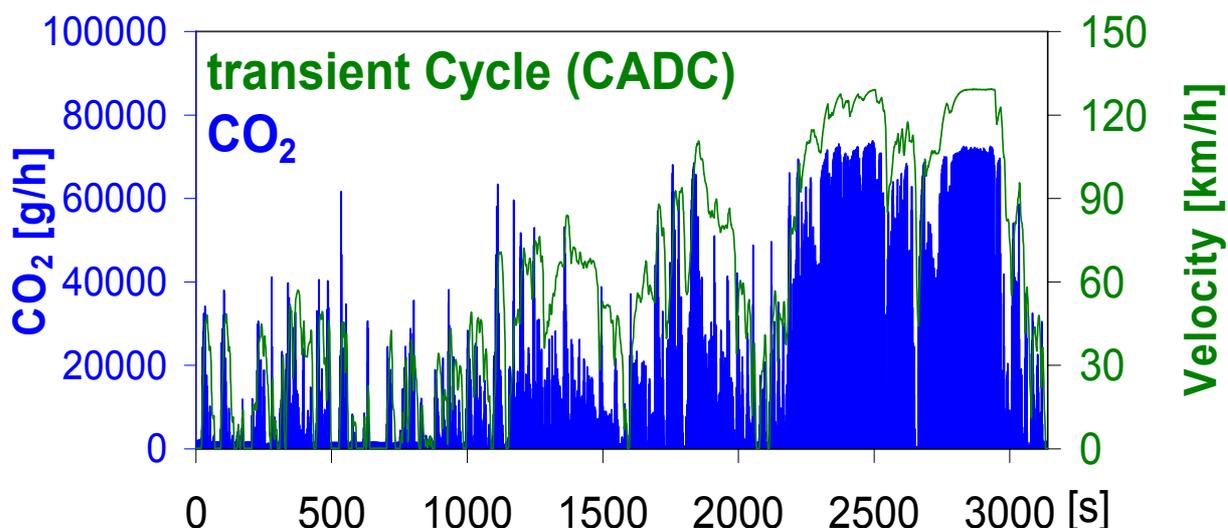


Figure 9 a CO₂ mass flow [g/h] and velocity monitoring for a Euro 2 light duty diesel vehicle (LDV) with oxidation catalyst (DOC) operated with high-sulphur (190 ppm) diesel-fuel during CADC.

