



WLTP DTP subgroup	
Date	11 June 2010
Title	Draft Nitrogen Dioxide (NO₂) measurement procedure
Working paper number	WLTP-DTP-02-06

1.0. Introduction

These guidelines were developed following in response to discussions at the 1st DTP (Develop Test Procedure) meeting held in Ann Arbor in April 2010. It was identified that a test procedure is required NO₂.

Once this proposal concept has been accepted by the DTP team, OICA will draft a proposal for the legislative text.

2.0. Background

2.1. Reason for the requirement

Revised and challenging air quality standards for NO₂ are in force since the beginning of 2010 in the European Union. As road transport contributes around half of the ambient NO₂, it is anticipated that a comparable means of determining the ratio of NO₂ to the total NO_x emissions will be required for the ongoing discussions. It is therefore proposed to develop such a procedure during the WLTP project in order to ensure worldwide harmonisation from the outset.

2.2. Existing legislation

In developing this draft test procedure, it was appropriate to review existing legislation that measures NO₂. Although no test procedure is known for the measurement of vehicle emissions, there is an existing practice for air quality measurements and this should form the basis for a proposal, at least to ensure possible correlation of results.

3.0. Measurement principle

Two alternative analyser concepts are proposed, these being Chemi-Luminescent Analyser (CLA) or Ultra-Violet Resonance Absorption (UV-RAS).

Contrary to the majority of today's light duty measurement procedures, and due to the uncertainty of NO to NO₂ ratios over time and the solubility of NO₂



in water, it is proposed to measure NO_2 directly rather than from CVS bags.

As NO_2 is seen as a pollutant emission, and therefore is expected to have the same dimension as NO_x (unit mass per unit of distance), it is recommended to adopt the modal measurement process that is currently applied to FID hydrocarbon measurements in ECE R83.

Draft proposal for the measurement of NO₂ in the exhaust from passenger cars

June 2010

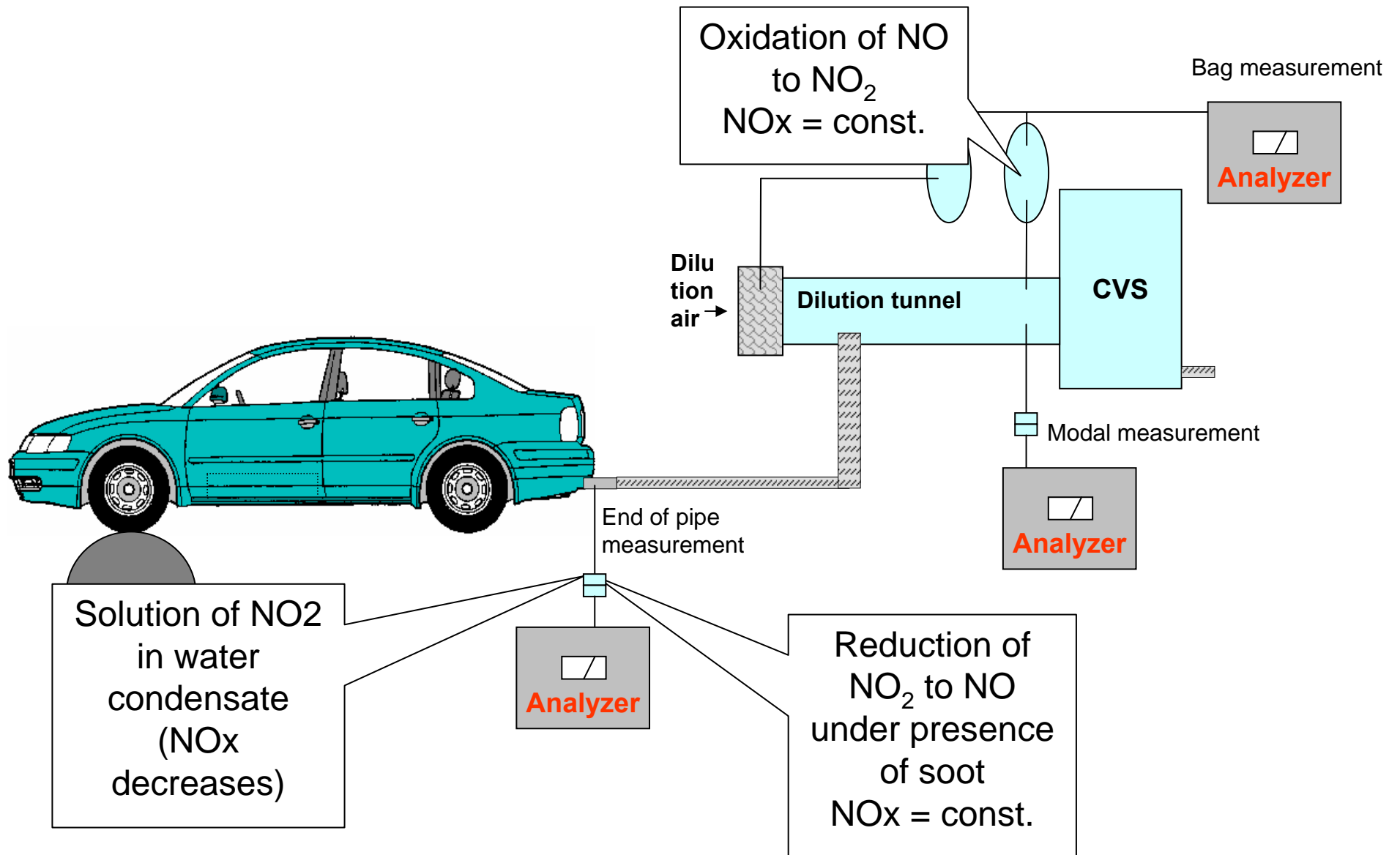
This work is intended to start discussions at the DTP work group level. Changes are likely as the technical experts review proposals made and then consolidate into agreed upon approaches."

