Calibration gas influence estimation
AVL Emission Test Systems, 2018
Your Emission is our Mission

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Introduction Notes

Statistic versus Tolerance:

- There is a “Tolerance” approach in most emission legislations:
  - A calibration gas tolerance is defined.
  - All other requirements and tolerances are related to the actual calibration gas. Most of that is done in form of a maximum allowed +/-x% deviation.
- A “Statistical” approach should be based on a measurement chain uncertainty evaluation, with uncertainties, repeatability’s and probabilities
  - more scientific correct
  - required by ISO 17025.
- Both are applicable, but will show different numbers:
  - The “Statistic” approach:
    - will result in higher % numbers, since it will include the whole measurement chain and the traceability back to a national standard.
    - is much more complex, especially in case of an emission laboratory.
  - The “Tolerance” approach is:
    - more simple
    - easier to validate (important for certification test approvals)

In this document we have reduced it as much as possible to calibration gas influences only, but as a minimum some evaluations from analyzers and linearization must be included.

Also note, that this is a general evaluation and is not based on a certain analyzer or gas manufacturer product.
Light Duty Emission Result calculation (GTR-15)

Example based on: ECE/TRANS/180 - Annex 7 Calculations (WLTP, GTR-15, Euro-6d temp), some calculations might be slightly different depending on actual test bed configuration, CO2 correction for 12V battery not shown, no PM and PN background correction applied (optional).

Specific humidity:
\[ H = \frac{6.211 \times R_a \times P_d}{P_b - P_d \times R_a \times 10^{-2}} \]

NOx humidity correction factor:
\[ KH = \frac{1}{1 - 0.0329 \times (H - 10.71)} \]

Fuel properties
\[ X = 100 \times \frac{x}{x + \frac{y}{2} + 3.76(x + \frac{y}{4} - \frac{2}{x})} \]

Dilution Factor
\[ DF = \frac{x}{C_{CO2} + (C_{Re} + C_{CO2}) \times 10^{-4}} \]

Concentrations, corrected [ppm]:
\[ C_i = C_e - C_d \times \left(1 - \frac{1}{DF}\right) \]

Particle Number Emission [#/km]:
\[ PN = \frac{V \times k \times (C_e + C_d - C_e \times \frac{d}{d}) \times 10^3}{d} \]

Particulate Mass Emission [mg/km]:
\[ PM = \frac{V_{mix} \times P_e}{V_{mix} \times k} \]

Gaseous Mass Emissions [g/km]:
\[ M_{phase} = \frac{V_{mix,phase} \times P_1 \times K_{phase} \times C_{phase} \times 10^{-6}}{C_{phase}} \]

Densities:
\[ P_i \quad @ \quad 273.15 \, K (0 \, ^\circ C) \quad \text{and} \quad 101.325 \, kPa: \]
- Carbon monoxide (CO): \( p = 1.25 \, g/l \)
- Carbon dioxide (CO2): \( p = 1.964 \, g/l \)
- Nitrogen oxides (NOx): \( p = 2.050 \, g/l \)
- Hydrocarbons:
  - for petrol (E0): \( p = 0.619 \, g/l \)
  - for petrol (E5): \( p = 0.632 \, g/l \)
  - for petrol (E10): \( p = 0.646 \, g/l \)
  - for diesel (B0): \( p = 0.620 \, g/l \)
  - for diesel (B5): \( p = 0.623 \, g/l \)
  - ...

Example based on: ECE/TRANS/180 - Annex 7 Calculations (WLTP, GTR-15, Euro-6d temp), some calculations might be slightly different depending on actual test bed configuration, CO2 correction for 12V battery not shown, no PM and PN background correction applied (optional).
Calibration gas and gas analyzer influences

Specific humidity:

\[ H = \frac{6.211 \times R_a \times P_d}{P_h - P_d \times R_h \times 10^{-2}} \]

NOx humidity correction factor:

\[ KH = \frac{1}{1 - 0.0329 \times (H - 10.71)} \]

Fuel properties:

\[ X = 100 \times \frac{x + \frac{y}{4} + 3.76 \left(\frac{x + \frac{y}{4}}{2}\right)}{x + \frac{y}{4} + 3.76} \]

\[ DF = \frac{X}{C_{CO2} + (C_{H2} + C_{CO2}) \times 10^{-4}} \]

