

Results questionnaire & review

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Content presentation

Provide an overview detailing:

—the types of impurities present in zero gases and their occurrence

—methods used to measure their concentration

—suitable purifier systems

with respect to the specifications for zero gas set in the EN-standards EN14211, EN14212 & EN14626 relative to the reference methods for the measurement of ambient air pollutants (NO_x , SO_2 & CO).

Data sources

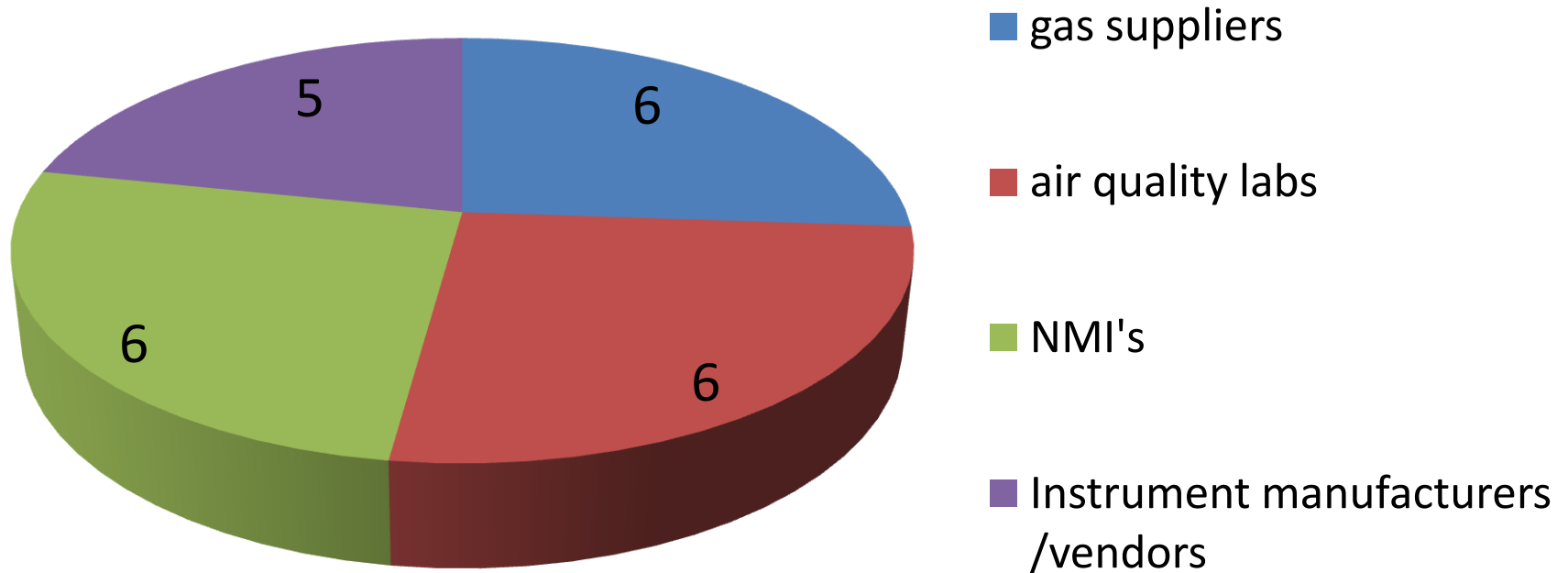
- returned questionnaires
- review of commercial purifier systems & zero air generators