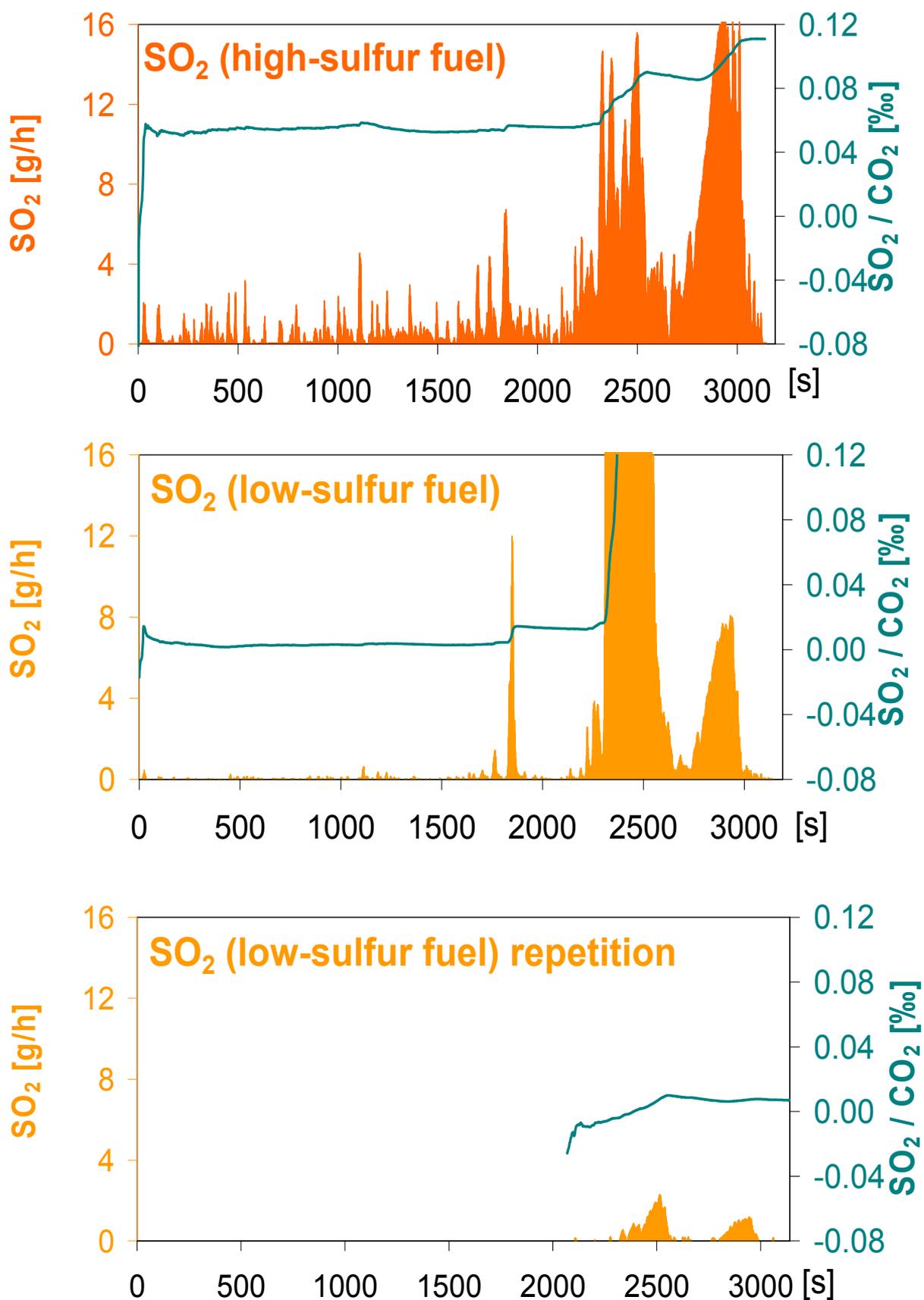


Figure 9 b-d SO₂ mass flow [g/h] and ratio of cumulated SO₂/CO₂-mass emissions [%] for a LDV with diesel oxidation catalyst (DOC) operated with low- (<10 ppm) and high-sulphur (190 ppm) diesel-fuel during CADC.

Conclusion

The formation of sulphur containing compounds is catalysed by strongly oxidizing exhaust gas treatment systems. These systems can convert sulphur present at trace levels in diesel exhaust to various SO_x components which accumulate to nano-particles. Depending on volatility of the obtained sulphur oxidation products, such compounds can accumulate in surface-rich systems such as DPFs or DOCs at lower operating temperatures. A later release at higher temperatures leads to the above described findings (storage and release phenomena). The formed H₂SO₄ condensates at lower temperature in CVS dilution tunnel during sampling for VERT VFT3 and will be deposited together with soot on the test filter. Thus, gravimetric determinations using PM result in negative filter efficiency whereas the number based filter efficiencies for solid nanoparticles (particle number) is usually >99 %. It can be concluded that particle number determinations are preferable, while particle mass determinations lead to wrong results.