Concentrations, corrected [ppm]:

\[ C_i = C_e - C_d \times \left(1 - \frac{1}{DF}\right) \]

Densities:

\[ \rho_i @ 273.15 K (0 \degree C) and 101.325 kPa: \]

- Carbon monoxide (CO) \( \rho = 1.25 \) g/l
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Example based on: ECE/TRANS/180 - Annex 7 Calculations (WLTP, GTR-15, Euro-6d temp), some calculations might be slightly different depending on actual test bed configuration, CO2 correction for 12V battery not shown, no PM and PN background correction applied (optional).
Calibration gas and gas analyzer influences

**Dominant influence:**
- is the calibration of the analyzer and the concentration measurement of the diluted exhaust bag.
- The uncertainty of the calibration gas effects the uncertainty of the final result directly (1:1).

**Second level (minor) influence:**
- is the dilution air background measurement used to correct the final result. Typically that are low concentrations and have less influence to the absolute result. (for emissions well below the criteria emissions that will be different, and for CO2 it is in all cases minor). Calibration gas uncertainty will even be partly compensated since it will effect the exhaust and dilution air bag concentration in the same way. (same calibration gas, same analyzer and range used).
- is effecting the dilution air background correction also via the dilution factor (DF) calculation. The DF is an estimation only (engine is running stochiometric and running all the time, which is not the case for Diesel or engines with Start/Stop or Hybrid vehicles). For CO2 it can be neglected.

**Additional notes:**
- When measuring low emission concentrations, the quality of the zero gas and the zero adjustment procedure (purging and stabilization) might be of similar or even more importance than the calibration gas quality. (see following pages)
- Calibration gas distribution can be an issue, problematic installations and/or operation might not ensure, that the calibration gas reaches the analyzer with the same quality as it was inside the bottle. (see following pages)
Uncertainty estimation: Concentration measurement

Statistical uncertainty evaluation of concentration measurement, ISO-17025 compliant

Conventional multi range analyzers (old)
- 95% Probability under the following assumptions
  - Zero Repeatability: 0,5% (95% Probability)
  - Span Repeatability: 0,5% (95% Probability)
  - Gas Divider: 1,0% (95% Probability)
- Calibration gas scenarios:
  Gas concentration at 80% of measurement range
  Gas with 99% probability:
  1. Scenario: Span Gas: 2,0% Lin. Gas: 2,0%
  2. Scenario: Span Gas: 2,0% Lin Gas: 1,0%
  3. Scenario: Span Gas: 1,0% Lin Gas: 1,0%

Single range analyzers (modern analyzer)
- With a good "Zero" point calibration
- Linearization points at the lower end of the range.
  - 95% Probability under the following assumptions
    - Zero Repeatability: 0,05% (95% Probability)
    - Span Repeatability: 0,5% (95% Probability)
    - Gas Divider: 1,0% (95% Probability)
    - Linearization Gas: 1,0% (99% Probability)
    - Span Gas Conc.: 1,0%, (99% Probability)

For details see: High Performance Linearization Procedures for Emission Analyzers, SAE No. 2000789; Dr. Ch. Weidinger, AVL; Dr. F. Kampelmühler, AVL
to be considered too

When we increase the span gas tolerance, then we need also to adjust:

- Increase of the limit of +/-2% for the “Total System validation test” (also known as Propane injection test, CFO).
  
  For this test, the calibration gases specification, propane purity, injection device calibration, CVS calibration, leaks and analyzer calibration are covered, so if the calibration gas has already an uncertainty of 2%, it will not work.

- Increase the limit of +/-2% for the Mid-Span gas test (currently limit is +/-2%)
  
  In this test 2 different gases are involved, the gas-divider and analyzer calibration is included. If the two gases have already +/-2% (worst case scenario would already be 4%.

- ... (needs some more investigation if there are others too)

Align with the GTR-19 (EVAP procedures):

- Hydrocarbon retention test of the chamber limit +/-2%.
- **Attention:** GTR-19 Draft still refers for the gas specifications to UNR-83, that should be changed to references to GTR-15
Calibration gas distribution

Calibration gas distribution quality:

- Calibration gas distribution is an issue too.

- Some distribution line installations (materials, diffusion, chemical reactions, ...) and operation (bottle exchange, purge, stabilization time, frequency of use, ...) might not ensure, that the “good” calibration gas of the bottle is reaching the analyzer with the same quality.