



<b>WLTP DTP subgroup</b>	
<b>Date</b>	<b>11 June 2010</b>
<b>Title</b>	<b>Draft Ammonia (NH<sub>3</sub>) measurement procedure</b>
<b>Working paper number</b>	<b>WLTP-DTP-02-07</b>

## **1.0. Introduction**

These guidelines were developed following in response to discussions at the 1<sup>st</sup> DTP (Develop Test Procedure) meeting held in Ann Arbor in April 2010. It was identified that a test procedure is required for the measurement of NH<sub>3</sub>. 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**

The measurement of NH<sub>3</sub> in the exhaust gas of vehicles with SCR systems is a possible indicator that the reagent is not being overdosed and hence that the system is in control.

### **2.2. Existing legislation**

In developing this draft test procedure, it was appropriate to review existing legislation that measures NH<sub>3</sub>. Although not yet adopted as legislation, the coming Euro VI regulation (for heavy duty vehicles and engines) from the EU will contain a test procedure for measurement of NH<sub>3</sub> and this has formed the basis for this proposal.

## **3.0. Measurement principle**

Two alternative analyser concepts are proposed as anticipated in the Euro VI legislation, these being Laser Diode Spectrometer (LDS) or Fourier Transform Infra-Red (FTIR).

Contrary to the majority of today's light duty measurement procedures, and due to the high reactivity and solubility of NH<sub>3</sub> with water, it is proposed to measure NH<sub>3</sub> directly rather than from CVS bags.

As NH<sub>3</sub> is seen as a control measure rather than a pollutant emission, and therefore is expected to have a volumetric concentration limit, it is recommended to adopt a simple averaging process as foreseen in the Euro VI legislation.



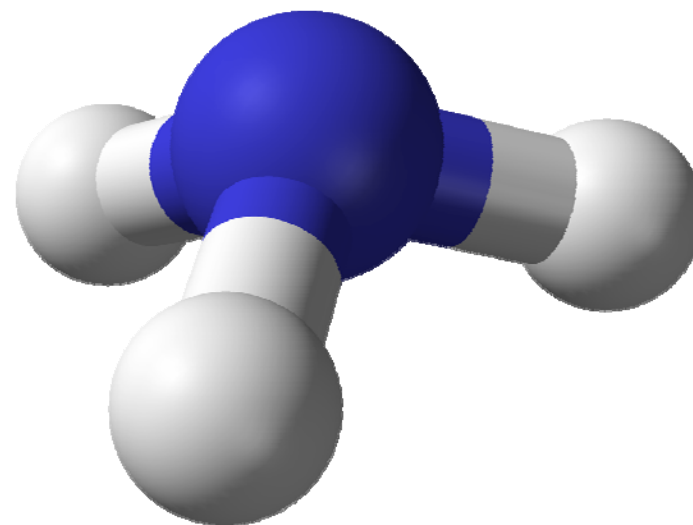
NH<sub>3</sub> Measurement  
method that could be applied to vehicles equipped with  
a SCR-system  
based on Euro VI comitology (heavy duty)

## **Draft Proposal**

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.

# Introduction: physical and chemical properties of ammonia (NH<sub>3</sub>)

- Colourless gas with characteristic pungent odour
- Polar molecule
- Reacts very well as base with acid substance (liquids, gases and surfaces)
- High solubility in water
- Melting point: -77,73°C
- Boiling point: -33,34 °C
- **IR spectroscopy**  
Major absorption bands  
3444, 3337, 1627, 950 cm<sup>-1</sup>
- **Mass Spectrometry**  
Masses of main fragments  
17 (100%)  
16(80%)  
15(9%)



# Measurement Principle

- 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)
- Following proposal of measurement method is based on proposal Euro VI comitology (heavy duty)

# Effects leading to measurement errors

- The following effects lead to loss of NH<sub>3</sub> during the measurement process and therefore should be avoided:
  - NH<sub>3</sub> show an high adsorption to polar surface. To minimize the effect piping and sample lines should be made of non sticky materials (e.g. PTFE, Stainless Steel, Subgroups to define ...)
  - Due to the high reactivity of NH<sub>3</sub> toward liquid water, condensation over the sampling line must be prevented.
  - Using instrument filter for NH<sub>3</sub> means to avoid high particulate load (significantly increased in presence of soot) before measuring; change of filter is recommended
  - Use the smallest possible filter

# Laser Diode Spectrometer (LDS)

- **Measurement principle**

The LDS employs the single line spectroscopy principle. The NH<sub>3</sub> absorption lines are chosen in the near infrared spectral range and scanned by a single-mode diode laser.

