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ENVIRONMENTAL AND POLLUTANTS GAS ANALYZERS

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Abstract – Air pollution exists where there are quantitative variations in the air composition or by the introducing of new pollutants. With the automobiles and industrialization increase there has been a need to control gas emissions before loading them into the environment. To this end, environmental and pollutants gas analyzers are used and it is necessary calibration by competent entities.

The main proposal of this communication is to demonstrate the importance of the calibration operation of these instruments as well as the calculation of associated uncertainties.

Keywords: Calibration, Metrological Control, Uncertainty, Certified Reference Material, Traceability.

1. INTRODUCTION

Air pollution is a major concern worldwide; it causes degradation of ecosystems, giving rise to the greenhouse effect, to climate change, the decrease in air quality and health problems in living beings.

In extreme case, the gases constituents of the atmosphere, in certain concentrations can cause death of persons, either by poisoning or by violence, they can cause accidents.

The gas analyzers are measurement instruments that detect the variation of gas concentration in the air composition in places where they are installed. This measurement instrument leads to a significant control of gaseous emissions to protect people and surveilling toxic gases properties and/ or fuels. To make the control of emissions are used environmental and pollutants gases analyzers, and to this end it is necessary that they are calibrated.

There are many types of emissions from these industries. At the Portuguese Institute for Quality are calibrated gas analyzers of:

- Carbon monoxide (CO) as a result of the exhaust of motor vehicles, industrial processes and incomplete combustion of wood, oil, gas and coal;
- Carbon dioxide (CO_2) as a result of burning gas, oil and coal;
- Nitric oxide (NO_x) as a result of power stations, factories of explosives, rockets, nitric acid and cars;
- Sulfur dioxide (SO_2) as a result of power stations, refineries, petrochemical, sulphuric acid factories;
- Hydrogen sulfide (H_2S) as a result of burning fossil fuels and the decomposition of organic matter.

The professional limits of exposure (ELV) to chemical agents, pollutants and environmental gases are set, in Portugal, by the Portuguese standard NP 1796/2004 [1]. Like other European Union countries, they are based on the limits proposed by the American Conference of Governmental Industrial Hygienists (ACGIH), 2006.

The Portuguese DL nº 78/2004 of April 3, the transposition into national law of Directive nº 96/62/CE, establishes measurements and procedures adequate to the pollution prevention and control from installations responsible for the pollutants discharge into the air. It establishes also a monitoring system. Finally, the Portuguese document Portaria nº. 80/2006 of January 23 sets the maximum and minimum mass thresholds applied to all emissions sources [2, 3].

Certified reference materials with traceability to national and international standards are used in the analyzers calibration. The instrument acceptance is based on the exposure limits values and on the instrument error. Different uses of gas analysis are performed:

- Carbon monoxide analyzers are used in network gas inspections;
- Oxygen is analysed in modified atmosphere within different industries, like the pharmaceutical and food ones;
- Pollutant gas analyzers are used by entities that make the gas emissions monitoring in industry;
- Exhaust gas analyzers are used to determine the concentration of particular gas compounds like carbon monoxide (CO), carbon dioxide (CO_2), oxygen (O_2) and hydrocarbons (HC) that make up the vehicle exhaust emissions.

2. ANALYZERS CALIBRATION

The standards used in analyzers calibration are certified reference mixtures traceable to IPQ and NMi (National Metrology Institute - The Netherlands) standards. The preparation of primary gas mixtures and certification of reference materials is made at the highest metrological level, using methods based on international standards ISO 6142 and ISO 6143 [4, 5].

2.1. Carbon Monoxide Analyzer

Generally these analyzers do not allow a direct admission of the gas and because of this the calibration is in a camera, ensuring that the measured value of the analyzer is only for the gas in question.

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The calibration begins by the choice of the standards. Once the limit is 50 ppm, the calibration is done with three certified reference material concentrations, a lower concentration and a higher than 50 ppm.

The calibration method is based on the use of these mixtures, with an adequate flow, in ascending order and are registered the values of measurement when they are stable. According to the metrological criterion established by the Amount of Substance Laboratory for carbon monoxide analyzers, is issued a calibration certificate when the measuring instruments have an measurement error less than 5 ppm for low and medium concentration, or a relative error less than or equal to 8 % for high concentration. If the criterion is not accomplished, an adjustment is made to the sensor with the prior consent of the client and after the calibration method is done [6, 7].

