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GAS ANALYZERS CALIBRATION BY DYNAMIC DILUTION FOR MONITORING AIR POLLUTION AND AIR EMISSIONS

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Abstract – The monitoring of air pollution and air emissions has suffered a great evolution during last decade in Portugal. In relation with this evolution, the necessary metrological control for the measurement equipments increased substantially, as required from the European Norm EN ISO/IEC 17025 [1].

This work compares two alternative methodologies to calibrate equipments for monitoring air pollutants emitted from ducts and stacks to the atmosphere. The traditional method, by comparing the calibration gases, Certified Reference Materials (CRM) with the equipment measurements and other method that consists in generate the calibration gas by dynamic dilution method from a high concentration CRM for each quantity.

The dilution systems that use Mass Flow Controllers (MFC) are very suitable on this field. They also give some technical advantages in calibration process, but a bigger expanded uncertainty is reached, influenced first by the MFC.

When comparing dynamic dilution and traditional calibration methods for some measurement reference equipments by Z' – score and E_n methods, the results were satisfactory.

Keywords: air pollution, air emissions monitoring, best measurement capability, dynamic dilution, gas analyzer's calibration, mass flow controllers and mass flow meters.

1. INTRODUCTION

The traditional methodology used in pollution gas analyzer's calibrations introduces directly the Certified Reference Materials (CRM) from the high pressure bottles to the analyzers. As a matter of fact, by using this method, a laboratory can achieve the Best Measurement Capability (BMC) in calibration. In other hand there is an increasing number of analyzers with different principles and ranges of measurement, different applications and specific calibration points, etc. This fact combined with the obligatory calibration of these equipments by an accredited entity, obligates a laboratory to have a high number of CRM (at least 5) for each quantity (gas) times the high number of possible calibration quantities (O_2, CO_2, NO, NO_2, CO, SO_2, CH_4, C_3H_8, H_2S, others) which is a technical/economic disadvantage.

The methodology of dynamic dilution for gases in the metrological area is a recent issue [2, 3, 4] and there are already available some dilution systems based on different principles and configurations [5].

Using a dynamic dilution system that works with MFC or with Mass Flow Meters (MFM), schemed in Fig. 1, is a practical way to avoid the disadvantage of the traditional method, reducing for just one or two CRM needed for each quantity.

To implement this calibration methodology in laboratory some important efforts are necessary in method validation and calibration of all equipments.

This work presents a dilution system example, the Best Measurement Capability (BMC) and some results of the method validation by Z'-score and E_n using the tracer method [2, 3, 5, 9].

2. METHODOLOGY

The concentration (C) of the calibration gas generated is given by the mass balance of the dilution system given by Equation 1. The dilution system is presented in Fig. 1 [8].

$$C = \frac{(C_S \times G_{VS} + C_Z \times G_{VZ})}{(G_{VS} + G_{VZ})} \qquad (1)$$

Where C is the concentration of calibration gas, G_V is the volumetric flow, and $_{S,\,Z}$ are Span gas and Zero gas.

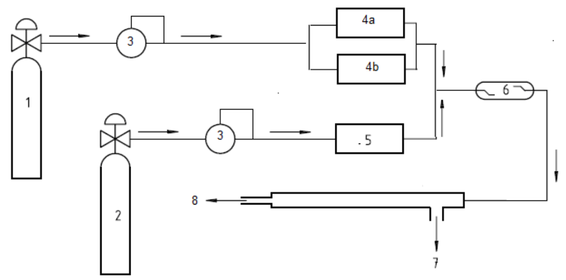

Fig.1. Dynamic dilution system.

(1 – Span gas, 2 – Dilution gas (N_2 or Air), 3 – Pressure regulator, 4a,b – Span gas mass flow controller, 5 – Dilution gas mass flow controller, 6 – Mixing camera, 7 – Exit to the analyzers, 8 – Exhaust).

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3. RESULTS

3.1. Calibration Examples

The dilution system was tested for a large number of gases (O_2, CO_2, NO, NO_2, CO, SO_2, CH_4, C_3H_8 and H_2S) that are normally measured in environmental emissions and air pollution. For each one it is possible to generate continuous concentrations for large measurement ranges. Some examples are given on Table 1.