Measurement of NO, NO₂ and NO_x Mass Emissions in the Exhaust of Light Duty Vehicles (LDV)

Effects leading to measurement errors:

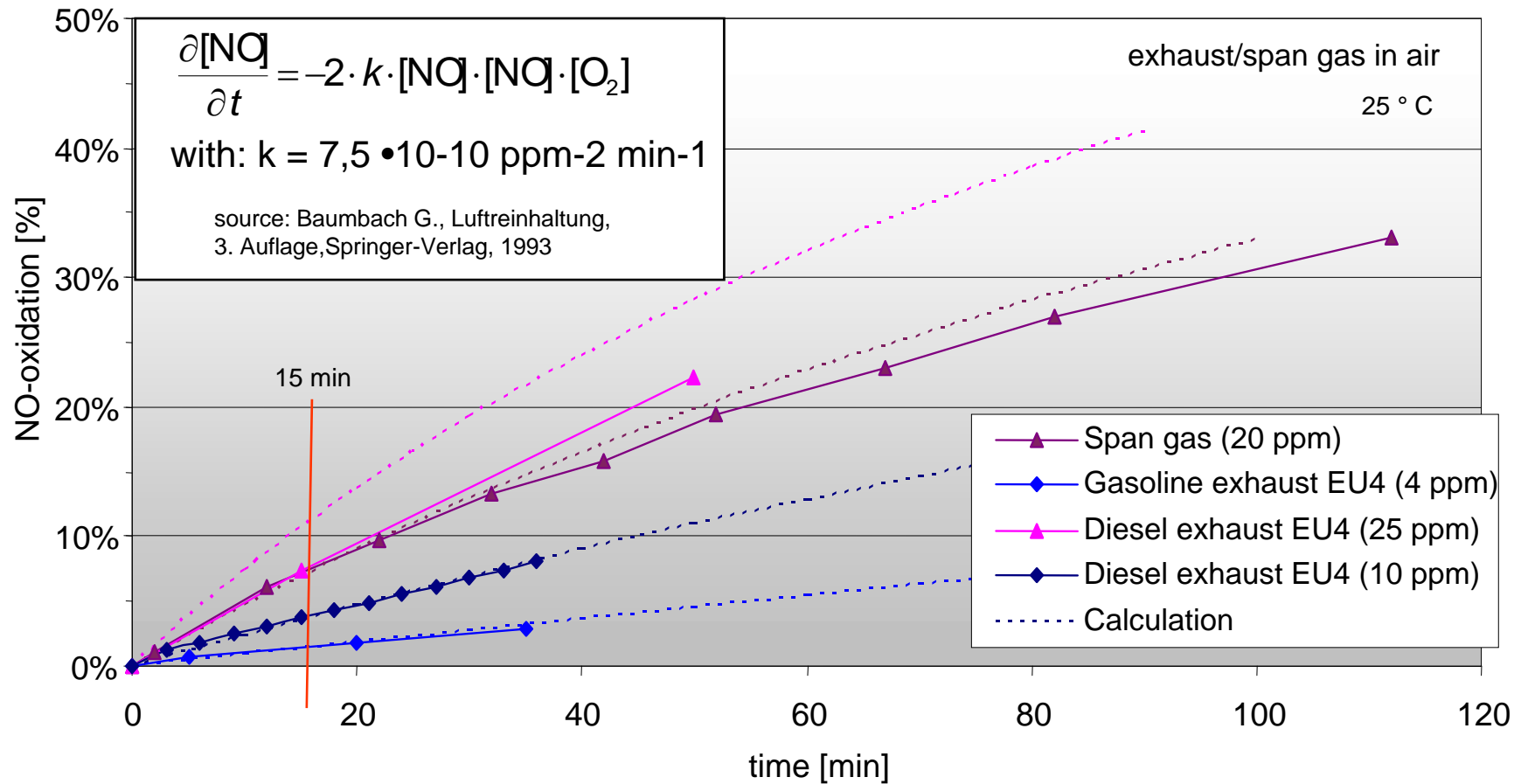
- Conversion of NO to NO₂ (NO_x remains constant)
In presence of oxygen at ambient conditions NO is oxidized to NO₂. Half life of NO at a concentration of 25 ppmv is of approx. 160 min.
- Conversion of NO₂ to NO (NO_x remains constant)
At elevated temperatures (> 150 °C) NO₂ is converted to NO. Conversion rate can be significantly increased in presence of soot (e.g. on filters).
- Solution of NO₂ in water condensate (NO_x decreases)
NO₂ is water soluble and can go into solution in presence of water condensate in the exhaust.

