

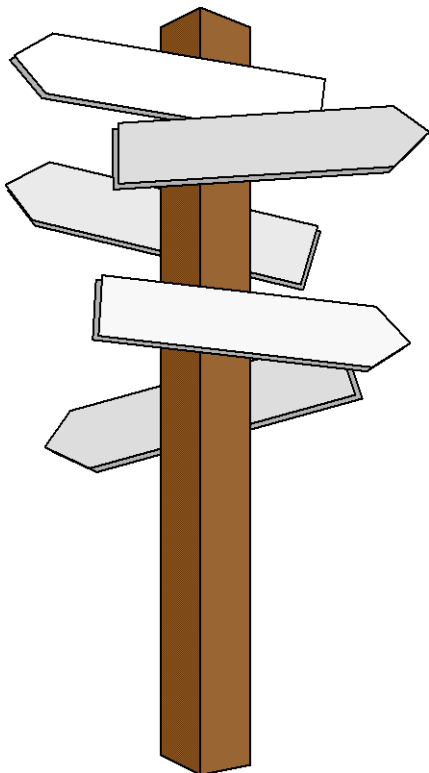
MacPoll Zero Gas

Requirements from EN Air Quality Standards

***Theo Hafkenscheid
RIVM-MIL
NL – BILTHOVEN***



Overview of presentation



- ▶ ***CEN/TC264 Air Quality***
- ▶ ***Uses of zero gases***
- ▶ ***Requirements for zero gases***
- ▶ ***Current practice***
- ▶ ***Conclusions***

CEN/TC 264 Air Quality

- ▶ ***<http://www.cen.eu/cen/Sectors/TechnicalCommitteesWorkshops/CENTechnicalCommittees/Pages/TCStruc.aspx?param=6245&title=CEN/TC%20264>***

CEN/TC 264 Air Quality

- ▶ ***Standardization of methods for air quality characterization of***
 - ▶ **Emissions into air**
 - ▶ ***Ambient air***
 - ▶ **Indoor air**
 - ▶ **Gases in and from the ground**
 - ▶ **Deposition**
 - ☞ **Measurement methods for air pollutants (particles, gases, odours, micro organisms)**
 - ☞ **Methods for the determination of the efficiency of gas cleaning systems.**

CEN/TC 264 Air Quality

- ▶ ***Established in 1990***
- ▶ ***Currently 27 active Working Groups and 1 Task Force***
- ▶ ***Zero gases highly relevant for standards of TC 264***
 - ▶ **Most stringent requirements for measurements of gases in ambient air (low ppb concentration levels)**



Zero gas

Applications of zero gases

- ▶ ***CEN/TC 264 WG12***
 - ▶ Has produced 5 (draft) standards for measurement of gases (NO_x, SO₂, O₃, CO, C₆H₆)
- ▶ ***Each standards contains sections on***
 - ▶ Type approval of monitoring equipment
 - ▶ QA/QC of measurements (calibrations, checks)
- ▶ ***For both zero gases are required***
 - ▶ For zero calibrations and checks
 - ▶ For dilution of high concentration calibration gas, span gas and test gases

Applications of zero gases

- ▶ ***Zero gas may be from***
 - ▶ **Cylinders**
 - ▶ **Zero-air generators**
- ▶ ***Quality of zero gases shall not adversely affect results of tests, checks and calibrations***
 - ▶ **Each standard contains purity requirements for zero gases**
- ▶ ***Zero gases in the field shall be checked against independent standard gases***

Applications of zero gases

- ▶ ***Zero gases are used by***
 - ▶ **Laboratories performing type-approval tests of monitoring equipment**
 - ▶ **Calibration laboratories of air quality monitoring networks**
 - ▶ **Field operators of air quality monitoring networks**
- ▶ ***Under different environmental conditions***

Requirements for zero gases

► Example: NO_x

Pollutant	Concentration
CO ₂	≤ 4,0 μmol/mol
O ₃	≤ 2,0 nmol/mol
NH ₃	≤ 1,0 nmol/mol
Water vapour	≤ 150 μmol/mol
NO	≤ 1,0 nmol/mol
NO ₂	≤ 1,0 nmol/mol

Type-approval testing of interferences

Pollutant	Concentration
CO ₂	≤ 400 μmol/mol
O ₃	≤ 2,0 nmol/mol
NH ₃	≤ 10 nmol/mol
Water vapour	≤ 150 μmol/mol
NO	≤ 1,0 nmol/mol
NO ₂	≤ 1,0 nmol/mol

Other type-approval tests

Requirements for zero gases

- ▶ ***Preferably one zero gas for laboratory applications and one for field applications***
 - ▶ **Laboratory gas to be used as transfer standard for field checks**
- ▶ ***Should combine all purity requirements !***
- ▶ ***Should have levels of impurities certified !***

Requirements for lab gas

Requirement	Component(s)
≤ 1 nmol/mol	NH ₃ , NO, NO ₂ , SO ₂ , xylenes, O ₃ , toluene
$\leq 0,1$ µg/m ³	Benzene
≤ 1 µg/m ³	Sum of interferences of benzene
$\leq 0,5$ nmol/mol	N ₂ O
$\leq 0,1$ µmol/mol	H ₂ S, CO
$\leq 4,0$ µmol/mol	CO ₂
≤ 150 µmol/mol	H ₂ O

