ZERO GAS REFERENCE STANDARDS

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CITAC Best Paper Award 2016

Introduction

- EMRP MacPoll Project

Goal:

Improve the traceability and comparability of measurement results of current air monitoring techniques

Introduction

- What is “zero gas”?

Air or N_2 with a specification for relevant impurities to meet the requirements of European air quality standards for the reference methods used to measure pollutants in air.

More generally, zero gas is usually a high purity source of the matrix gas being measured, where components of relevance to the measurements are present at negligible amount fractions or are quantified so as to not cause a systematic bias.

Introduction

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- Is there a universal “zero gas”?

Table 1 Specifications of the zero gas for type approval of nitrogen monoxide, nitrogen dioxide, sulphur dioxide, ozone and carbon monoxide analysers. Values have been obtained from standards EN 14212 (sulphur dioxide), EN 14211 (nitrogen monoxide and nitrogen dioxide), EN 14625 (ozone) and EN 14626 (carbon monoxide)

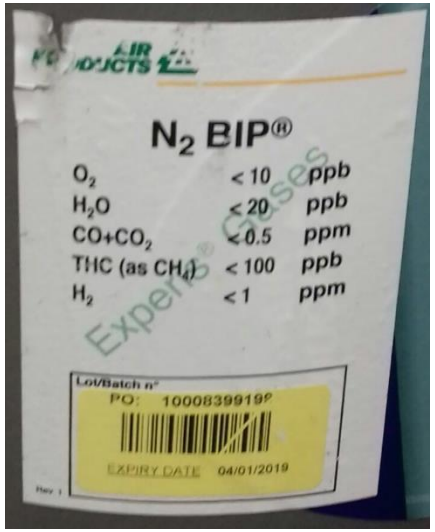
	Amount fraction for interference tests (nmol mol^{-1})				Amount fraction for other tests (nmol mol^{-1})			
Impurity	SO_2	NO/NO_2	O_3	CO	SO_2	NO/NO_2	O_3	CO
CO_2	—	≤4000	—	≤4000	—	≤400 000	—	≤400 000
O_3	—	≤2	≤1	—	—	≤2	≤1	—
H_2S	≤100	—	—	—	≤100	—	—	—
NH_3	≤2	≤1	—	—	≤10	≤10	—	—
NO	≤1	≤1	—	≤1	≤1	≤1	—	≤1
NO_2	≤1	≤1	—		≤1	≤1	—	—
N_2O	—	—	—	≤0.5	—	—	—	≤0.5
m-Xylene	≤1	—	≤1 (xylenes)	—	≤1	—	≤1 (xylenes)	—
Toluene	—	—	≤1	—	—	—	≤1	—
H_2O	≤150 000	≤150 000	≤150 000	≤150 000	≤150 000	≤150 000	—	≤150 000
SO_2	≤1	—	—	—	≤1	—	—	—
CO	—	—	—	≤100	—	—	—	≤100

Introduction

- Our paper: **Zero gas reference standards** *Anal. Methods* (2016) 8, 3014-3022

Description of the problems

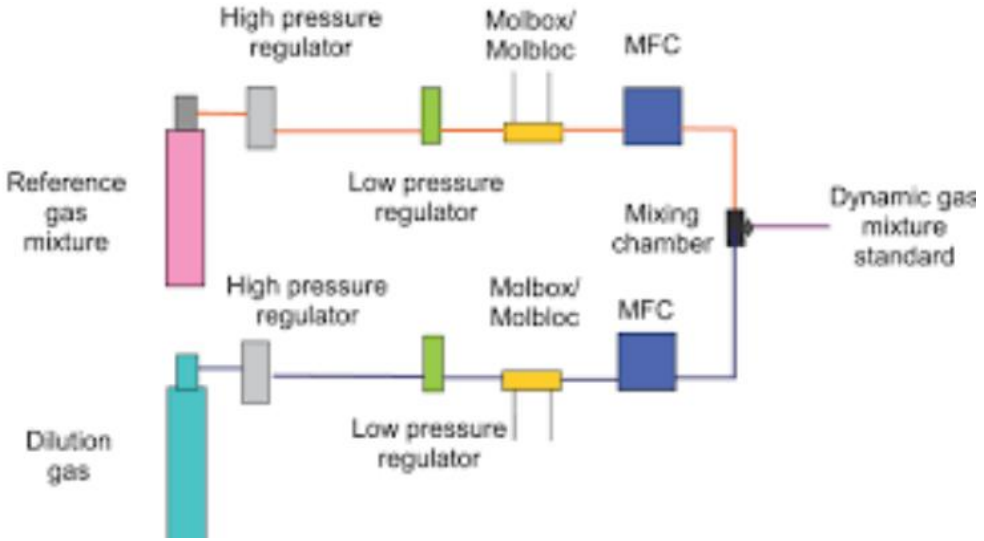
- We need to know the amount of impurities to properly **assess the uncertainty** of measurements.
- Impurities in commercial high purity gases reported as **a maximum value with no uncertainty**.
- Zero air generators and filters degrade with use and time.



