WEIGHING UNCERTAINTY CONTRIBUTIONS DURING PREPARATION OF PRIMARY GAS STANDARDS BY GRAVIMETRY

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Abstract: Primary gas standards (PSMs) are essential to society as provide traceability in the gas area. These standards are prepared by the gravimetric method, one of the most precise and accurate methods for preparing PSMs. This study aims to present the effects of weighing uncertainties related to the gravimetric process of developing a primary gas standard mixture, in order to simplify some procedures used in gas metrology.

Key words: primary gas standard mixture, gravimetry, traceability, weighing, certified reference material.

1. INTRODUCTION

In recent years the necessity concerning the quality in most different areas has significantly increased, what makes accuracy of results to be of extreme importance. International standards of comparison and normalized procedures are already being taken up in several science branches. Trustworthy and accurate analysis of gas composition, for instance, is of great value in several sectors, such as energy, environment, legislative and health ones. Nevertheless, in Brazil there is still a lack of production of these international standards, what still takes to the importation of these special gas mixtures.

The Laboratory of Gas Analysis (LABAG) at INMETRO is part of the Chemical Metrology Division (DQUIM) of the Brazilian National Metrology Institute (NMI), and it acts in the development of new analytical methodologies for gas mixtures production and certification process, in order to establish the traceability chain to all the gas industry sectors in Brazil.

The achievements made by the gas metrology laboratory from INMETRO are the growth in gas calibrations performed and the developments of certified reference material (CRM) demanded by the national industry, as well as the support not only the needs for traceability from the society, but also from most of South America. In the past years, LABAG's group followed a step-by-step approach to implement facilities for the analysis and preparation of gravimetric reference material of gas mixtures, known as Primary Standard Gas Mixtures (PSM's).

Primary standard gas mixtures (PSM's) are the basis for disseminating traceability for the analysis of gases. One way to prepare them is by gravimetry, which consists in weighing stable gases or volatile liquids into high-pressure cylinders, in agreement to the described concepts of the International Organization for Standardization ISO 6142:2001 - *Gas Analysis - Preparation of calibration gas mixtures - Gravimetric method* [1].

Although the principle and execution of the gravimetric method to prepare PSMs are not complicated, the uncertainty of the gravimetric method is so small that a seemingly minor error can result in an incorrect amount fraction of the PSM. There are many sources of error when using this method, but one of the most important is the error related to the weighing.

Based on the previous study proposed by Milton [2], it was observed that contributions from weighing uncertainty regarding the use of mass pieces in order to correct the buoyancy effect are insignificant in the final gravimetric uncertainty. It is presented that the amount of fraction of the resulting mixture is not influenced by changes in buoyancy due to linear expansion of the cylinder.

Therefore, with the objective to prevent the importation necessity, diminishing the cost and bringing more agility in the production of gas mixtures, LABAG is working in the development of several CRMs, placing INMETRO in the selected group of National metrology producers of primary reference gas mixtures.

Nowadays, Labag is producing binary and multicomponent mixtures of automotive emission standards, such as carbon dioxide (CO2), carbon monoxide (CO), and propane (C3H8) in nitrogen, and methane (CH4) in synthetic air. Afterwards, it intends to produce also standards, such as ethanol for breath analysis and natural gas.

2. PURPOSE

The increasing necessity concerning trustworthy and accurate results in gas area, impacts directly in the traceability establishment in analysis related to quality control of air, energy and health areas, enclosing techniques researching, such as gas chromatography and infrared spectrometric, focusing in the determination and quantification of different matrices in gas state and in the gravimetric preparation of gravimetric gas mixtures standards (PSM's), in order to make Certified Reference Material or primary reference gas mixture (PRM's) available.

This paper aims to present a simplification during the gravimetric process of developing primary gas standard

mixtures (PSM's), calculating the effects in uncertainty estimative during weighing of the components of the mixture. The use and the optimization of the production procedure of these gravimetric reference material is an important tool in the implementation of various aspects of measuring quality.

3. STATE OF ART

3.1 GAS MIXTURES AS REFERENCE MATERIALS

According to the ISO Guide 34 definition [4], a reference material (RM) is a substance that has one or more features that are homogenous and well described, so that they can be used for calibrating a measuring device, validating a measuring method or determining chosen parameters of the materials. A RM can be either a pure substance or a mixture of components, and it may be solid, liquid or gaseous. A certified reference material (CRM) is a material that carries a certificate. To each certified parameter an uncertainty should be assigned at a given confidence level. The applicability of a procedure for a precise determination of the material parameters has to be confirmed several times and each time accepted independently. Certificates are issued by recognized bodies.