In Table 1 are indicated the results of calibration of carbon monoxide analyzer.

Table 1. Results for the calibration of carbon monoxide analyzer in ppm, before and after adjustment.

Adjustment	True Value (ppm)	Instrument Indication Average (ppm)	Expanded Uncertainty (±)	Measurement Error (ppm)
Before Adjustment	25,3	19	1 (k=2,00)	-6
	51,1	41	1 (k=2,00)	-10
	75,6	63	1 (k=2,00)	-13
After Adjustment	25,3	23	1 (k=2,00)	-2
	51,1	51	1 (k=2,00)	0
	75,6	76	1 (k=2,00)	0

Table 1 shows that the metrological criterion was not accomplished, so it was necessary to make an adjustment to the sensor.

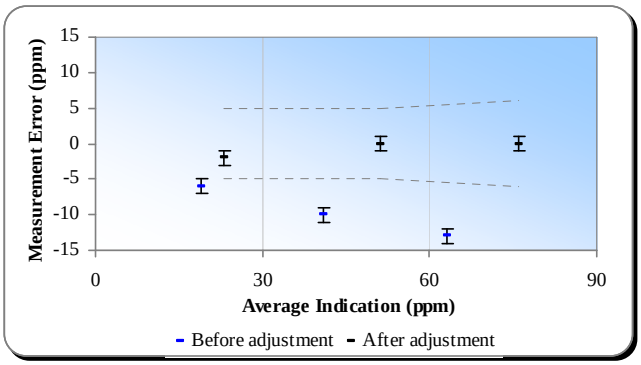

Fig. 1. Results of the calibration of the carbon monoxide analyzer, before and after adjustment.

In Fig. 1 are represented the calibration results of the carbon monoxide analyzer.

The measurement error is the difference between the average of indication measuring instrument and the true value.

2.2. Pollutants Gas Analyzers

For this type of analysis the calibration is done with five certified reference mixtures to cover the work range. The calibration procedure is based on the use of these five mixtures, with an adequate flow, in ascending order and are registered the values of measurement when they are stable.

According to the metrological criterion established by the amount of substance laboratory for pollutants gas analyzers is issued a calibration certificate for the case of the relative error is less than or equal to 10 %. Similarly if the criterion is not accomplished an adjustment is made to the sensor with the prior consent of the client [6, 7].

In Table 2 are recorded the results of calibration of pollutants gas analyzers.

Table 2. Results for the calibration of pollutants gas analyzer for CO, NO, NO_2, SO_2 sensors in ppm and O_2 in %.

Gas	True Value	Instrument Indication Average	Expanded Uncertainty (±)	Measurement Error
CO (ppm)	100,3	101	1 (k=2,00)	1
	487	489	4 (k=2,02)	2
	739	735	5 (k=2,00)	-4
	1476	1451	10 (k=2,00)	-25
	3997	3781	36 (k=2,14)	-216
O_2 (%)	5,09	5,01	0,04 (k=2,00)	-0,08
	7,98	7,86	0,02 (k=2,00)	-0,12
	10,11	10,00	0,04 (k=2,00)	-0,11
	15,01	15,02	0,04 (k=2,00)	0,01
	20,88	21,15	0,06 (k=2,00)	0,27
NO (ppm)	47,0	47	2 (k=2,00)	0
	249	247	2 (k=2,00)	-2
	400	396	2 (k=2,00)	-4
	753	751	4 (k=2,00)	-2
	1019	1016	6 (k=2,00)	-3
NO_2 (ppm)	100	106,0	3,4 (k=2,02)	6
	200	206,3	5,5 (k=2,00)	6,8
	300	316,7	5,8 (k=2,00)	17,1
	400	430,7	9,3 (k=2,00)	30,3
	500	528,0	9,4 (k=2,00)	28
SO_2 (ppm)	23,1	14	1 (k=2,00)	-9
	47,9	40	1 (k=2,00)	-8
	182	163	2 (k=2,00)	-19

Table 2 shows that the analyzer has a relative error below 10 % for the CO, O_2, NO and NO_2 sensors and a relative error more than 10 % for the SO_2 sensor. In this case is necessary to make an adjustment to the SO_2 sensor.
The results after adjustment are presented in Table 3 and are represented in Fig.2.

Table 3. Results in ppm after adjustment for the calibration of the SO_2 sensor.

