A comparison of EPA and EN requirements for nitrogen oxide chemiluminescence analyzers

J. Barberá[1], M. Doval[1], E. González[1], A. Miñana[1] & F. J. Marzal[2]
[1]*Departamento de Ingeniería Química, Universidad de Murcia, Spain*
[2]*Departamento de Ingeniería Térmica y de Fluidos, Universidad de Cartagena, Spain*

Abstract

Nitrogen oxides analyzers currently used for measuring air quality in European countries meet the standard ISO 7996:1985, which does not establish any special feature for such equipment, except the analytical technique implemented. Nevertheless, most of them are designated as "Reference methods" by the Environmental Protection Agency of the United States. Future European legislation in this matter establishes as reference method for measuring these pollutants that described in EN 14211:2005, where a number of tests for chemiluminescence analyzers are described. In this paper, we compare the requirements of both documents, evaluating the suitability of each and their approach.
Keywords: chemiluminescence, nitrogen oxides, EPA, type approval tests, EN 14211:2005.

1 Introduction

Following the "Better Regulation" initiative for updating and simplying community legislation, the *Proposal for a Directive on ambient air and cleaner air for Europe* [3] aims at integrating in a single document the Directives 96/62/EC [4], 99/30/EC [5], 2000/69/EC [6], 2002/3/EC [7] and the Decision 97/101/EC [8]. Moreover, the Proposal establishes the complete control of particulate matter ($PM_{2.5}$) and also stipulates new reference documents for the measurement of regulated pollutants in air, as shown in table 1.

The standards of the Proposal of Directive, except for those related to particulate matter and lead, include a new and wide-ranging section about

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Table 1: Reference documents currently used and those set by the Proposal of Directive for measuring pollutants.

Pollutant	Analytical Method	Normas	
		In force	Proposal of Directive
Sulfur dioxide	Ultraviolet fluorescence	ISO 10498	EN 14212 : 2005
Particulate lead	Atomic absorption spectrometry or Inductively coupled plasma mass spectroscopy	EN 12341 : 1999	EN 14902 : 2005
Benzene	Gas cromatography	------------	EN 14662 : 2005
Carbon monoxide	Non-dispersive infrared spectroscopy	------------	EN 14626 : 2005
Particulated matter PM_{10}	Gravimetric determination	EN 12341 : 1999	EN 12341 : 1999
Particulate matter $PM_{2.5}$	Gravimetric determination	------------	EN 14907 : 2005
Ozone	Ultraviolet photometry	ISO 13964:1998	EN 14625 : 2005
Nitrogen oxides	Chemiluminescence	ISO 7996:1985	EN 14211 : 2005

requirements to be met by the analyzers, known as “Type-Approval Test”, which aims at assuring data quality from the networks measuring ambient air pollution. “Type- Approval Tests” include a number of tests in the laboratory and field and the calculation of the expanded uncertainity, which must be lower than that specified in the corresponding legislation.

Independently, the Environmental Protection Agency from the US certifies the analyzers for measuring air pollutants as Reference or Equivalent Methods [9]. In the next section and regarding nitrogen oxides analyzers, the main differences, advantages and drawbacks of the proposed tests in both documents are discussed.

2 EPA and EN requirements for chemiluminescence nitrogen oxides analyzers

2.1 Performance parameters and criteria required by EPA

The performance parameters and their criteria described in the Code of Federal Regulations by EPA are compiled in table 2.

2.2 Performance parameters and criteria required by EN 14211:2005

Regarding the performance characteristics required to obtain the “Type-Approval Test” certificate, characteristics evaluated in laboratory (table 3) and those tested in field (table 4) must be distiguished.

Table 2: Performance parameters and criteria for nitrogen oxides analyzers established by EPA. All the tests are carried out with NO_2.

Performance parameter	Performance criteria
Range	0-500 ppb
Noise	
At zero	≤ 5 ppb
At 80% URL	≤ 5 ppb
Lower detectable limit	≤ 10 ppb
Interference equivalent	
Each interferant	≤ 20 ppb
Water vapour	
Sulfur dioxide	
Nitric oxide	
Ammonia	
Total interferant	≤ 40 ppb
Zero drift, 12 and 24 hours	≤ 20 ppb
Span drift, 24 hours	
20% of URL	≤ 20%
80% of URL	≤ 5%
Lag time	≤ 20 min
Rise time	≤ 15 min
Fall time	≤ 15 min
Precision	
20% of URL	≤ 20%
80% of URL	≤ 30%
NO_2 efficiency converter(1)	≥ 96 %

(1)From EPA [10].

2.3 Comparison between EPA and EN requirements in laboratory tests

2.3.1 General considerations about performance parameters, performance criteria and experimental procedures

As can be deduced from tables 2 to 4, tests targets are, in some cases, similar but neither performance criteria nor experimental procedures are.

Firstly, it is noticeable that EPA does not carry out any field tests, unlike some of the tests proposed in EN 14211:2005.

