

Gaseous Metrology Developed in INMETRO

C. R. Augusto, C.C. Ribeiro, V. S. Cunha.

Instituto Nacional de Metrologia, Normalização e Qualidade Industrial
Av. Nossa Senhora das Graças, 50 Xerém, 25250-020, Rio de Janeiro, Brasil.
craugusto@inmetro.gov.br

ABSTRACT

The Laboratory of Gas Analysis (LABAG) is integral part of the Chemical Metrology Division of the Brazilian NMI and it acts in the development of new analytical methodologies for the gaseous mixtures certification process. Labag also destines part of its activities to the study of the transference of the traceability to the secondary standards using Primary Standards of Gaseous Mixtures - PSM, and started the production of these PSM in Brazil. The objective of this work is to present the activities that are being development in gas metrology in Brazil, the methodologies for certification of composition of gaseous standards, the process to produce Primary Standard of Gaseous Mixtures recently started, the laboratories results with its participation in key comparisons of CCQM/BIPM, the registrations CMC in BIPM/Appendix C and the organization of comparisons of the laboratories of the Brazilian companies.

1. INTRODUCTION

The Laboratory of Gas Analysis (LABAG) integrates the Chemical Metrology Division of INMETRO/BRAZIL. It acts in the development of analytical methodologies for gaseous mixtures certification process, and, as well as, it is making possible the production of PSM in Brazil. Its mission is to establish a system that guarantees and promotes the traceability to the international system of the gaseous chemical measurements, in order to support the industrial development of the technological and scientific centers of Brazil.



Fig. 1. Gas chromatography (CG) with FID and TCD.

INMETRO started activities in the field of Metrology in Chemistry in 2000. The work in gas analysis was one of the first area's to work on and in the past years the group followed a step-by-step approach to implement facilities for the analysis and preparation of PSM. First priority was the analysis of natural gas mixtures and automotive type mixtures. For both type of analysis the laboratory participated in

relevant comparisons. As a final step the laboratory is also investing in facilities for the gravimetric preparation of reference gas mixtures.

The objective of this work is to present LABAG's infrastructure that supports the activities in development in gas metrology in Brazil: the methodologies for certification of composition of gaseous standards, the process to recently start producing Primary Standard Gas Mixtures, the participation in key comparisons of CCQM/BIPM, the registrations CMC in BIPM/Appendix C and the organization of comparisons of the laboratories of Brazilian companies.

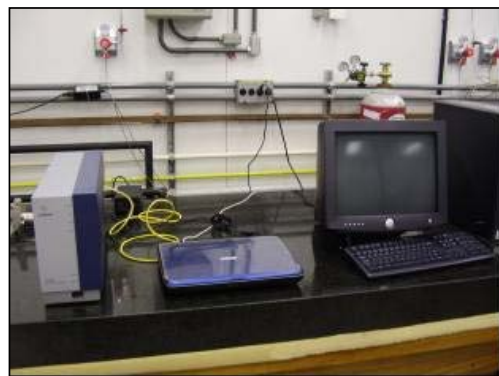


Fig. 2. Micro - Gas chromatography (Micro CG).

2. ACTIVITIES BEING DEVELOPMENT IN LABAG

2.1. Reserch Line

Traceability establishment in analysis related to quality control of air and natural gas.

Researches and development in gravimetry, gas chromatography and infrared spectrometry focusing the analyte determination and quantification in different matrices in gaseous state.

And development of Primary Standards of Gaseous Mixtures – PSM production.

- Analyzers of non-dispersive infrared to determine CO, CO₂, NO_x, SO_x and ethanol and analyzer of chemiluminescence to determine NO_x;
- Filling station, vacuum pump for cylinders, cylinder rolling machine and mass comparators, to prepare PSM.



Fig. 3. Non-dispersive infrared and quimi-luminescent analyzers.



Fig. 5. Mass Comparator - 50kg.



Fig. 4. Mass Comparators.

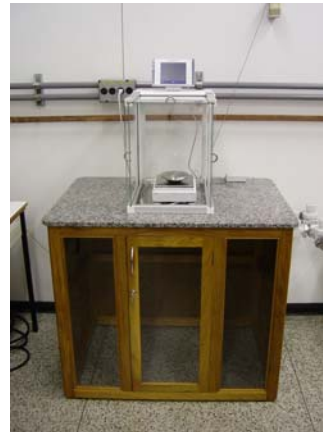


Fig. 6. Mass Comparator 10 100 g.