True Value (ppm)	Instrument Indication Average (ppm)	Expanded Uncertainty (±)	Measurement Error (ppm)
23,1	23	1 (k=2,00)	0
47,9	48	2 (k=2,00)	0
182	181	2 (k=2,00)	-1
320	320	3 (k=2,00)	0
457	458	4 (k=2,00)	1

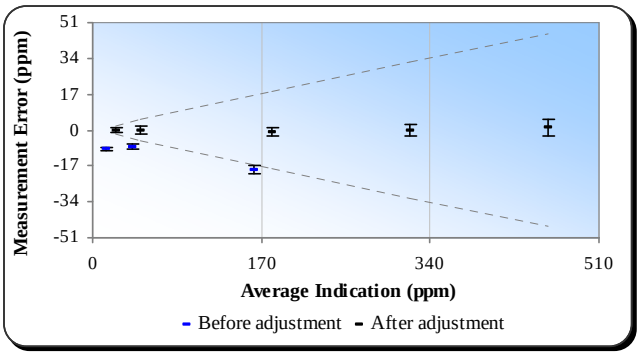

Fig. 2. Results of the calibration of the SO_2 sensor, before and after adjustment.

2.3. Exhaust Gas Analyzers

These analyzers are submitted to a series of metrological control operations (pattern approval, initial verification, subsequent verification, extraordinary verification).

Certified reference mixtures (CO + CO_2 + O_2 + HC in nitrogen), according to ISO 3930 (OIML R99) are used in metrological control for exhaust gas analyzers. They also satisfy the requirements in Portuguese document Portaria n. º 20/2007 of October 5 [8].

The pattern approval is the acceptance of a specific brand and model of the measuring instrument. This operation of metrological control is valid for a period of 10 years, unless otherwise specified in the order of Daily Republic.

The initial verification is done when an instrument is new and seeks to determine its compliance with the model approved in advance and is made in accordance with a set of tests referenced in the Recommendation of OIML R99 (ISO 3930) [9].

These tests are the determination of the calibration curve using three mixtures corresponding to the low, medium and high concentration, in carrying out a leakage test and a test of waste HC.

The subsequent verification is valid for a year and aims to see if the measuring instruments maintains metrological quality within the tolerances set by the maximum allowable OIML R99 [9].

The instruments are sealed, at then end of the verification, in accordance with the Order of the Daily Republic of pattern model and deliver up a verification certificate.

The instruments are approved when the errors observed for each reading is within the maximum permissible errors (EMA) set in OIML R99 for the initial verification, these are indicated in Table 4:

Table 4. Table of EMA according to OIML R99 [9].

Class	Type of EMA	CO (%)	CO_2 (%)	HC (ppm)
Class I	Absolute	± 0,06 %	± 0,5 %	± 12 ppm
	Relative	± 5 %	± 5 %	± 5 %
Class II	Absolute	± 0,2 %	± 1 %	± 30 ppm
	Relative	± 10 %	± 10 %	± 10 %