Without a doubt, preparation of proper RM used for analyzing gaseous samples is particularly difficult; and so much attention has been paid to research on the development of this kind of RM, and its definition should be well known by the gas area.

Primary Reference Gas Mixture (PRM's) are prepared gravimetrically to the highest level of precision by National Standards Institutes using guideline ISO 6142:2001 [1]. The accuracy level of PRM's is the highest commercially available mixture. These PRM's are therefore not mend for direct use as working standard calibration gas analyzers, but more as reference standard to which working standards are traceable to.

Certified reference material (CRM's) are prepared in compliance with ISO guidelines and are certified by National Standards Laboratory or an Accredited Laboratory using guideline ISO 6143:2001 [3]. In this comparison, the method of multi point calibration is applied, where the analyzer is calibrated using PRM's. The accuracy level of a CRM is less than a PRM, and its use is mend for daily calibration of analyzers or as reference point for other mixtures (traceability).

Working reference materials (WRM's) consist of gas mixtures prepared by laboratories, certified according to guidelines of ISO 6143:2001 using at least a CRM as reference mixture.

In addition, there are reference materials (RM's), which are gas mixtures with sufficiently well known properties in order to be used to verify an instrument or a measurement method.

The growing requirements, indispensable in a competitive world market, concerning the accuracy of measurements, enclosing their traceability and worldwide comparability, constitute a considerable challenge for the National Institute of Metrology (INM) with its responsibility for ensuring the scientific background for the consistency and accuracy of all measurements in the State. Several Reference Materials (RMs) and Certified Reference Materials (CRMs) are widely used to establish the necessary comparability and traceability of chemical measurement results.

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 potential demands, identifying the impediments in national industry and establishing the priority activities for the development of PSM's. After the production, characterization, stability study and, finally, certification of the produced standards, it's possible to supply the PRM's.

Considering the gas area demand, Labag is developing several certified reference materials (PRM's) that are described on Table 1. Recently, in 2010, Labag participated, along with several recognized and expertise NMIs, in Inmetro first key-comparison regarding the production of primary standard gas mixture – Euramet 1113. This comparison aimed to produce an environment multicomponent primary mixture automotive emission in nitrogen, which analyte components are carbon monoxide, carbon dioxide and propane.

3.2 PSM PREPARE – THE GRAVIMETRIC METHOD

LABAG prepares PSMs by gravimetrical addition of each component, in according to the ISO method, that have been widely agreed upon [1]. This method consist in transferring stable gases or volatile liquids, denominated as parent gases (pure gases or gravimetrically prepared mixtures of known composition) quantitatively from supply cylinders into the PSM high-pressure cylinder. The amount of gaseous component added from the parent gas is determined by weighing after each successive addition. The mass fraction of each component in the final mixture is then given by the quotient of the mass of that component to the total mass of the mixture. The gravimetric method scheme for preparing primary standard gas mixtures by gravimetry is presented in Figure 1.

This procedure is carried out using a turbomolecular vacuum pump, filling station with electronically polishing pipes, valves and manometers. To achieve the intended composition of the mixture, the parameter mass is required. A more direct way of targeting the desired masses is by use of a balance on which the cylinder is placed is placed to observe the difference in mass which occurs during transfer. This special device is known as mass comparator balance (Figure 2).

The traceability of the composition of the gas mixture to the SI is guaranteed by the use of calibrated instrumentation, as well as, calibrated masses and tracked to a national standard, used in a mass comparator, when it was intended to get the mass of the gaseous component added to the cylinder.

Table 1 – Ranges of Labag's Certified Reference Mixture

Category	Measurand (quantity: amount of substance fraction)		Matrix	Dissemination range of measurement capability	Range of Expanded Uncertainty (k=2, 95%)	Measurement Technique
	Analyte	Unit				
Environment	Automotive Emission1		N2			
	CO	cmol/mol		0,1- 10,0	1,0 – 1,0	GC TCD2 /NDIR3
	CO2	cmol/mol		0,5 – 15,0	0,75 – 0,75	GC TCD / NDIR
	C3H8	μmol/mol		200 - 3500	0,5 – 0,5	GC FID4 / NDIR
	CO	μmol/mol	N2	1 - 100	3 - 2	GC TCD / NDIR
	CH4	μmol/mol	Synt. Air	50 - 500	2 – 1	GC FID (with methanizer)
Forensic	Ethanol	μmol/mol	N2	50 - 500	BEING DEVELOPMENT	
Energy	Natural Gas	μmol/mol	CH4	diverse	BEING DEVELOPMENT	

