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TRACEABILITY IN GAS MIXTURE

M.T. Lopez Esteban and T.E. Fernandez Vicente
Reference Gases Laboratory, Spanish Center of Metrology
E-28760 Tres Cantos, Madrid, Spain

Abstract: The 20th Conférence Générale des Poids et Mesures (1995), invited National Metrology Laboratories and other organizations (national and international), to collaborate wich the Comité International and the new Comité Consultatif in establising world-wide traceability at the highest level for measurement in chemistry.

In 1998 the Spanish Center of Metrology began a new project with the objective, inside its performance field related to the obtainment, development and difussion of the national measurement standards, of beginning the necessary works to develop an aspect never contemplated before in the chemical field, and inside it especifically the primary standard mixtures certification in order to assure traceability in gas mixture.

Keywords: Traceability, gas mixture

1 INTRODUCTION

In 1998 was published, in the Spanish Legislation, a legal document which regulates the State Metrological Control of the instruments for measuring vehicle exhaust emissions [1]. This legislation has as objective the protection of the environment, and human health and safety. The reliability in the results of quantitative chemical analysis is also very important for international trade [2].

The aforementioned Metrological Control includes the aspects related to type-approval and verifications, either initial or after the reparation and/or modification or periodical.

The Metrological Control showed the necessity of analyzing and certifying the gas mixture bottles in order to give traceability to the measures.

2 DEVELOPING THE PROJECT

The project consists of two parts. In the first place the Metrological Control of the instruments for measuring vehicle exhaust emissions, and in second place and subdivided in two, on one hand the necessity of the analysis, the certification and the assurance of the traceability of gas mixture already mentioned, and for other it is sought to carry out the putting in cylinders of special gas mixture in the own Reference Gases Laboratoy of the Spanish Center of Metrology.

As a previous step to the realization of the project, there were carried out the following general actions:

2.1 Location

Election of the working area and the facilities in those that will carry out the project: Election of the laboratory location; realization of the modifications and necessary works in the facilities in those that will be carried out the instruments for measuring vehicle exhaust emissions tests, as well as the analyses of gas mixture and the putting in cylinders of the same ones (system and control of environmental conditions; forced gas extraction; conductions for pure gases; annexed installation for pure gas bottles, and all those necessary ones for the correct operation of the laboratory).

2.2 Study of Legislation

Relative legislation to the State Metrological Control and applicable standard according to that was under consideration. It is a spanish standard [3] that provides for the realization of tests for the confirmation of the conformity of the implied measure instruments, like the climatic, mechanics and the electricians and electromagnetic ones, all them at some certain severity levels, among others. The tests are performanced in certain environmental conditions and using gas mixtures of defined content. It also contemplates the maximum errors allowed by measuring under working conditions for an instrument of certain class of accuracy, expressed as absolute value or relative. This spanish standard is equivalent to the OIML R.99 [4].

2.3 Agreements with Manufacturers

Meetings with spanish manufacturers of gas mixtures to reach agreements for the realization of projects to short, half and Iong-term have taken place. Among the activities developed in the frame of these agreements stands out the realization of visits that have carried out technicians from the Spanish Center of Metrology Laboratory, to manufacturers' plants of production of pure and special gases that have their factories in Spain, with the purpose of knowing their facilities, their activity fields and methods of special gas mixture preparation.

There were visited the laboratories for control where analysis technique used for gas mixture certification, validation methods, analysis equipments calibration and treatment of results with expression of the uncertainty were discussed.

These manufacturers of gas mixtures are suppliers of those used according to that demanded in the relative spanish standard to the tests that give execution to the State Metrological Control of the instruments for measuring vehicle exhaust emissions.

2.4 Encounters with other Organizations

Meetings with technicians from Portugal and Holland metrological institutes with the objective of verifying the equivalence of tests that are carried out to the analysers for measuring vehicle exhaust emissions, as well as to know the analysis methods of gas mixture bottles and the necessary equipment for their performance.

3 METROLOGICAL CONTROL

3.1 Metrological Control tests

Performance of type-approval, initial verification, verification after reparation and/or modification and periodic verification tests, with the purpose of giving execution to the State Metrological Control of the instruments for measuring vehicle exhaust emissions. It is necessary to use gas mixture bottles which concentrations as is defined in the legislation for the performance of these tests.

3.2 Standards Operating Procedures (SOP's)

Elaboration of technical procedures relative to type-approval and verification tests, as well as technical instructions relative to the manipulation of gas bottles previously to their use in the State Metrological Control of the instruments for measuring vehicle exhaust emissions tests. For this purpose, spanish, european and international normatives have been studied and consulted, as well as available OIML documents and recommendations, and operating instructions of equipments under test.

3.3 Equipment

Acquisition of needed equipment to carry out the tests that includes, the gas mixture bottles provided by national manufacturers, flow meter, baroclimatic camera, equipments for the electronic and electromagnetic tests performance and all the necessary accessories.

3.4 Training

Training in the Nederlands Meetinstituut (NMi) for three weeks in the field of type-approval and verification performance tests of analysers for measuring vehicle exhaust emissions or automotive mixtures that use the non dispersive infra red technique (NDIR).

4 ANALYSIS, CERTIFICATION AND ASSURANCE OF THE TRACEABILITY IN GAS MIXTURE

4.1 Equipment

With the purpose of checking and certifying each component of these mixtures content, CO, CO_2, O_2, total hydrocarbons and NO_x specific gas analysers have been acquired, as well as a gas chromatograph with workstation.