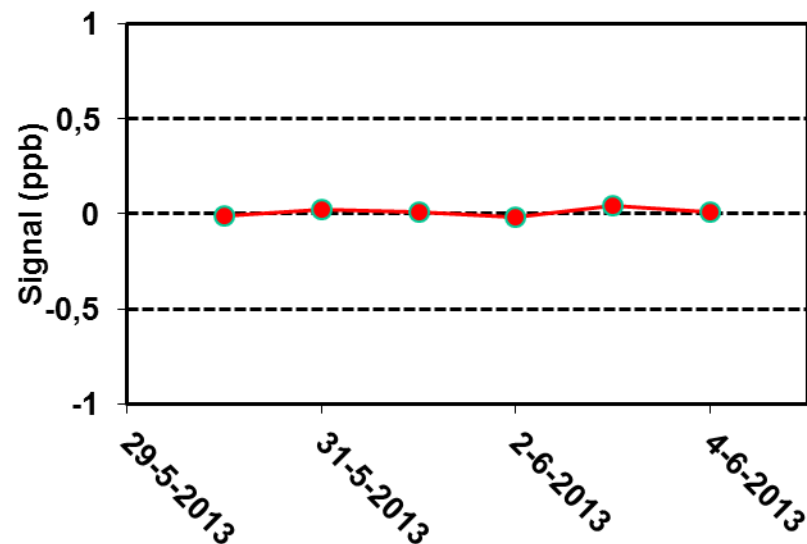
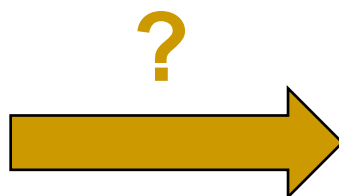
Requirements for other zero gases

Requirement	Component(s)
≤ 1 nmol/mol	NO, NO ₂ , SO ₂ , xylenes, O ₃ , toluene
≤ 10 nmol/mol	NH ₃
$\leq 0,1$ $\mu\text{g}/\text{m}^3$	Benzene
≤ 10 $\mu\text{g}/\text{m}^3$	Sum of interferents of benzene
$\leq 0,5$ nmol/mol	N ₂ O
$\leq 0,1$ $\mu\text{mol}/\text{mol}$	H ₂ S, CO
≤ 400 $\mu\text{mol}/\text{mol}$	CO ₂
≤ 150 $\mu\text{mol}/\text{mol}$	H ₂ O

Requirements for zero gases

- ▶ ***2012 WG12 standards allow for use of monitors with different ranges (generally lower) when type approved***
 - ▶ **Requirements for zero gases should be scaled accordingly !**
- ▶ ***CEN/TC 264 WG12 will produce a standard for measurement of ozone precursors***
 - ▶ **Need for stringent requirements for levels of interferences !**

Current practice



Current practice

- ▶ ***Most networks and laboratories use zero-air generators***
 - ▶ “Unlimited” supply of zero air
 - ▶ Substantial choice of manufacturers
- ▶ ***Quite different specifications***
 - ▶ Sometimes qualitative
 - ▶ < 0,1 ppb, < 0,5 ppb, < 1 ppb for NO_x, SO₂, CO, O₃
 - ▶ Sometimes information for other components (e.g., THC)
 - ▶ Sometimes information for H₂O

Current practice

- ▶ *Zero air in cylinders with appropriate specifications are scarce*
 - ▶ Mostly aimed at use as GC FID gas

- ▶ *When levels are given, how are these measured ?*
 - ▶ What equipment ?
 - ▶ How calibrated ?
 - ▶ Calibration standards with traceable compositions ?

Current practice

- ▶ *Most networks and laboratories are unable to do (im)purity checks/determinations*
 - ▶ **Other than below limit of detection of own equipment**
- ▶ *Rely on manufacturer's specifications*
 - ▶ **Supported by information on maintenance**
- ▶ *Attempt to find supporting evidence from inter-laboratory comparisons*



Conclusions

Conclusions

- ▶ *EU Standards for measurement of gaseous air pollutants contain stringent requirements for purities of zero gases*
- ▶ *Users rely on specifications of producers of generators or cylinder zero gas*
- ▶ *If given, it is unclear how these specifications are determined*
- ▶ *Users have little or no means to determine qualities of zero gases themselves*

Conclusions

- ▶ ***Need for (network of) institutes capable of testing/certifying zero gases at required specifications***
 - ▶ **Gas metrology laboratories ?**
 - ▶ **National Reference Laboratories for air quality monitoring ?**
 - ▶ **Common, harmonized methods and calibration standards ?**
- ▶ ***Need for comparisons of zero gases***

Questions

- ▶ ***Are such low levels of impurities measurable ?***
- ▶ ***If so, by whom ?***
 - ▶ **Gas metrology laboratories ?**
 - ▶ **Producers ?**
 - ▶ **What should monitoring networks do ?**
- ▶ ***If so, at what costs ?***
- ▶ ***Will costs be balanced by benefits ?***
 - ▶ **Would require studies into effects of using “old” and “new” technology zero gases**



Thank you !