

WLTP-DTP Subgroup Additional Pollutants
DTP3 Vienna 12/13 Oct.

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Progress report

DTP3 –meeting Vienna 12/13 Oct.

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Additional pollutants subgroup - Members list

Chair:

Co-chair:

Mörsch	Oliver	Daimler
Astorga-Iloren	Covadanga	JRC
Akard	Mike	Horiba
Andersson	Jon	Riccardo
AOYAMA	Yuichi	JASIC-contact
Berg	Olle	Volvo Cars
Bigi	Laura	PSA
Born	Michael	BMW NA
Bosteels	Dirk	AECC
Charafeddine	Kamal	Porsche
Dijkhuizen	Arjan	TME
Engelejringer	Kurt	AVL List GmbH
Hill	Less	HORIBA
Holmstrom	Maria	Saab
Jemma	Carl	Riccardo
Kirchner	Ulf	Ford Europe
Laroo	Chris	USEPA
Loo	Jeff	GM
May	John	AECC
Momique	Jean-Claude	PSA

Nagy	Don	GM
Nyman	Bjorn	Saab
Petit	Alain	Renault
Petrofski	Alexander	Volvo Cars
Ramacher	Bjoern	Volkswagen Group
Renders	Johan	EC
Sanchez	James	EPA
Sawada	Yutaka	JAMA
Schuster	Norbert	Ford Europe
Sherman	Mike	Ford
Silvis	Willian	AVL
Simon	Nakia	Chrysler
Steininger	Nikolaus	EC
Strobel	Karsten	GM Europe
Thiel	Wolfgang	BMW AG
Vavra	Christian	MAHA-AIP
Walker	Patrick	GM Europe
Witt	Susanne	UBA
Yassine	Mahmoud	Chrysler

Additional pollutants subgroup – Terms of reference

The Additional Pollutants subgroup shall be responsible for the development of test procedures for pollutants not currently regulated such as NO₂, NH₃, N₂O including measurement equipment and formulae for the measurement for light duty vehicles.

Scope of Activity

The subgroup will undertake the following tasks on the basis of procedures in existing legislation and expert knowledge within the group:

1. Agree on additional pollutants to be addressed.
2. Identify appropriate measurement methods for each of the pollutants.
3. Describe measurement and calibration procedures and calculations based on existing legislation and on output from lab procedure subgroup.
4. Drafting of legislation text.

Meeting schedule

- First Meeting:** Telephone/Web Conference
Date: 20th July 2010
16 participants
- Second Meeting:** Telephone/Web Conference
Date: 20th July 2010
20 participants
- Third Meeting:** Face to face meeting at JRC/Ispra
(planned) Date: 9/10 Dec. 2010
registration ongoing

Pollutants to be addressed

NH₃, NO₂, N₂O, Ethanol, Aldehydes (Formaldehyde, Acetaldehyde)

Open issue:

Definition in 1st meeting:

Further components if tasked.

Group does not by itself define further pollutants to be addressed.

Annotation from Nikolaus Steininger 27.09.10:

Group should also define components, since no input from outside is to be expected. Input for VOC in context with new fuels is needed. If required from Group further expertise is needed / issue to be addressed at Vienna

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Measurement Methods for additional pollutants