Influencing Factors on NO/NO₂ Ratio



Oxidation of NO to NO₂ in the CVS bag

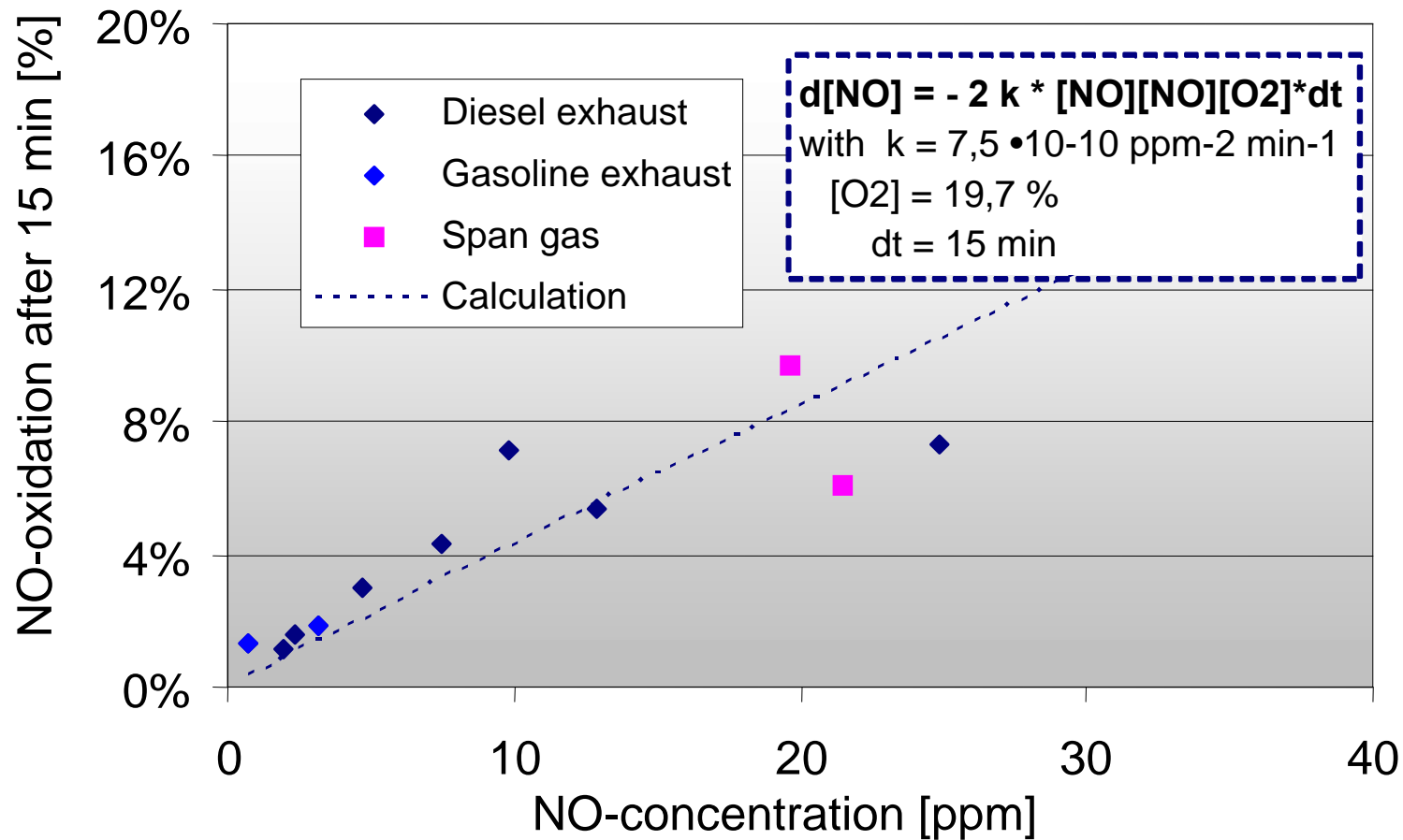
Comparison of measurement and theoretical approach