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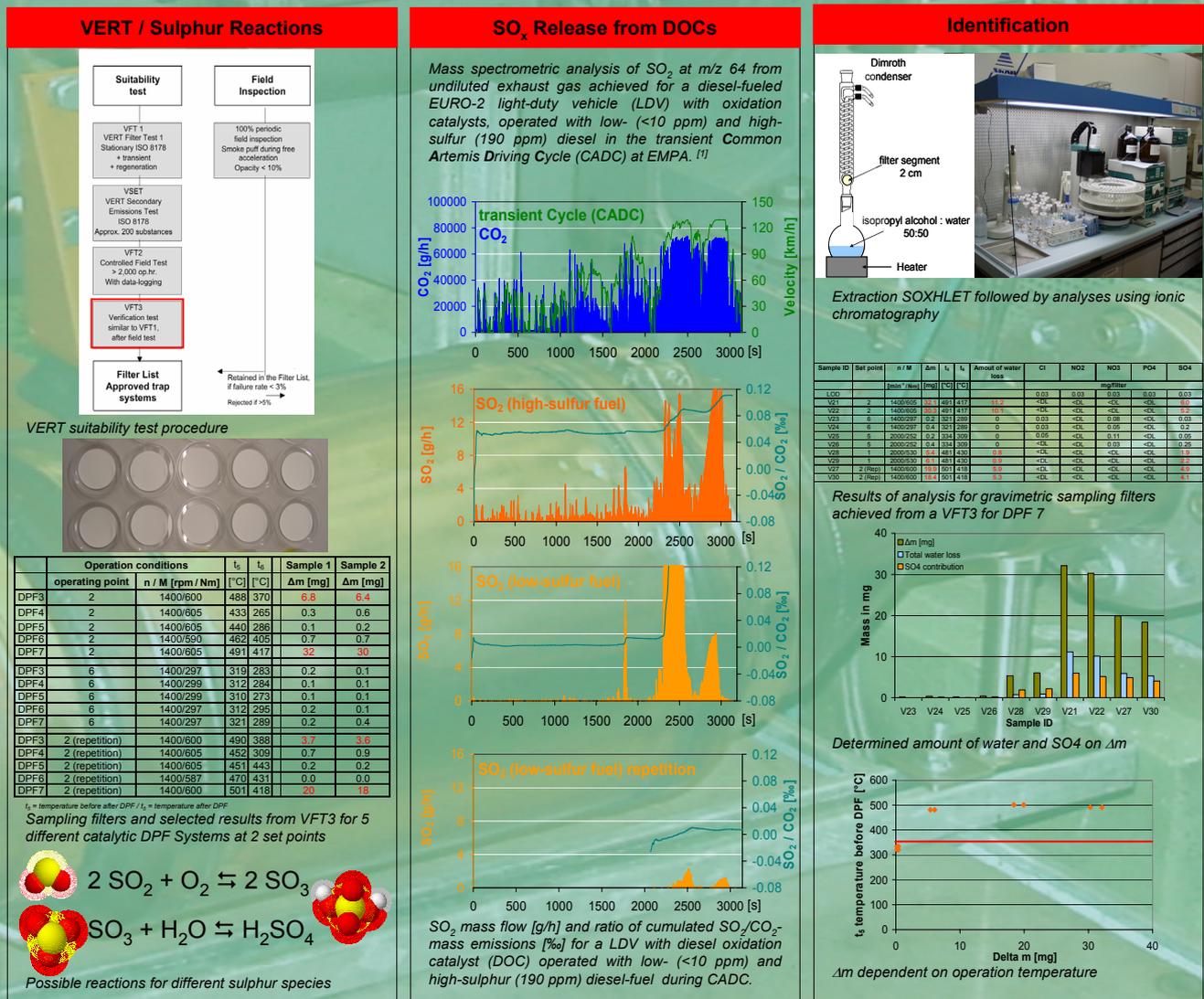
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Conclusion: The formation of sulphur containing compounds is catalysed by strongly oxidizing exhaust gas treatment systems. These systems can convert sulphur present at trace levels in diesel exhaust to various SO_x components which accumulate to nano-particles. Depending on volatility of the obtained sulphur oxidation products, such compounds can accumulate in surface-rich systems such as DPFs or DOCs at lower operating temperatures. A later release at higher temperatures leads to the above described findings (storage and release phenomena). The formed H₂SO₄ condensates at lower temperature in CVS dilution tunnel during sampling for VERT VFT3 and will be deposited together with soot on the test filter. Thus, gravimetric determinations using PM result in negative filter efficiency whereas the number based filter efficiencies for solid nanoparticles (particle number) is usually >99 %. It can be concluded that particle number determinations are preferable, while particle mass determinations lead to wrong results.

References:
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