On the other hand, tests established by EPA are focused on NO_2 whereas EN tests are designed for NO, except in the case of converter efficiency, which is carried out for NO_2 and response time and averaging effort, for both NO and NO_2. This is explained by the fact that NO_2 is measured by reduction to NO so, if conversion efficiency is appropriate, the measurement procedure is common to both species. Evaluating the performance characteristics with NO_2, instead of NO, avoids introducing the standard uncertainty of the reduction process but could lead to mistakes in the NO_2 channel when evaluating certain performance characteristics.

As regards performance criteria, the European standard is much more demanding than EPA. In most cases, these criteria are defined by absolute figures so it is necessary to express them as relative values, since the concentrations of the pollutants used for tests are not the same, in order to establish a correct comparison. The performance parameters of both documents that can be compared are displayed in table 5 with their respective performance criteria in relative value, where it can be easily seen that EPA is much more

Table 3: Laboratory performance parameters and their criteria established in EN 14211:2005 for chemiluminescence nitrogen dioxide analyzers.

Performance parameter	Performance criteria	
	NO	NO_2
Range	0-962 ppb	0-261 ppb
Response time for NO channel:		
Rise response time	≤ 180 s	
Fall response time	≤ 180 s	
Difference between rise and fall response times	≤ 10 s or ≤ 10 % relative difference	
Response time for NO_2 channel:		
Rise response time		≤ 180 s
Fall response time		≤ 180 s
Difference between rise and fall response times		≤ 10 s or ≤ 10 % relative difference
Repeteability		
at zero level	≤ 1 ppb	
at the hourly limit value	≤ 3 ppb	
Lack of fit to linear		
Largest residual different from zero	≤ 4 %	
Zero residual	≤ 5 ppb	
Sensitivity to sample gas pressure	≤ 8 ppb/kPa	
Sensitivity to sample gas temperature	≤ 3 ppb/K	
Sensitivity to surrounding temperature	≤ 3 ppb/K	
Sensitivity to electrical line voltage	≤ 0.3 ppb/V	
Cross-interferences		
Water vapour	≤ 5 ppb	
Carbon dioxide	≤ 5 ppb	
Ammonia	≤ 5 ppb	
Ozone	≤ 2 ppb	
Averaging effort	≤ 7 %	≤ 7 %
Short term drift, 12 hours		
At zero	≤ 2 ppb	
At the span level	≤ 6 ppb	
Differences in response between sample and calibration port, if applicable	≤ 1 %	
NO_2 efficiency converter		≥ 98 %

Table 4: Field performance parameters and their criteria established in EN 14211:2005 for chemiluminescence nitrogen dioxide analyzers.

Performance parameter	Performance criteria	
	NO	NO_2
Long term drift, 3 months		
At zero	≤ 5 ppb	
At the span level	≤ 5 %	
Reproducibility		≤ 5 %
Period of unattended operation	3 months or less if manufacturer indicates a shorter period	> 90 %
Period of availability	> 90%	

permissive than EN. The response time and interferences criteria are especially striking.

Differences in test procedures are also found. Whereas EN establishes the number of individual or independent measurements to be taken in each test without specifying any special sequence for their execution, EPA requires at

Table 5: Performance criteria comparison for analogous EPA and EN tests.

Performance parameter	Performance criteria	
	EPA	EN
Response time for NO_2		
Rise response time	≤ 35 min (20 min lag time + 15 min rise time)	≤ 180 s
Fall response time	≤ 35 min (20 min lag time + 15 min fall time)	≤ 180 s
Repeteability (EN) or noise (EPA)		
At zero level	≤ 5 ppb	≤ 1 ppb
At span	≤ 1.25%	≤ 0.6 %
Interferences		
Water vapour[(1)]	≤ 20 %	≤ 1 %
Ammonia[(2)]	≤ 20 %	≤ 1 %
Total interferences	≤ 40 %	≤ 3.4 %
Short term drift		
Zero, 12 hours	≤ 20 ppb	≤ 2 ppb
Span		
12 hours	-	≤ 0.9 %
24 hours		
20% URL	≤ 20 %	-
80% URL	≤ 5 %	-

(1) Concentration used by EPA, 20000 ppm; concentration used by EN 19000 ppm.
(2) Concentration used by EPA, 100 ppb; concentration used by EN, 200 ppb.

least seven days for carrying them out, and establishes which tests should be repeated following a strict sequence.

In the next section, most significant differences between both documents are described.

2.3.2 Certification range

Regarding the certification range of both documents, that established in EN 14211:2005 for NO_2 (0 to 261 ppb) is the most coherent since it is 1.25 times the highest limit for this gas in the legislation, that is, the alert threshold (208 ppb). Nevertheless, as was mentioned before, NO_2 is hardly ever used in EN tests as most of them are described for NO, with the certification range in this case of 0 to 962 ppb. This range, as well as that proposed by EPA, is excessively high since in real environments, concentrations are not likely to exceed 200 to 300 ppb, being typically less than 100 ppb.