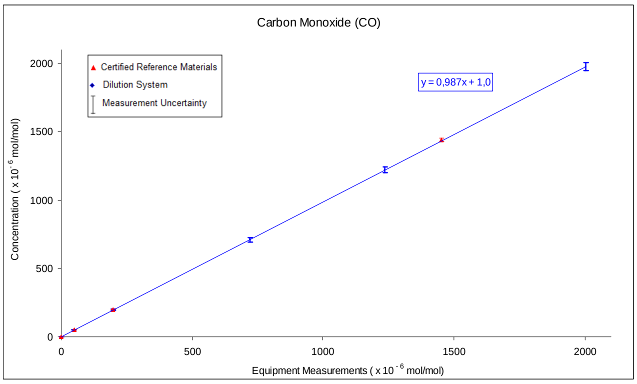

Fig. 2. Calibration function for carbon monoxide and 3 CRM.

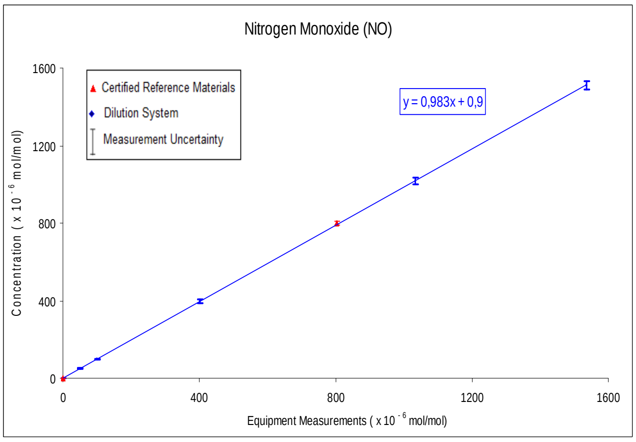

Fig. 3. Calibration function for nitrogen monoxide and 1 CRM.

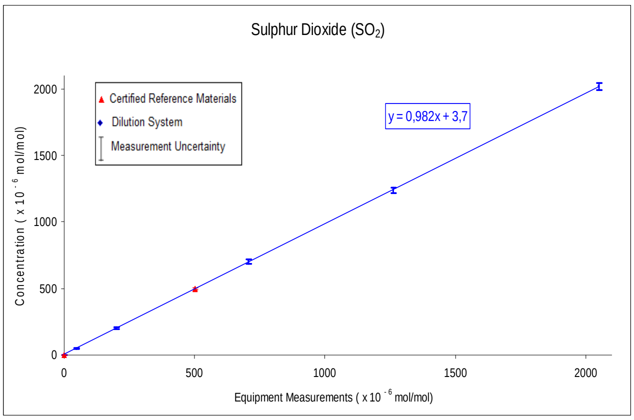

Fig. 4. Calibration function for sulphur dioxide and 1 CRM.

The Figs. 2, 3, 4, 5, 6 and 7, show the results for a calibration functions using the dilution system and some typical equipments for measuring Carbon Monoxide (CO) by Non-dispersive infrared spectrometry (NDIR) [10], Nitrogen Monoxide (NO) by Chemiluminescence [11], Sulphur Dioxide (SO_2) and Carbon Dioxide (CO_2) by NDIR, Oxygen (O_2) by Paramagnetism [12] and Propane (C_3H_8) by Continuous Flame Ionisation Detector method (FID) [13].

The figures show also the results for some gases used as tracer (CRM) in method evaluation [2].

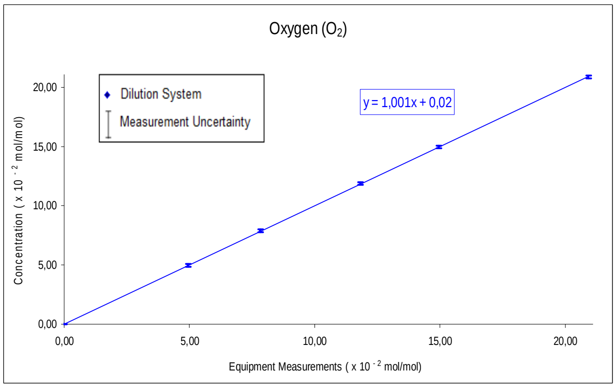

Fig. 5. Calibration function for oxygen.

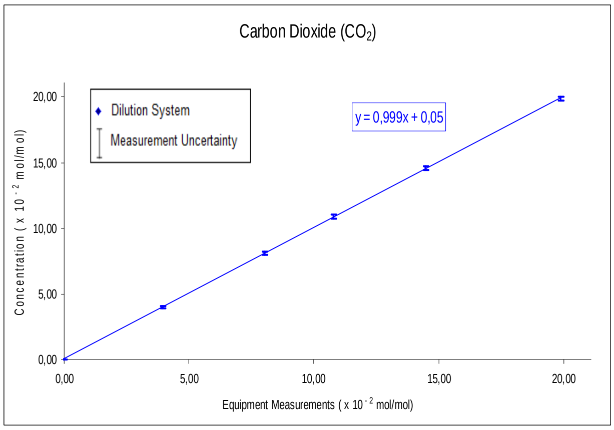

Fig. 6. Calibration function for carbon dioxide.