- **There are no reference standards for zero gases.**

Description of the problems

- How reference gas mixtures are prepared?



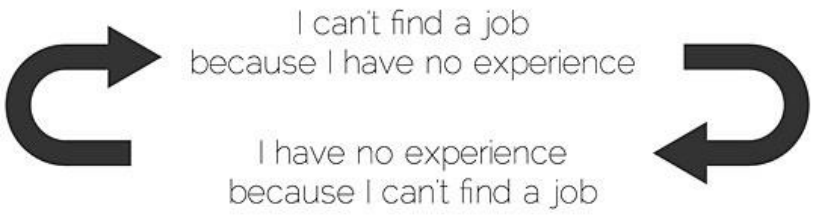
H-P Haerri, T Macé, J Waldén, C Pascale, B Niederhauser, K Wirtz, V Stovcik, C Sutour, J Couette and T Waldén (2017) *Measurement Science and Technology*, 28 (3)

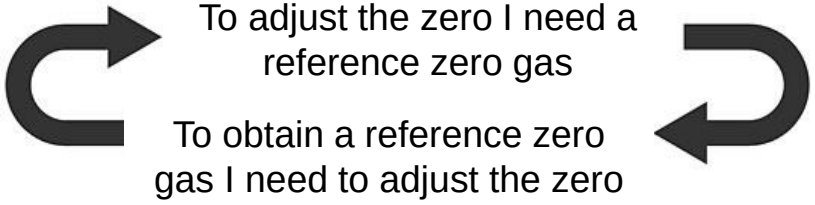
Description of the problems

Quantification of target components in balance gases is essential but very challenging due to:

- The **detection limits** of current analytical techniques.
- The difficulty of establishing a **real zero response** against which to compare.
- Moreover, absolute analytical methods also require a zero gas to define the baseline.

Catch 22 situation





Current solutions

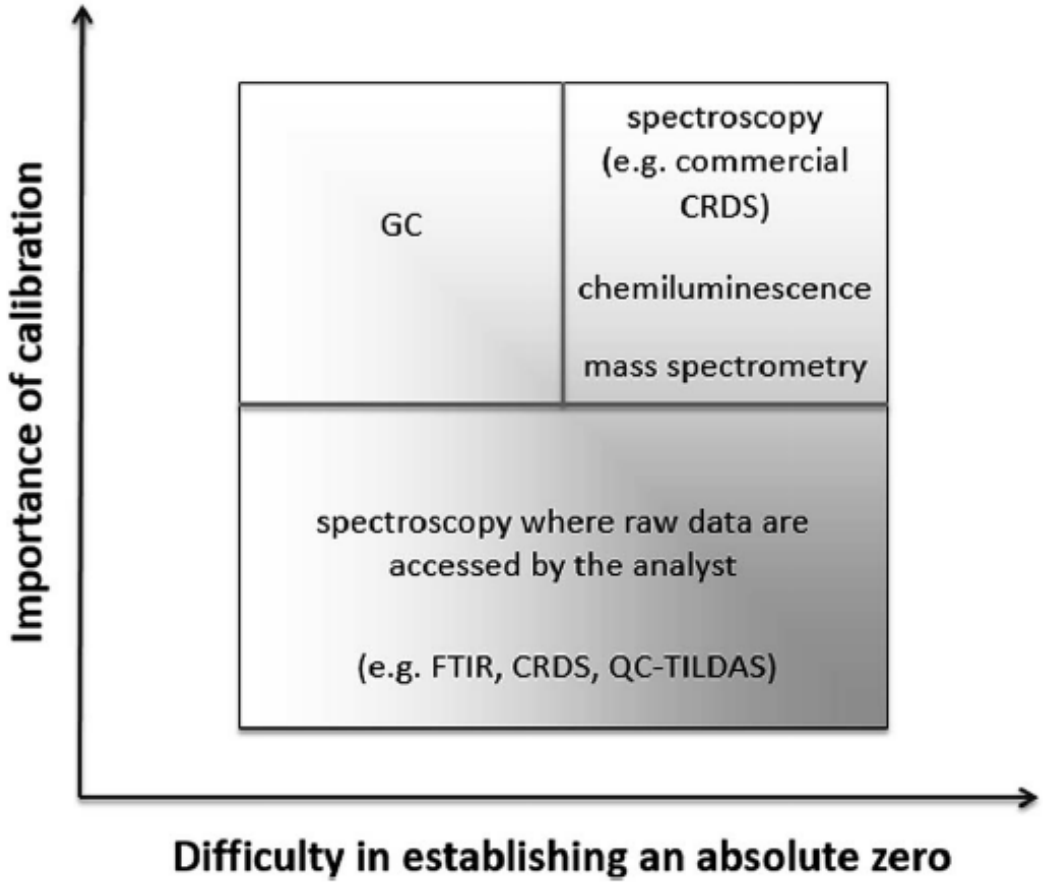
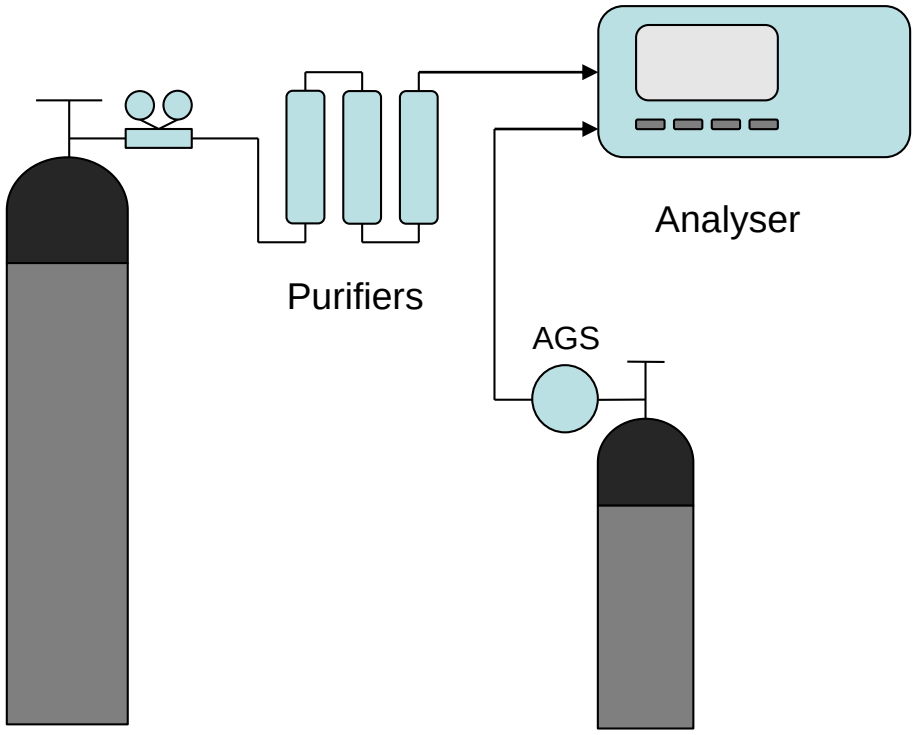