Pollutant	Method	Base	bag	diluted	raw	online	off line	Robustness	Paper Nr.	Problems
NO2	CLD	ECE Reg. 83		x		x		very good	WLTP-DTP-02-06e	
	QCL			x		x		not yet available	WLTP-DTP-AP-02-02	not yet available
	UV-RAS			x		x		good	WLTP-DTP-02-06e	
	FTIR			x		x		fair		LoD
N2O	NDIR	CFR	x			x		fair	WLTP-AP-02-01 b	cross interference and LoD
	QCL		x			x		not yet available	WLTP-DTP-AP-02-02	not yet available
	Photo Acoustic		x			x		poor		cross interference and stability
	GC-ECD	CFR	x				x	good	WLTP-AP-02-01 b	off line
NH3	LDS	ECE Reg. 49			x	x		poor	WLTP-DTP-02-07e	only concentration
	FTIR				x	x			WLTP-DTP-02-07e	only concentration
	QCL				x	x		not yet available	WLTP-DTP-AP-02-02	not yet available
Ethanol	Photo Acoustic		x			x		good		
	GC-FID	CARB		x			x			off line
Aldehydes	Impinger + HPLC	EPA/625/R-96/-1-b		x			x	good	WLTP-DTP-AP-02-06	off line
	FTIR				x	x				only concentration, LoD for dilute
	QCL			?		x		not yet available		not yet available
VOC?	GC-FID	CARB	x				x	?		off line, complex, LoD
	?									
?										

General guidelines

- agree on performance criteria
 - LoD
 - cross interference
 - rise time
 - ...
- allow alternative methods
- base on existing legislation where suitable
- avoid raw measurement where possible

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WLTP-DTP-AP-02-01a: Definitions

- **LoD (Limit of Detection)**

The LoD is the smallest quantity that can be reliably (99%) distinguished from zero

DIN32645 / Skoog&Leary „Principles of Instrumental Analysis“: $LoD = \text{avg. (blank)} + 3 \times \text{std. dev. (blank)}$

- **LoQ (Limit of Quantification)**

Das LoQ is the smallest quantity at which two different concentrations can be distinguished reliably.

DIN32645: $LoQ = 3 \times LoD$ or $LoQ = 10 \times \text{std. dev. (blank)}$

Skoog&Leary „Principles of Instrumental Analysis“: $LoQ = 10 \times \text{std. dev. (blank)}$

- **Interpretation of the Values according DIN32645**

Result	Interpretation	further Information
$x < LoD$	Not measured	$< 2 \times LoD$
$LoD \leq x < LoQ$	measured	
$LoQ \leq x$	Sufficient	Within confidence region

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WLTP-DTP-02-06e:

Mass emissions of NO, NO_x and NO₂ in emission test cycle:

- **NO:** CVS with modal measurement of NO in the diluted exhaust gas and integration over the cycle/phase
-> NO concentration.
NO_x: Measurement of NO_x-concentration from CVS bag (standard method)
-> NO_x concentration.
NO₂: Difference of NO_x and NO concentration.
- Analyzer: CLD or DUV-RAS (see SAE-Paper 2004-01-1830).
- Working groups to recommend sampling technologies to avoid aqueous condensation in dilute modal sample streams.
- For NO_x, NO and NO₂ gas density of $\rho_{\text{NO}_2} = 1.913 \text{ g/cm}^3$ at 20^o C is applied.