1 multicomponent mixture of CO, CO2 and Propane
2 gas chromatography with thermal conductivity detector
3 non dispersive infra-red
4 gas chromatography with flame ionization detector

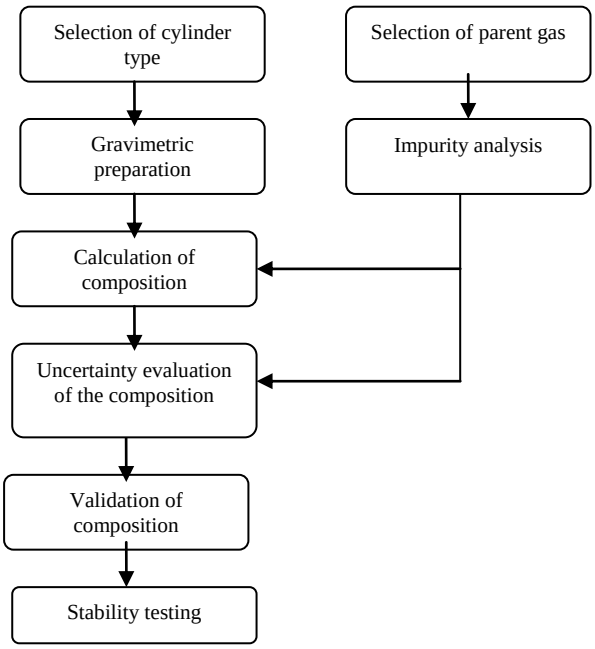

Fig. 1. - Flowchart of primary gas standard preparation

Fig. 2. – Mettler mass comparator balance

The uncertainty in the values of the amount fractions of the components introduced in such PSMs is limited by a combination of the uncertainty in the weighing process together with the uncertainty in the purity of the gases and their molecular weights. For binary mixtures of stable compounds, these gravimetric uncertainties are generally less than 0,05% and may be as small as 0,005%. (relative to value) [2, 6].

A number of sources of error influence the uncertainty of the final result. They should be taken into account or neglected, depending on the equipment and method uses and on the degree of uncertainty in the final result which can be tolerated. There are 4 (four) main components incorporated in the gravimetric uncertainty: errors from the balance, from the mass pieces, from the cylinder and from gas components. Related to the balance are uncertainties contributions, such as: resolution of the balance, linearity, drift, zero point, and effect of location of the cylinder on the pan. Related to the gas components are: residual gas, leakage, molar mass and purity of parent gases. Related to cylinders are: typical changes in mass due to handling and adsorption phenomena occurring when the cylinder is at constant temperature. Some of these uncertainty contributions in each step of weighing are presented in Figure 3. The most significant ones that should be paid attention are underlined in the scheme of the uncertainty contributions in the weighing process.

Another uncertainty contribution comes from buoyancy effects that arise from the multiplicative effect of differences in atmospheric conditions between weightings and differences in the volumes of the items being weighed. To minimize the influence of the last uncertainty contribution mass pieces are used during the weighing. As both cylinders (sample mixture and reference) are used all along the weighing process, it should be counted the buoyancy effects only for the mass pieces used.

The mass and its respective uncertainty from each component are obtained from a mass comparator (Mettler XP10003S, max.: 10,1 kg, d.: 1mg), which registers the mass from the unknown cylinder which has the PSM being prepared and a reference cylinder. Those two cylinders are

weighed against each other with the necessary mass pieces added on the balance. The mass recorded from any weighing on a balance pan is given by the difference between the apparent mass suspended from the arm.

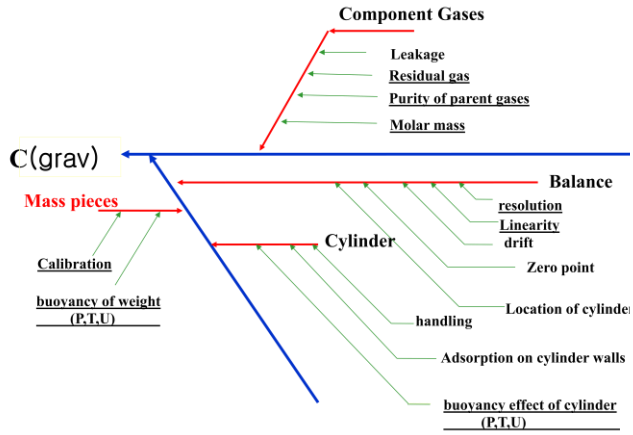

Fig. 3. – Uncertainty sources during each weighing process

For this study, it was gravimetrically prepared a PSM of carbon monoxide in nitrogen with a nominal concentration of 100 x 10^{-6} mol/mol. During the weighing of each component of the mixture, the first one was using the mass pieces required for the total mass difference in the final pressure, and another register of the weighing results without the mass pieces added to the balance. The mass pieces used for this weighing were 500 g and 100 g. Both weightings were performed under same room conditions, which were around: 21 ^{o}C, 1005 hPa and 59 %RH.