Fig. 1 Classification of analytical techniques as a function of their need for calibration and an absolute zero.

Current solutions

- What is currently done at NPL in the field of air quality?

  Standard addition method



Applicable to “relative” analytical techniques

Circular approach

Current solutions

- What is currently done with absolute spectroscopy?

The capability of these techniques depends on:

- Their limits of detections
- Their traceability to the SI

Project EURAMET 934 provided guidelines to underpin a future standard for SI traceability (TILSAM method)

https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

Comparison of generators and filters

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- In field, automated analysers of air pollutants are usually zeroed with purified compressed air.

Table 3 Manufacturer specifications for the zero air generators

	Flow (L min^{-1})	NO (nmol mol^{-1})	NO_2 (nmol mol^{-1})	NO_x (nmol mol^{-1})	CO (nmol mol^{-1})	SO_2 (nmol mol^{-1})
ZAG 1	1–5	<0.5	<0.5		<50	<0.5
ZAG 2	1–20	<0.5	<0.5			<0.5
ZAG 3	8			<0.01		<0.01

Table 5 Manufacturer specifications for two commercial purifiers

	Gases purified	Impurities removed	Outlet amount fraction	Maximum flow rate	Regeneration
PURIFIER 1	Compressed dry air, N_2, O_2	H_2O, CO, CO_2 organics (C > 4), SO_2, NO_x, HCl, H_2S, NH_3 and amines, hydrocarbons with heteroatoms such as Si, halogens, P, B, S, or metals	<1.0 nmol mol^{-1}	50 slpm	In factory
PURIFIER 2	Compressed dry air, N_2, O_2, He	SO_2/SO_x, H_2S, toluene, CO/CO_2, NH_3, H_2O, acid gases, alcohols, amines, ammonia, hydrocarbons, H_2O, NO_x, siloxanes	<0.5 nmol mol^{-1}	25 slpm	In factory or field

Comparison of generators and filters

- The three air generator tested in this work complied with the requirements of the relevant standards with the exception of one of them for NO_2.
- The two purifiers met the manufacturer specifications, except for CO and filter 2. However, output concentrations were below the limits set by the relevant EN standards.

Conclusions

- The availability of zero gas reference standards is primarily limited by the **limits of detection** of current “absolute” analytical methods and their traceability to the SI.
- Methods to quantify target impurities in balance gases using dynamic dilution and metrology grade air or N_2 to zero the analysers has been proved to give good results for air quality applications.
- Performance of zero gas generators and purifiers meets air quality EN standards requirements, but need routine maintenance.
- More demanding applications will require target gas impurities in zero gas to be more precisely determined but this will only be achieve in parallel with the improvement in sensitivity of analytical techniques.

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