Questionnaire

WORKSHOP ZERO GASES

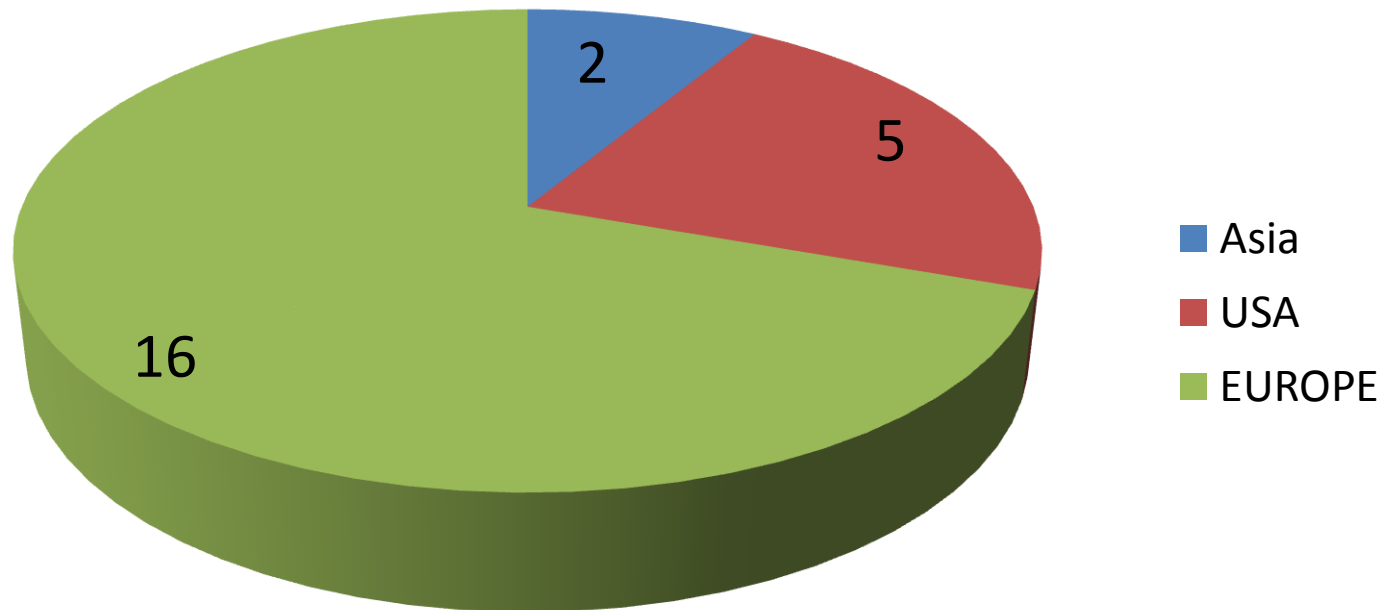
Air		Air			Air		Air		
Pollutant	Standard	Concentration	Company product ¹	Specify type of product	Specs (in ppb)	Analytical method	Instrument (technique)	LoD (ppb)	Calibration method
<i>example 1</i>	<i>EN14211:2012 & EN14626:2012</i>	<i>≤ 4.0 ppm</i>	<i>analysis method</i>	<i>see instrument</i>	<i>0-5000 ppb</i>	<i>CRDS</i>	<i>near-IR CRDS spectrometer model 56CT</i>	<i>3</i>	<i>gas cylinders</i>
<i>example 2</i>	<i>EN14211:2012 & EN14212:2012</i>	<i>≤ 1.0 ppb</i>	<i>purifier</i>	<i>model abc123</i>	<i><1 ppb</i>	<i>chemiluminescence</i>	<i>NOx analyzer model 75JP</i>	<i>0.5</i>	<i>gas phase titration</i>
<i>example 3</i>	<i>EN14211:2012 & EN14212:2012</i>	<i>≤ 1.0 ppb</i>	<i>cylinder</i>	<i>nitrogen 5.0</i>	<i><1 ppb</i>	<i>chemiluminescence</i>	<i>NOx analyzer model 75JP</i>	<i>0.5</i>	<i>gas cylinders</i>
CO ₂	EN14211:2012 & EN14626:2012	≤ 4.0 ppm	cylinder/purifier/generator/analysis method						
O ₃	EN14211:2012	≤ 2.0 ppb	cylinder/purifier/generator/analysis method						
NH ₃	EN14211:2012	≤ 1.0 ppb	cylinder/purifier/generator/analysis method						
	EN14212:2012	≤ 2.0 ppb	cylinder/purifier/generator/analysis method						
	EN14211:2012 & EN14212:2012	≤ 10 ppb	cylinder/purifier/generator/analysis method						
Water vapour	EN14211:2012 & EN14212:2012 & EN14626:2012	≤ 150 ppm	cylinder/purifier/generator/analysis method						
NO	EN14211:2012 & EN14212:2012 & EN14626:2012	≤ 1.0 ppb	cylinder/purifier/generator/analysis method						
NO ₂	EN14211:2012 & EN14212:2012	≤ 1.0 ppb	cylinder/purifier/generator/analysis method						
H ₂ S	EN14212:2012	≤ 0.1 ppm	cylinder/purifier/generator/analysis method						
m-Xylene	EN14212:2012	≤ 1.0 ppb	cylinder/purifier/generator/analysis method						
SO ₂	EN14212:2012	≤ 1.0 ppb	cylinder/purifier/generator/analysis method						
N ₂ O	EN14626:2012	≤ 0.5 ppb	cylinder/purifier/generator/analysis method						