- **Installation**

The analyzer shall be installed either directly in the exhaust pipe (in-situ) or within an analyzer cabinet using extractive sampling in accordance with the instrument manufacturers instructions. If installed in an analyzer cabinet, the sample path (sampling line, pre-filter(s) and valves) shall be made of stainless steel or PTFE and shall be heated to [TBD] in order to minimize NH<sub>3</sub> losses and sampling artefacts. In addition, the sampling line should be as short as practically possible. Influence from exhaust temperature and pressure, installation environment and vibrations on the measurement shall be minimized, or compensation techniques be used. If applicable, temperature conditioned air used in conjunction with in-situ measurement for protection of the instrument, shall not affect the concentration of any exhaust component measured downstream of the device, or sampling of other exhaust components shall be made upstream of the device.

- **Cross interference**

The spectral resolution of the laser shall be within 0.5 cm<sup>-1</sup> in order to minimize cross interference from other gases present in the exhaust gas

# Fourier Transform Infrared (FTIR) analyzer

- **Measurement principle**
- The FTIR employs the broad waveband infrared spectroscopy principle. It allows simultaneous measurement of exhaust components whose standardized spectra are available in the instrument. The absorption spectrum (intensity/wavelength) is calculated from the measured interferogram (intensity/time) by means of the Fourier transform method.
- **Installation and sampling**
- The FTIR shall be installed in accordance with the instrument manufacturer's instructions. The NH<sub>3</sub> wavelength (see slide 2) shall be selected for evaluation. The sample path (sampling line, pre-filter(s) and valves) shall be made of stainless steel or PTFE and shall be heated to [TBD] in order to minimize NH<sub>3</sub> losses and sampling artefacts. In addition, the sampling line should be as short as practically possible.
- **Cross interference**  
The spectral resolution of the NH<sub>3</sub> wavelength shall be within 0.5 cm<sup>-1</sup> in order to minimize cross interference from other gases present in the exhaust gas

# Emission test procedure

- **Checking the analyzers**

Prior to the emissions test, the analyzer range shall be selected. Emission analyzers with automatic or manual range switching are permitted. During the test cycle, the range of the analyzers shall not be switched.

Zero and span response shall be determined, if the provisions of Section 'Determination of analyzer drift is not required' do not apply for the instrument. For the span response, a NH<sub>3</sub> gas that meets the specifications of Section 'NH<sub>3</sub> calibration gas' shall be used. The use of reference cells that contain NH<sub>3</sub> span gas is permitted. The analyzer shall be operated in a mode that minimizes the total system response time.

- **Collection of emission relevant data**

At the start of the test sequence, the NH<sub>3</sub> data collection shall be started, simultaneously. The NH<sub>3</sub> concentration shall be measured continuously and stored with at least 1 Hz on a computer system.

- **Operations after test**

At the completion of the test, sampling shall continue until system response times have elapsed. Determination of analyzer's drift according to Section 'Analyzer drift' is only required, if the information in Section 'Determination of analyzer drift is not required' is not met.



# Emission test procedure

- **Analyzer drift**  
As soon as practical but no later than 30 minutes after the test cycle is complete or during the soak period, the zero and span responses of the analyzer shall be determined. The difference between the pre-test and post-test results shall be less than 2 per cent of full scale.
- **Determination of analyzer drift is not required,**
  - if the zero and span drift specified by the instrument manufacturer in Sections 'Zero drift' and 'Span drift' meets the requirements of Section 'Analyzer drift', and if
  - the time interval for zero and span drift specified by the instrument manufacturer in Sections 'Zero drift' and 'Span drift' exceeds the duration of the test.