The measured values show a fair to good agreement with the theoretical approach (calculation).

Oxidation of NO to NO₂ in CVS bag after 15 min

Influence of NO concentration



Bag measurement yields increased NO₂ value due to oxidation of NO.

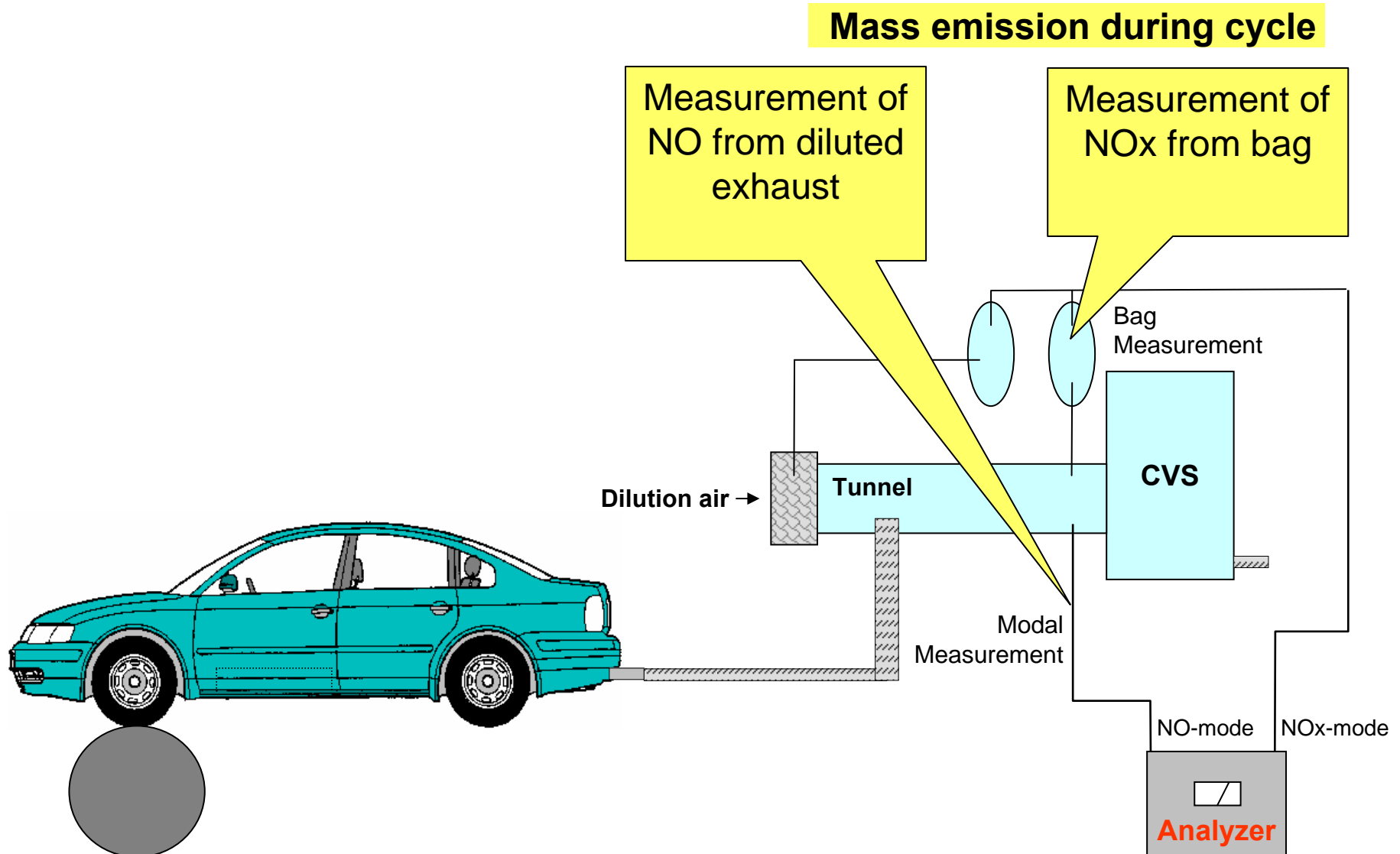
Conclusions

- In the diluted exhaust NO partly oxidizes to NO₂.
- The reaction rate depends on the NO concentration (for T = const).
- To avoid systematic error, residence time has to be minimized
→ modal measurement of NO

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° C is applied.