Returned questionnaires



In total 23 questionnaires were returned (>20% of total sent out)

Geographical distribution



Analytical methods: CO

Techniques (ranking based on frequency of use)

- 1) NDIR (Horiba, Thermo Scientific)
- 2) Gas chromatography
- 3) Laser spectroscopy (CRDS/CEAS/TDLS)

Respondent	DETECTION LIMITS (ppb)			
	<u>Air Quality labs</u>	<u>NMI's</u>	<u>Instr. Manufacturers</u>	<u>Gas Producers</u>
1.	0,5*	0,5	<1	5
2.	10	1	<2	20
3.	40	1	<100	50/50
4.	<50	10		
5.	<80			
6.	<100			

*=NOAA

Gas mixtures: CO

Specifications of zero gas by gas producers

Respondent	SPECIFICATIONS (ppb)
1.	<50
2.	<50
3.	<100
4.	100
5.	<500

Notes:

- specs based on the best grade zero gas produced
- results nitrogen and air combined
- EN-standards: CO < 0.1 ppm

Respondent	DETECTION LIMITS (ppb)			
	Air Quality labs	NMI's	Instr. Manufacturers	Gas Producers
1.	0,5*	0,5	<1	5
2.	10	1	<2	20
3.	40	1	<100	50/50
4.	<50	10		
5.	<80			
6.	<100			

Analytical methods: SO₂

Virtually always measured using fluorescence
(Horiba, Thermo Scientific, Teledyne)

Respondent	DETECTION LIMITS (ppb)			
	<u>Air Quality labs</u>	<u>NMI's</u>	<u>Instr. Manufacturers</u>	<u>Gas Producers</u>
1.	0,05	0,05	0,025 [#]	0,5
2.	<0,5	0,5 [*]		5
3.	0,5	1		10
4.	<1	3		
5.	<1			

*laser spectroscopy

[#]accumulation + ion chromatography

Gas mixtures: SO₂

Specifications of zero gas by gas producers

Respondent	SPECIFICATIONS (ppb)
1.	<5
2.	<5
3.	<50
4.	<100

Notes:

EN-standards: SO₂ < 1 ppb

-specs based on the best grade zero gas produced

-results nitrogen and air combined

Respondent	DETECTION LIMITS (ppb)			
	<u>Air Quality labs</u>	<u>NMI's</u>	<u>Instr. Manufacturers</u>	<u>Gas Producers</u>
1.	0,05	0,05	0,025 [#]	0,5
2.	<0,5	0,5 [*]		5
3.	0,5	1		10
4.	<1	3		
5.	<1			

Analytical methods: NO

Virtually always measured using chemiluminescence
(Thermo Scientific, Environnement-SA, Horiba)

Respondent	DETECTION LIMITS (ppb)			
	<u>Air Quality labs</u>	<u>NMI's</u>	<u>Instr. Manufacturers</u>	<u>Gas Producers</u>
1.	0,05	0,1	0,35	0,4
2.	<0,4	0,4	10	5
3.	0,5	0,5*		5
4.	0,5	1		10
5.	<1			

*laser spectroscopy

For NO₂ some specified slightly higher detection limits.