# Data Evaluation

- The average NH<sub>3</sub> concentration (ppm/test) shall be determined by integrating the instantaneous values over the cycle. The following equation shall be applied:

$$c_{\text{NH}_3} = \frac{1}{n} \sum_{i=1}^{i=n} c_{\text{NH}_3,i} \quad (\text{in ppm/test})$$

where:

$c_{\text{NH}_3,i}$  is the instantaneous NH<sub>3</sub> concentration in the exhaust gas, ppm  
 $n$  is the number of measurements

# Analyzer Specification

- **Linearity requirements**

- The analyzer shall comply with the following linearity requirements:

Intercept  $b \leq 0.5 \%$  max

Slope  $m$  0.99 - 1.01

Standard error  $SEE \leq 1 \%$

Coefficient of determination  $r^2$  max  $\geq 0.998$

- The linearity verification shall be performed at least every 12 months or whenever a system repair or change is made that could influence calibration.

- **Linearity verification**

At least 10 reference values shall be introduced to the measurement system, and the measured values shall be compared to the reference values by using a least squares linear regression. For maximum limits see above.

- **General requirements**

The measurement systems shall be warmed up according to the recommendations of the instrument manufacturer. The measurement systems shall be operated at their specified temperatures, pressures and flows according to the recommendations of the instrument manufacturer.

# Analyzer Specification

- **Procedure**

The linearity verification shall be run for each normally used operating range with

(a) The instrument shall be set at zero by introducing a zero signal. For gas analyzers, purified synthetic air (or nitrogen, see specification of gases) shall be introduced directly to the analyzer port.

(b) The instrument shall be spanned by introducing a span signal. For gas analyzers, an appropriate span gas shall be introduced directly to the analyzerport.

(c) The zero procedure of (a) shall be repeated.

(d) The verification shall be established by introducing at least 10 reference values (including zero) that are within the range from zero to the highest values expected during emission testing. For gas analyzers, known gas concentrations shall be introduced directly to the analyzer port.

(e) At a recording frequency of at least 1 Hz, the reference values shall be measured and the measured values recorded for 30 s.

(f) The arithmetic mean values over the 30 s period shall be used to calculate the least squares linear regression parameters according to equation  $y = mx + b$

where:

y = actual value of signal

m = slope of the regression line

x = reference value of signal

b = y intercept of the regression line

(g) The linear regression parameters shall meet the above requirements

(h) The zero setting shall be rechecked and the verification procedure repeated, if necessary.

# Analyzer Specification

- With the prior approval of the approval authority, less than 10 reference points are permitted, if an equivalent accuracy can be demonstrated.
- For the linearity verification, a NH<sub>3</sub> gas that meets the specifications of Section ‘NH<sub>3</sub> calibration gas’ shall be used. The use of reference cells that contain NH<sub>3</sub> span gas is permitted.
- Instruments, whose signals are used for compensation algorithms, shall meet the above linearity requirements
- Linearity verification shall be done as required by internal audit procedures, by the instrument manufacturer or in accordance with ISO 9000 or ISO 17025 requirements.
- **Analyzer specifications**  
The analyzer shall have a measuring range and response time appropriate for the accuracy required to measure the concentration of NH<sub>3</sub> under transient and steady state conditions.

# Analyzer Specification

- **Minimum detection limit**  
The analyzer shall have a minimum detection limit of  $< 2$  ppm under all conditions of testing.
- **Accuracy**  
The accuracy, defined as the deviation of the analyzer reading from the reference value, shall not exceed  $\pm 3$  per cent of the reading or  $\pm 2$  ppm, whichever is larger.
- **Zero drift**  
The drift of the zero response and the related time interval shall be specified by the instrument manufacturer.
- **Span drift**  
The drift of the span response and the related time interval shall be specified by the instrument manufacturer.
- **System response time**  
The system response time shall be  $\leq 20$  s.
- **Rise time**  
The rise time of the analyzer shall be  $\leq 5$  s.
- **NH<sub>3</sub> calibration gas**  
A gas mixture with the following chemical composition shall be available. NH<sub>3</sub> and purified nitrogen The true concentration of the calibration gas shall be within  $\pm 2$  per cent of the nominal value, and shall be traceable to national or international standards. The concentration of NH<sub>3</sub> shall be given on a volume basis (volume percent or volume ppm). The expiration date of the calibration gases stated by the manufacturer shall be recorded.

# Alternative Systems

- Other systems or analyzers may be approved by the approval authority, if it is found that they yield equivalent results.
- "Results" refer to average cycle specific NH<sub>3</sub> concentrations