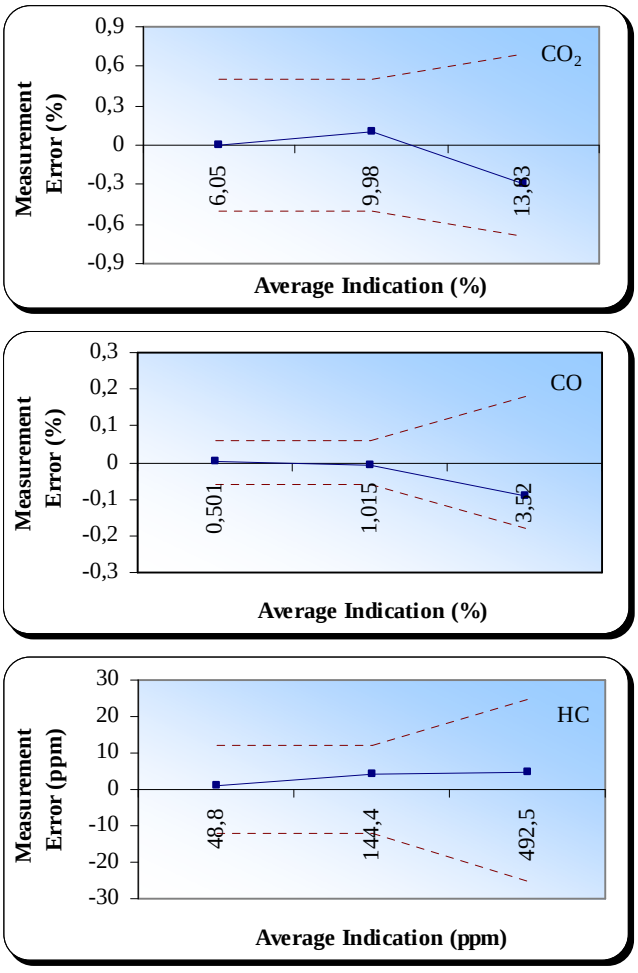

Fig. 3. Results in the initial verification for Class I where dashed lines represent the maximum permissible errors.

In Fig. 3, as example, are indicated the results of an approval test for an exhaust gas analyzer.

2.4. Calculation of Uncertainty

The uncertainties have been calculated in accordance with the "Guide to the expression of uncertainty of measurement in calibration laboratories" [11]. The measurement of uncertainty associated with estimates of the quantities of entry, is evaluated according to the assessment method called the "Type A and Type B". In this case the evaluation of standard uncertainty is Type A, since it can be applied when several independent observations have been made for one of the input quantities of *Xi* under the same conditions of measurement.

It is considered that the input quantities, *Xi* repeatedly measure is the quantity *Q*, which in the calibration of gas analyzers matches to the values of reading the instruments for various gases.

When n observations (n> 1) are statistically independent, the estimate of the quantity *Q* is given by the arithmetic mean of the observed values individually, q_j (where, j = 1,.., n), whose expression is:

$$\bar{q} = \frac{1}{n}\sum_{j=1}^{n} q_j \qquad (1)$$

The experimental variance, s^2 (q) of value q_j is given by:

$$s^2(q) = \frac{1}{n-1}\sum_{j=1}^{n}(q_j - \bar{q})^2 \qquad (2)$$

Where the variance square root is the experimental standard deviation, *s* (q).

The uncertainties of measurement that influence the calibration of analyzers results from the combination of three sources of uncertainty: the uncertainty of the standard deviation of measurement, uncertainty of the division and the uncertainty of the reference material.

The uncertainty of the standard deviation of measurement is related to the dispersion of results and is calculated using the following mathematical expression:

$$u_{disp} = \frac{s(q)}{\sqrt{n}} \qquad (3)$$

Where *s (q)* is the standard deviation and *n* is the number of readings.

The uncertainty of the division is related to the resolution of the analyzer and is given by:

$$u_{div} = \frac{\mathrm{Re}\,solution}{\sqrt{12}} \qquad (4)$$

The uncertainty of the reference material is related to the uncertainty of certified gas mixture and is given by half of the expanded uncertainty of the standard:

$$u_{padr} = \frac{U}{2} \qquad (5)$$

The combined uncertainty results from the square root of the sum of the squares of the different types of uncertainties, specifically:

$$u_c = \sqrt{u_{disp}^2 + u_{div}^2 + u_{padr}^2} \qquad (6)$$

The expanded uncertainty, presented in the calibration certificate, is expressed by the combined uncertainty, multiplied by a coverage factor in order to correspond to a confidence interval of approximately 95 % [11]:

$$U = k \times u_c \qquad (7)$$

The value of k is determined by calculating the degree of freedom number, ν_{eff}, given bye Welch-Satterthwaite equation:

$$\nu_{eff} = \frac{u_c^4}{\sum_{j=1}^{n}\frac{u_j^4}{\nu_j}} \qquad (8)$$

Where, u_j is the standard uncertainty related to standard deviation of measurement, equipment resolution and reference material. ν_j are the degrees of freedom associated with uncertainties.

For a given system, the degree of freedom number is dependent on the variations of standard deviation uncertainties, since the reference material and division uncertainty for each measurement is the same. This dependence on variations of standard deviation uncertainties consequently results in different coverage factors.

In the calibration certificate are presented the measurement result and the associated expanded uncertainty, *U*, expressed as ($q \pm U$).

4. CONCLUSIONS

Analysis of Fig. 1 and 2, for results of carbon monoxide analyzer and pollutants gas analyzers respectively, evidence that the analyzer after the adjustment meets the metrological criterion, for which was issued a calibration certificate.

The results of the exhaust gas analyzers, Fig. 3, show that the analyzer was approved because the averages of the measured values are within the maximum permissible errors.

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