An observation of the linearity of the balance was also performed for a wide range of mass pieces, in order to evaluate the linear expansion correction of the cylinder during weighing.

As it was presented before, the final uncertainty of PSM's is limited by the uncertainty of their gravimetric preparation. As the total uncertainty is the sum of squared contributions, a contribution equaling less than 1/10 of the largest contribution can be safely neglected [1].

A general observation of the most important uncertainty contributions was performed, in order to evaluate the relative contribution of the buoyancy effect against the other contributions. For this study, only uncertainties derived from the balance (weighings) were considered and compared to the ones derived from the buoyancy effect in the mass pieces.

4. RESULTS

The verification of the balance was performed by studying the linearity of the mass comparator in the same ambient conditions from the weightings. This verification is presented in figure 4, and it was done for all work range. Considering the trend line, it can be seen from R^2 that the results from the balance weighing are very satisfactory.

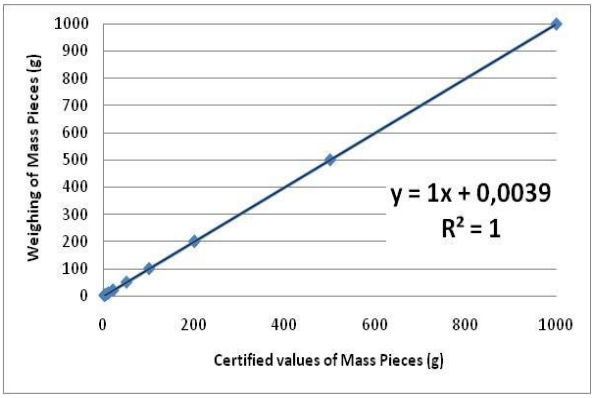

Fig. 4. – Mass Comparator Linearity

In Table 2 it can be observed the results obtained from weighing the mixture to be prepared of carbon monoxide in nitrogen (3 weighing out of 2 components). These results were acquired through the software ISO 6142 (NMi Van Swinden Laboratorium B.V., version 3.0.0.1) developed and validated by VSL, which is based on the procedures to estimate PSM final uncertainty from the Norm ISO 6142:2001. It was performed two different weightings: one adding mass pieces and another without them, to evaluate the effects of using it during the weighing step of the gravimetric process. It can be seen that there is no significantly difference between the gravimetric uncertainty (u_g) with/without the mass pieces. This is confirmed when evaluating the relative final gravimetric uncertainty obtained (u_g/fraction*100) that is a hundred times higher (0,03%) than the difference from each procedure.

Table 2. Effects of mass pieces on weighing

	mol.fraction (x10^{-6} mol/mol)	u_g (x10^{-6} mol/mol)	relative uncertainty (%mol/mol)
with Mass Pieces	99,65054951	0,031440147	0,03155040
without Mass pieces	99,64916502	0,03143981	0,03155050

Therefore, it is concluded that the weighing step during gravimetric procedure to prepare PSMs can be simplified by not considering the use of mass pieces while weighing, as this contribution is much lower compared to the total balance uncertainty contributions.

Nevertheless, a special attention should be paid regarding each contribution of the combined uncertainty for the gravimetric process. Calculations and estimative should be done in order to know exactly what uncertainty contribution from buoyancy effect itself, and not only in the final results of the standard mixture.

5. CONCLUSIONS

This paper describes several aspects regarding the importance of use of gas CRMs, as well as, new developments in the process for the production of these type of CRMs.

The accurate weighing of gas into high-pressure cylinders plays a central role in providing traceability for primary gas mixtures. The uncertainties in the masses of successive components added to such mixtures are significantly correlated. We show that a consequence is that the amount fraction of the resulting mixture is not influenced by changes in buoyancy due to the linear expansion of the cylinder. Thus, the correction for linear cylinder expansion applied to the calculated mass fraction is sufficiently small to be ignored in the examples given here, which are typical of many practical applications in gas metrology. This result provides a useful simplification to some procedures used in gas metrology.

Nevertheless, this result will require more careful consideration. Although the results obtained were satisfactory, more complex studies are necessary and they are already being developed. Such studies will make it possible to identify the contribution of each uncertainty of the produced primary gas standards. Besides, statistical evaluations are also already in progress, therefore they are basic tools for the assessment of the metrological trustworthiness of measurements.

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