4.2 Additional equipment

To assure the reproducibility of taking the sample, and with the purpose to performance automatic analysis, there were also acquired some samplers and the appropiate software that allows connecting several gas mixture bottles, determinate the number of analysis repetitions to performance for each

sample, in the required working conditions. It also allows the registration of variations produced during the analysis.

4.3 Standards Operating Procedures (SOP's)

Technical instructions relative to the handling of these equipment have been elaborated, as well as the performance of their verification and calibration.

4.4 Primary Reference Materials (PRM's)

The reference materials used for specific analysers and the gas chromatograph calibration, are binary mixtures, with each component of interest in N_2, as gas balance, in different content so that the range of interest is covered. The supplier of these standards is the NMi.

4.5 Training

Training in the Nederlands Meetinstituut (NMi) for three weeks in the field of gas Metrology, with the purpose of acquisition of knowledge relative to gas mixture preparation; gas mixture verification and certification; gas chromatography analysis of automotive gas mixtures; automotive gas mixtures analysis with specific analysers; purity analysis that use the Fourier transform infrared spectrophotometry technique and mass spectrophotometry analysis.

4.6 Validation of methods

Validation of analysis methods used for gas mixture composition certification, according to international standards.

4.7 Comparisons

Participation in interlaboratory comparison exercises, first of all national and international level in the future.

A gas manufacturer is in charge of the gas mixture preparation for the performance of these comparison exercises, in order to assure that all gas mixtures cylinders have identical content for each component. This content is certificated by NMi. In this way, each participant is provided with a gas mixture bottle.

4.8 Traceability

At national level, the Reference Gases Laboratory of the Spanish Center of Metrology will have guaranteed international traceability through the working gases (provided by spanish manufacturers) chemical analysis that will be calibrated with reference gases certified by the NMi or another laboratory of similar characteristics.

Also, the transfer of this traceability towards the manufacturers of calibration gas mixtures, with the objective that they will be integrated in the national calibration chain for the production of calibrated reference gas mixtures. This way, the readiness of these reference materials qualifies the laboratories users to calibrate or to evaluate the accuracy of their gas analyses.

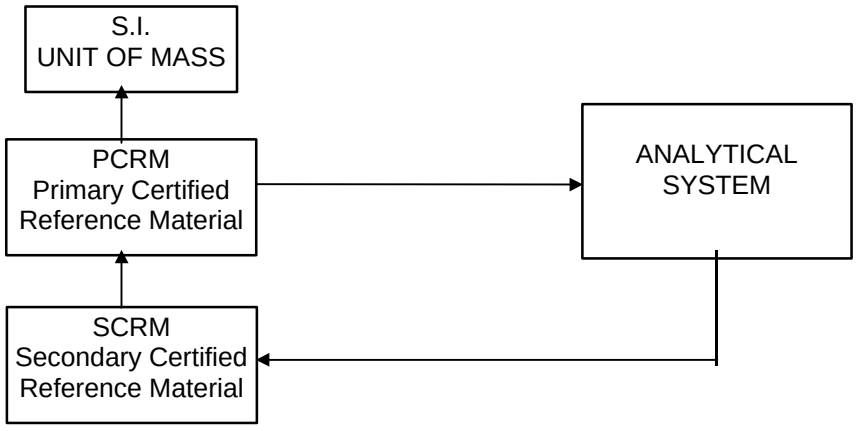

Figure 1. Traceability in gas mixture scheme

5 GAS MIXTURE PREPARATION

The objective to half term, is to acquire the necessary equipment to develop methods of preparation for gravimetric primary gas mixtures.

Take part in international comparison exercises that allow the obtainment of mutual recognition among National Institutes of Metrology about results in putting in cylinders and certified gas mixture, as well as demonstrate the traceability of those mentioned primary gas mixture and confirm the technical competence as reference laboratory for Metrology of gases.

To performance this second part of the project, the laboratory is provided with an additional location, because there are more equipments needed. This laboratory is endowed with a very controlled air conditioning system as well as a forced gas extraction.

To develop this project, we are going to perform these stages:

5.1 Equipment

It would be necessary to have an additional location, and more equipments, like filling stations, high accuracy balances and comparators as well as working standards of mass with the appropiate class of accuracy, empty (rented or bought) cylinders and high concentration gases to put in cylinders to get dilutions.

5.2 Training

Training in a Metrology Institute or Organization where this subject is being already worked, with the purpose to study in depth the application of the techniques for the preparation of gas mixtures for gravimetric method and purity analysis.

5.3 Standards Operating Procedures (SOP's)

Technical procedures and instructions will be elaborated and validated, all of them relative to putting in cylinders the gas mixture, as well as their analysis and subsequent certification.

5.4 Comparisons

Periodic participation in interlaboratory comparison exercises, either at national or international level.

Participation in periodic tests with other National Institutes of Metrology for the mutual recognition of results.

Transfer traceability, at national level, to the gas mixture bottles filled in our laboratory which are used for the analysers for measuring vehicle exhaust emissions calibration.

Give technical assistance, in matter of certification, to manufacturers of gas mixtures with the objective of certifying the filled bottles during manufacturing.

REFERENCES

[1] Ministerial Order 1998.04.15 that regulates the Metrological Control of the State of the instruments for measuring petrol vehicle exhaust emissions.
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AUTHORS: M. Teresa LOPEZ ESTEBAN and Teresa E. FERNANDEZ VICENTE, Reference Gases Laboratory, Spanish Center of Metrology, Calle del Alfar 2, E-28760 Tres Cantos, Madrid, Spain, Phone Int. +34 91 8074751, Fax Int. +34 91 8074807, E-mail: mtlopez@mfom.es