Gas mixtures: NO

Specifications of zero gas by gas producers

Respondent	SPECIFICATIONS (ppb)
1.	<5
2.	<10
3.	<20
4.	20
5.	<100

Notes:

-EN-standards: NO < 1 ppb

Respondent	DETECTION LIMITS (ppb)			
	Air Quality labs	NMI's	Instr. Manufacturers	Gas Producers
1.	0,05	0,1	0,35	0,4
2.	<0,4	0,5*	10	5
3.	0,5	0,4		5
4.	0,5	1		10
5.	<1			

Analytical methods: H₂O

100

A variety of techniques is used:

...roscopy (CRDS/TDLS), crystal oscillator, chemical (DL not indicated), dew point, P₂O₅.

P
Z
E
R
O
G
A
S
E
S

Respondent	DETECTION LIMITS (ppb)			
	Air Quality labs	NMI's	_____	<u>Gas Producers</u>
5.				100
6.				100

Gas mixtures: H₂O

Specifications of zero gas by gas producers

Respondent	SPECIFICATIONS (ppb)
1.	20
2.	<500
3.	<500
4.	<500
5.	<1000

Notes:

- EN-standards: H₂O < 150 ppm
- specs based on the best grade zero gas produced
- results nitrogen and air combined

Respondent	DETECTION LIMITS (ppb)			
	Air Quality labs	NMI's	Instr. Manufacturers	Gas Producers
1.	~200 (technique?)	5	1	10
2.		1300	1,5	20
3.			2	20
4.			<3000	100
5.				100
6.				100

Calibration & Accreditation



Calibration

- mostly using gas cylinders (few mention use of PRM's), often in combination with dilution
- other methods: permeation or gas phase titration

Accreditation

- Some mention ISO 17025 accreditation



Gas purifiers (1)

In the review, specifications of gas purifiers from 10 suppliers were compiled (data mainly taken from the Internet).

SPECIFICATIONS (in ppb)*					
CO		NO _x		SO ₂	
typical	lowest	typical	lowest	typical	lowest
1	0,5	1	<0,1	0,5	<0,001



*Some manufacturers specify the removal efficiency (normally 99.5-99.9%). For a 1 ppm challenge the level of remaining impurity is 1-5 ppb.

Gas purifiers(2)

SPECIFICATIONS (ppb)							
CO ₂		NH ₃		HC as CH ₄		H ₂ O	
typical	lowest	typical	lowest	typical	lowest	typical	lowest
1	<0,1	1	<0,005	1	<0,5	1	<0,1

Zero air generators (1)

Specifications of zero gas analyzers from 21 suppliers were compiled (data mainly taken from the Internet).

SPECIFICATIONS (in ppb)					
CO		NO _x		SO ₂	
typical	lowest	typical	lowest	typical	lowest
50-100	10	0,5-100	0,1	0,5	0,1



Note: specifications of zero air generators are frequently based on the specifications of the purifiers.

Zero air generators (2)

SPECIFICATIONS							
CO ₂ (ppm)		O ₃ (ppb)		HC as CH ₄ (ppb)		H ₂ S (ppb)	
typical	lowest	typical	lowest	typical	lowest	typical	lowest
5-10	1	0,5	0,4	0,5-100	0,4	0,5	0,1

Other specified compounds include BTEX and NH₃.

Concluding remarks (1)

- For CO various techniques used: NDIR/GC/laser
- NO_x / SO₂ dominated by CLD /fluorescence
- For H₂O laser spectroscopy mostly frequently used

Concluding remarks (2)

- On average, detection limits analytical equipment gas producers are higher than of other groups.
- Zero air generator specifications often sub ppb except for CO and CO₂.
- Filter specifications often extremely low (How validated? Sampling issues?).

Thanks to VSL colleagues, WP2 partners MACPoll & Tanil Tarhan (UME-TUBITAK)!