2.2. Infrastructure

LABAG encloses two areas, which are described as: a gravimetry room, where PSM are prepared, and a verification and certification part of the PSM produced.

The equipments available to develop the activities in order to attend the internal Brazilian market expectations are:

- Gas Chromatographs (GC) with methane catalyst column and coupled with thermal conductivity and flame ionization detectors and Micro - Gas Chromatograph (Micro GC), used to analyze Natural Gas and Gaseous Emissions;



Fig. 7. Vacuum set-up.



Fig. 8. Filling Station.

2.3. Gas Certification Process

In order to attend the internal market demand for certified reference material with traceability to the International System of Units – SI – LABAG certifies the gases commercially produced in Brazil following the norm ISO6143:2001 - Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures.

The certification of INMETRO guarantees the traceability, the quality and the reliability of the product produced in Brazil, either in national and international market, what means a significant advantage to the gas industries.

Mentioning a specific branch of the gas sector, the natural gas market can be considered as an important beneficiary segment with the certification and, consequently, with the metrological reliability.

LABAG emphasizes the mixture certification of:

- Automotive gas emissions measurements (CO/CO₂/Propane): binary and multi – component mixtures;
- Methane in synthetic air or in azote;
- Natural gas.

2.4. The Production of Primary Standards of Gaseous Mixtures – PSM

Excellency in gas metrology is only found at some National Metrology Institutes (NMIs). In order to begin the gravimetry production in Brazil, it was

necessary to establish agreements with other NMIs, as well as, evaluating the Brazilian, identifying the impediments in national industry and establishing the priority activities for the development of Primary Standards of Gaseous Mixtures – PSM.

Using reference materials is an important tool in the accomplishment of several aspects in quality measurement. They are also used in validation method, calibration and uncertainty measurement prediction.

The gravimetric preparation of gaseous mixtures uses analytical purity gases, and it allows the Laboratory to attribute a composition value to the main reference component.

Initially, LABAG will produce standards of automotive emissions, like carbon dioxide, propane and methane, Afterwards, it intends to produce multi component standards , like natural gas ones.

2.5. Participation in International Comparisons

LABAG participates in international comparisons to guarantee and demonstrate its competence in gas measurement.

Some of the international comparisons that the laboratory participated are presented below:

- SIM 8.12 P - 1st and 2nd rounds – Measurement of greenhouse gas emissions vehicles (2004 and 2006).
- CCQM the K23, a, b and c - Measurement of natural gas (2004/2005).
- CCQM the K52 - Measurement of greenhouse gases - carbon dioxide (2006).
- EUROMET - Measurement of natural gas (2007).

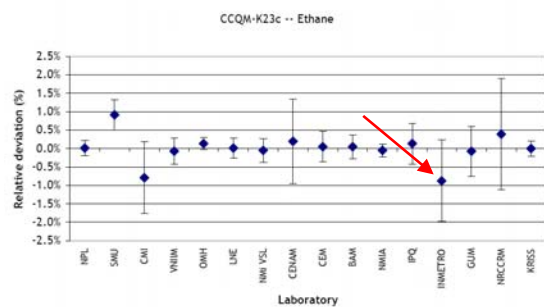


Fig. 9. Degrees of equivalence for ethane (Mixture III).

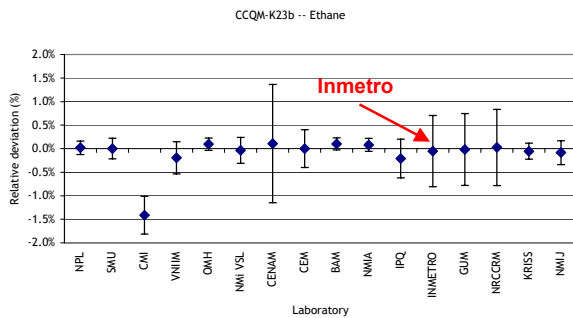


Fig. 10. Degrees of equivalence for ethane (Mixture II).