2.3.3 Response time

This test shows important differences from one document to the other. EN establishes 180 seconds as the maximum time to pass from zero concentration to 90% of the introduced concentration (770 ppb) and the same time to pass from 770 ppb to 10% of this value when changing to sample zero air.

As far as EPA is concerned, it defines the response time as the necessary to obtain a reading of 95% of the introduced concentration (400 ppb) from zero air and must be, at most, 35 minutes which is not admissible taking into account that there are commercially available nitrogen oxides analyzers with response times as low as 30 seconds.

2.3.4 Short term drift

This test also shows how EPA is less restrictive than EN. When sampling zero air, the short term drift performance criteria established by EPA is 20 ppb, whereas in EN it is 2 ppb, which is ten times below the permitted value of the American agency.

Something similar happens with the span concentration. Whereas EPA allows a 20% variation when using a concentration equal to 20% of the upper range limit (URL) (100 ppb) and 5% when using a concentration of 80 % of the URL (400 ppb), EN allows a maximum drift of 0.9% for a test concentration of 670 ppb. Leaving apart the discussion about whether EN drift criteria are adequate or not, a short term drift of 20% in 100 ppb (hourly limit value for the protection of human health) is not admissible since the uncertainity of the readings would be higher than that permitted in the legislation (±15%).

2.3.5 Interferences

Each document establishes four interferent gases, water vapour and ammonia being the two common interferences in both. Water vapour is a specie that is always present in the environment but ammonia is not likely to be found except in industrial fields.

It has been tested experimentally that certain NO converters are able to oxidize ammonia to nitric oxide giving, as a result, a positive signal in the NO_2 channel without interfering with NO. This interference is not taken into account in the EN standard since it evaluates only NO readings, which remain the same in the presence of ammonia, for which this part of the standard should be reviewed. On the other hand, EPA studies the interference of ammonia on NO_2 but only at zero concentration as it assumes that NO_2 and ammonia can react to produce NO.

As has been previously stated [11], water vapour is able to absorb part of the released energy in the chemiluminescence reaction because of its absorption strip in the infrared region. The greater or lesser degree of interference depends on the type of photomultiplier tube used but, can only be totally eliminated with great difficulty since the excited NO_2 emission strip and the water vapour absorption strip practically overlap.

Carbon dioxide and ozone are the two gases that complete the interferences established in the EN standard. Carbon dioxide absorbs infrared radiation but at higher wavelengths, which makes it possible to totally eliminate the interference using a suitable photomultiplier tube.

As regards ozone, it is well-known that this gas reacts with NO to produce NO_2 so if the NO reading diminishes when mixing with ozone, it is not because of interference but due to a reaction between them. This reaction is commonly used to produce NO_2 standard concentrations by means of gas phase titration. The EN standard needs to be reviewed in this respect.

Nitric oxide and sulfur dioxide are the other two gases that EPA specifies as interferences in the NO_2 measurement process, but this *a priori* should not be especially problematic.

2.3.6 Lower detectable limit

This performance parameter is only taken into account by EPA and gives relevant information about the analytical method. Since the annual limit value for the protection of human health is 21 ppb it is essential that analyzers give reliable readings at these low concentration levels.

2.3.7 Lack of fit

This test checks the capacity of the analyzer to give proportional readings to different concentrations, this being one of the basic features of any analytical method.

Although this test is not included among the tests set by EPA, the American agency establishes as a previous step before carrying out all the tests the calibration of the analyzer with, at least, seven points of concentration, correcting the readings by means of the calculated straight line.

2.3.8 Sensitivity coefficients to device characteristics and ambient parameters

One of the most clearest difference between both protocols is that EN 14211:2005 incorporates the evaluation of the analyzer response for a number of performance parameters, such as sensitivity to variations in the sample temperature and pressure, the surrounding air temperature and the line voltage. Even though the two last variables can be controlled in the networks by means of thermal conditioning and voltage stabilizators, respectively, the first can only be controlled with difficulty and, thus, it is necessary to know the influence they have on the measurement process to evaluate their contribution to the expanded uncertainity and decide whether corrections should be made.

3 Conclusions

We have compared the requirements of EPA and EN 14211:2005 for nitrogen oxides analyzers. The latter document will be the first one to impose a number of requirements to be met by this type of analyzers when the Proposal for a Directive on ambient air and cleaner air for Europe comes into force. The performance characteristics are more numerous than those set by EPA to certified the equipments as reference methods for measuring nitrogen dioxide. In cases where the tests are comparable, the performance criteria are much more demanding in EN than in the EPA document. All of this will involve important changes for most of the equipment used at present in European countries to meet the aforementioned requirements. Nevertheless, some of the performance parameters or their criteria must be reviewed and, when necessary, modified.

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