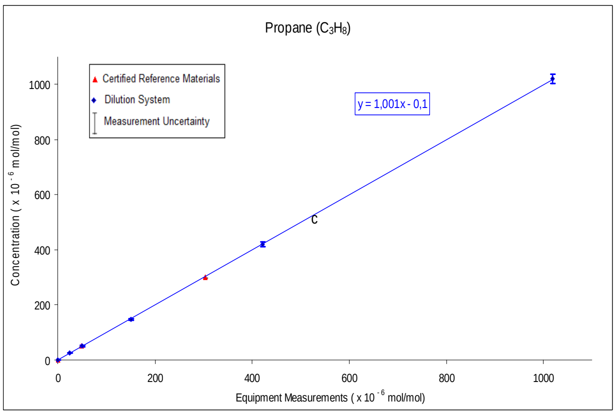

Fig. 7. Calibration function for propane and 2 CRM.

3.2. Best Measurement Capability's

The Best Measurement Capability (BMC) is defined in the document EA-4/02 [7] as, *the smallest uncertainty of measurement that a laboratory can achieve within its scope (…), when performing routine calibrations (…) nearly ideal measuring instruments designed for the measurement of that quantity (…).*

The BMC was calculated according the GUM [6]. For the dilution system used (Equation 1) the BMC is given as a polynomial 3rd degree equation (where C is the concentration) given in Table 1.

Table 1. Quantity, Calibration Range and Best Measurement Capability

Quantity	Units	Calibration Range	Best Measurement Capability (BMC) expressed as Expanded Uncertainty (k=2)
O_2	10^{-2} mol/mol	2 to 21	$BMC = 2{,}74\cdot10^{-05}\cdot C^3 - 1{,}52\cdot10^{-03}\cdot C^2 + 2{,}52\cdot10^{-02}\cdot C - 2{,}73\cdot10^{03}$
CO_2	10^{-2} mol/mol	2 to 20	$BMC = 2{,}85\cdot10^{-05}\cdot C^3 - 1{,}42\cdot10^{-03}\cdot C^2 + 2{,}49\cdot10^{-02}\cdot C - 4{,}38\cdot10^{03}$
CO	10^{-6} mol/mol	10 to 5000	$BMC = 4{,}37\cdot10^{-10}\cdot C^3 - 5{,}13\cdot10^{-06}\cdot C^2 + 2{,}25\cdot10^{-02}\cdot C - 6{,}45\cdot10^{02}$
SO_2	10^{-6} mol/mol	10 to 5000	$BMC = 3{,}87\cdot10^{-10}\cdot C^3 - 4{,}59\cdot10^{-06}\cdot C^2 + 2{,}26\cdot10^{-02}\cdot C - 1{,}30\cdot10^{02}$
NO	10^{-6} mol/mol	20 to 2500	$BMC = 1{,}19\cdot10^{-09}\cdot C^3 - 7{,}20\cdot10^{-06}\cdot C^2 + 2{,}35\cdot10^{-02}\cdot C + 6{,}76\cdot10^{02}$
C_3H_8	10^{-6} mol/mol	10 to 3000	$BMC = 9{,}82\cdot10^{-10}\cdot C^3 - 7{,}19\cdot10^{-06}\cdot C^2 + 2{,}24\cdot10^{-02}\cdot C + 8{,}81\cdot10^{01}$

4. DILUTION METHOD EVALUATION

The dynamic dilution method performance was evaluated by the Z'=Z'- score and Normalized Error, E_n, according to the international reference ISO 13528:2005 [14].