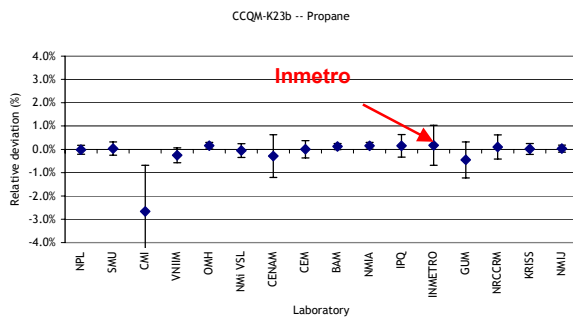


Fig. 11. Degrees of equivalence for propane (Mixture II).

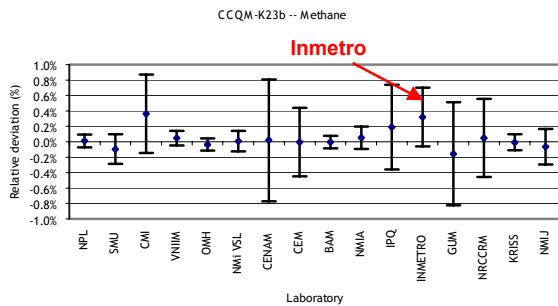


Fig. 12. Degrees of equivalence for methane (Mixture II).

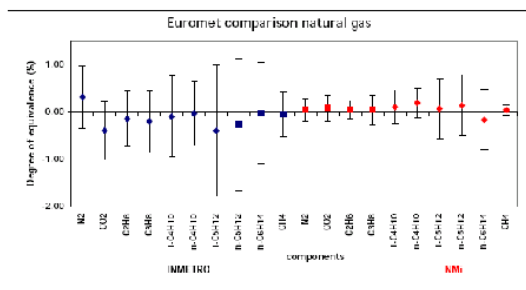


Fig. 13. Degrees of equivalence for natural gas.

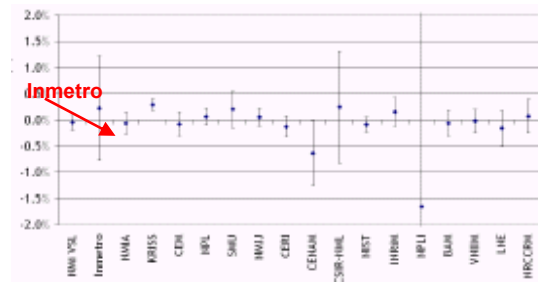


Fig. 14. Degrees of equivalence for carbon dioxide.

Analyzing the graphics showed on Figs. 9 and 10, it is possible to compare Inmetro results on two key comparisons occurred on two years, 2004 and 2005, to measurement natural gas. From the first participation of a CCQM/BIPM key comparison that occurred on 2004, when LABAG was not still totally structured for measurement gaseous samples, up to now, it is possible to observe that it has been presenting an upgrading in the optimization of methodologies, reducing measurement standard deviations and consequently the measurement uncertainty.

2.6. National Comparisons Coordination

LABAG coordinates comparisons (Proficiency Testing) in Brazil seeking to evaluate national laboratories, approximate industries to the quality market exigencies and disseminate metrological culture.

The emphasis of its comparisons is described below:

- Natural gas composition,
- Gaseous emissions: methane, propane, carbon monoxide and carbon dioxide

3. RESULTS AND DISCUSSION

From the first participation of LABAG in a CCQM/BIPM key comparison to measurement of gaseous samples (occurred in 2004) up to now, as can be observed in the graphs, the Laboratory has been presenting an upgrading in the optimization of methodologies which has been contributing to reduce the measurement standard deviations and consequently the measurement uncertainty.

Recently, LABAG was audited by Peer-Review accomplishing a necessary stage to the request of service register in the Appendix C of Bureau International des Poids et Mesures (BIPM), denominated of Capacity in Measurement and

Calibration (CMC) and the services list include natural gas and gaseous emissions measurement.

4. CONCLUSIONS

In general, the search of certified reference materials exceeds the offer in terms of the range of materials and of availability.

There are many aspects in the gas analysis to be developed at the laboratory, studies about the integration, process to improve the preparation, homogeneity, stability and characterization of PSM has been produced by the laboratory.

These fundamental aspects will enlarge the gaseous availability of PSM in Brazil and in the exterior.

The participation in the comparisons key of CCQM/BIPM made possible that LABAG/INMETRO is capable to maintain the traceability to the International System Units - SI, to give technical support, to guarantee the quality of the measurements of the national laboratories in way to turn them internally harmonica and acceptable internationally, contributing to the reliability of the analyses.

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