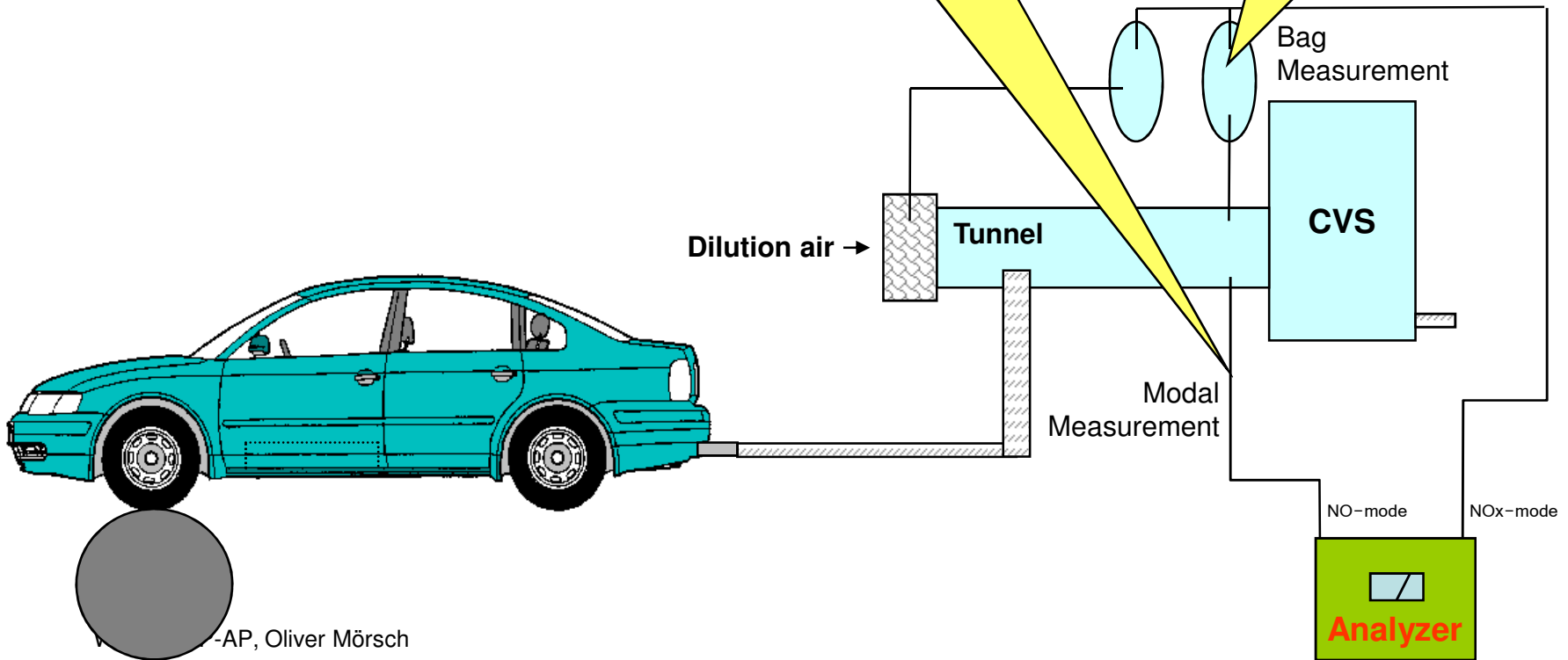
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WLTP-DTP-02-06e: Proposed setup for NO₂ determination

Mass emission during cycle

Measurement of NO from diluted exhaust

Measurement of NO_x from bag



WLTP-DTP-02-06e: Measurement Principle for NH₃

- Ammonium measurement method that could be applied to vehicles equipped with a SCR-system
- Two measurement principle for raw exhaust emission measurement may be used
 - Laser Diode Spectrometer
 - Fourier Transform Infrared (FTIR) analyzer)
- Due to high reactivity and physical properties of ammonia the effect of sampling should be minimised
 - In-situ method
 - Minimal effect of sampling artefact
 - End of pipe measurement
 - Extractive Method
 - Use of PTFE or stainless steel for piping
 - Temperature of piping system and the filter $T > [\text{TBD}] \text{ } ^\circ\text{C}$ to prevent condensation
 - Minimize sample volume removed from the raw exhaust and correct other emissions measurements for this removal or separate the SCR-control test from the emission test
 - Sampling line should be clean before use (including change of filter)
- proposal of measurement method is based on proposal Euro VI comitology (heavy duty)

WLTP-DTP-AP-02-01a: Requirements for a reliable **N2O** measurement method

- actual emission limit for N2O: 0,010 g/mi
- measurement from bag → non or quasi continuous measurement is sufficient
- For a reliable measurement of air bag LoQ has to be at 300ppb (typicall background concentration)
→ LoD has to be in the order of 30 ppb
- No or little cross interference at typical bag concentrations:

2,5% CO2	20ppm THC
2,5% H2O	5ppm CH4
200ppm CO	5ppm NOx

- an offset of 0,1ppm in the measurement of the air bag results in a 30% error at limit level