Proposed setup for NO₂ determination



Text based on Reg. 83

Sampling System Requirements

- The sampling system response time (from the probe to the analyser inlet) shall be no more than [TBD] seconds.
- The modal NO analyser shall be used with a constant flow (criteria for constant flow TBD) system to ensure a representative sample, unless compensation for varying CFV or CFO flow is made.

Nitrogen oxide (NO) analysis:

- The analyzer shall be either of the chemi-luminescent (CLA) or the ultra-violet resonance absorption (UV-RAS) type.
- The analyzers shall have a measuring range compatible with the accuracy required to measure the concentrations of the exhaust gas sample pollutants.
- Measurement error shall not exceed 2 per cent (intrinsic error of analyzer) disregarding the true value for the calibration gases.
- For concentrations of less than 100 ppm, the measurement error shall not exceed 2 ppm.
- The ambient air sample shall be measured on the same analyzer with an appropriate range.
- No gas drying device shall be used before the analyzer.

Text based on Reg. 83

- NO concentrations shall be calculated from the integrated NO analyzer reading, corrected for varying flow if necessary.

- Determination of NO

The average NO concentration is calculated as follows:

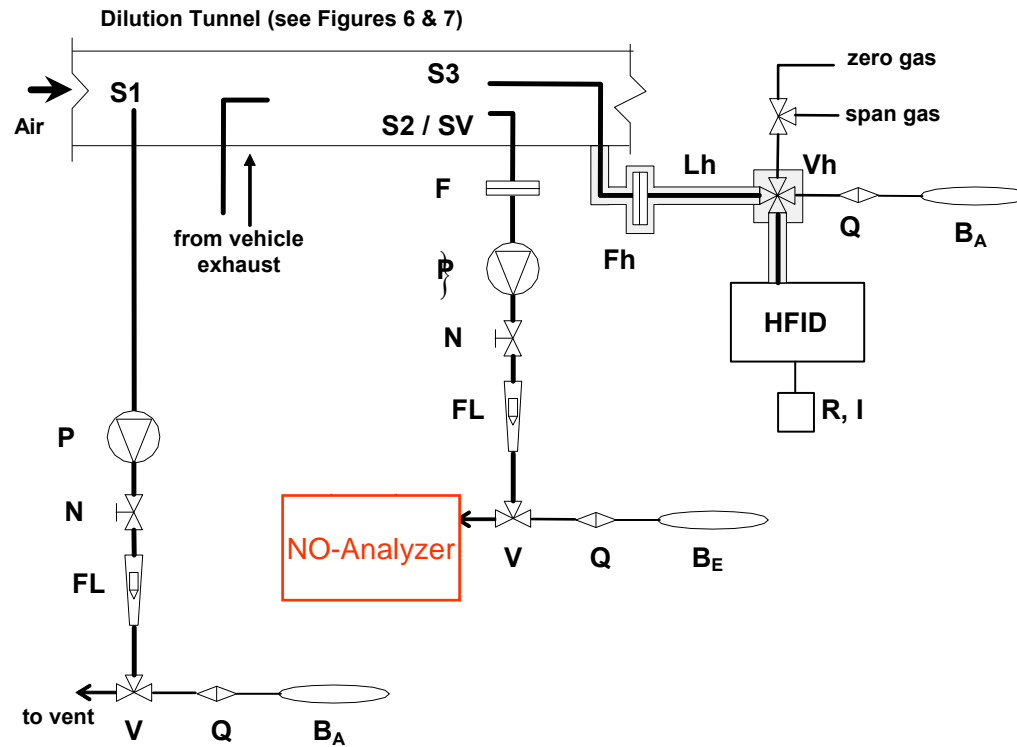
$$C_e = \frac{\int_{t_1}^{t_2} C_{NO} \cdot dt}{t_2 - t_1}$$

where:

$\int_{t_1}^{t_2} C_{NO} \cdot dt$ = integral of the recording of the modal NO analyzer over the test (t_2-t_1)

C_e = concentration of NO measured in the diluted exhaust in ppm.

Figure based on Reg. 83



Reg. 83 Figure 10: Gaseous Emissions Sampling Schematic
(addition for modal NO measurement)