The Z' is calculated according the Equation 2,

$$Z' = \frac{(x_{dil} - x_{ref})}{\sqrt{U_{ref}^2 + \sigma^2}} \qquad (2)$$

where x_{dil} is the equipment measurement for the concentration generated by the dilution system, x_{ref} is the equipment measurement for the certified CRM, U_{ref} is the measurement uncertainty of CRM and σ is the experimental standard deviation given by the Equation 3, that for a Maximum Error (E) of 2 % of the concentration in a rectangular probability distribution is,

$$\sigma = \frac{x_{ref} \times E/100}{\sqrt{3}} \qquad (3)$$

The Z' classifies the dilution method performance as:

$|Z'| \leq 2$ satisfactory
$2 < |Z'| \leq 3$ doubtful
$|Z'| > 3$ unsatisfactory

With the uncertainties and the BMC calculated, is also possible to evaluate the dilution method performance by E_n calculated according the Equation 4,

$$E_n = \frac{(x_{dil} - x_{ref})}{\sqrt{U_{dil}^2 + U_{ref}^2}} \qquad (4)$$

where x_{dil} is the equipment measurement for the concentration generated by the dilution system, given by the linear regressions of Figs. 2, 3, 4 and 7, x_{ref} is the equipment measurement for CRM, U_{ref} is the measurement uncertainty of the CRM and U_{dil} is the uncertainty of the dilution system, BMC, given in Table 1. The E_n classifies the dilution method performance as:

$|E_n| \leq 1$ satisfactory
$|E_n| > 1$ unsatisfactory.

Table 2. Results of the dynamic dilution method performance (Z' and E_n)

Quantity	Principle of Measurement	CRM ($x10^{-6}$ mol/mol)	Equipment Readings (x_{ref}) ($x10^{-6}$ mol/mol)	Expanded Uncertainty (U_{ref}) ($x10^{-6}$ mol/mol)	Equipment Readings (x_{dil}) ($x10^{-6}$ mol/mol)	Expanded Uncertainty (U_{dil}) ($x\ 10^{-6}$ mol/mol)	σ	Z'	E_n
CO	NDIR [EN 15058:2006]	50,5	50,2	0,8	50,9	1,1	0,6	0,7	0,5
CO	NDIR [EN 15058:2006]	199,8	199	2,0	199	4,2	2,3	0,0	0,0
CO	NDIR [EN 15058:2006]	1442	1451	12	1424	24	16,8	-1,3	-1,0
NO	Chemiluminescence [EN 14792:2005]	800	804	12	787	15	9,3	-1,1	-0,9
SO_2	NDIR [-]	497,9	502	4,8	494	10	5,8	-1,1	-0,7
C_3H_8	FID [EN 13526:2001]	49,99	49,2	0,47	49,9	1,5	0,6	0,9	0,4
C_3H_8	FID [EN 13526:2001]	301,6	303	3,0	301,8	7,0	3,5	-0,3	-0,2

5. CONCLUSIONS

This dynamic dilution methodology can be applied for almost all gases normally measured in environmental emissions. For each one it is possible to generate continuous concentrations for large ranges as given on Table 1.

The BMC reached in calibration by the whole dilution system is a polynomial 3rd degree equation, for which the expanded uncertainties are sometimes two times larger than the traditional calibration methodology.

The response of MFC is different for different gases, specially the ones with high concentrations (10^{-2} mol/mol). This has to be considered in a laboratory method validation, because the response factor of the MFC is different from the gases normally used in calibration of MFC (N_2 or Air).

The dynamic dilution method gives some advantages: it is only necessary one dilution system and one CRM (high concentration) for each gas according the method validation and the MFC ranges; for each gas it is possible to generate a continuous range of calibration points between the calibration limits, it is an interesting technical advantages on this field.

There are also some disadvantages: significant efforts are needed for the method implementation and method validation; there is a necessity for metrological control of extra equipments inside the laboratory that contribute for a larger expanded uncertainty in calibration [5, 6], influenced firstly by MFC of the dilution system.

With the application of Z'- score and E_n for both methodologies of calibration, the result is satisfactory for all compared quantities.

With tests and calibrations of three different dilution systems, we also conclude that special study should be made to the reproducibility of MFM and MFC. Regular calibration of the dilution system is necessary and crucial.

NOMENCLATURE

BMC – Bets Measurement Capability
C – Concentration of the gas generated by dynamic dilution system
CRM – Certified Reference Materials
C_s – Concentration of Span gas
C_Z – Concentration of Zero gas
E_n – Normalized Error
FID – Flame Ionisation Detector
GUM – Guide to Expression of Uncertainty in Measurement
G_{vs} – Volumetric flow of Span gas
G_{vz} – Volumetric flow of Zero gas
k – Coverage factor
MFC – Mass Flow Controllers
MFM – Mass Flow Meters
NDIR – Non-dispersive infrared spectrometry
U_{ref} – Measurement uncertainty of CRM
U_{dil} – Expanded uncertainty of the dynamic dilution system
x_{dil} – Equipment measurement of concentration generated by the dynamic dilution system
x_{ref} – Equipment measurement of CRM
Z' – Z'score
σ – Experimental standard deviation

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