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The use of dynamic dilution by Mass Flow Controllers in the environmental monitoring of CO₂: calibration issues and strategies

M Sega^{1,2}, F Pennecchi¹, F Rolle¹ and P G Spazzini¹

¹ Istituto Nazionale di Ricerca Metrologica - INRIM, Strada delle Cacce 91, 10135 Torino, Italy

E-mail: m.sega@inrim.it

Abstract. Gaseous pollutants determination in atmosphere is usually carried out by comparison methods with dedicated analysers, which need to be calibrated with proper certified reference gas mixtures. Dynamic dilution allows the generation of gas mixtures which can be employed either to calibrate the analysers or to validate gas mixtures contained in high pressure cylinders. The dynamic dilution is often achieved by using Mass Flow Controllers (MFCs) due to their ease of use and good level of reliability. The MFC sensors are based on heat exchange equations, therefore the response of these instruments is sensitive to the nature of the flowing gas. The different response can be taken into account through a so-called Gas Correction Factor (GCF), which can be computed when the gas properties are known. Neglecting the use of proper GCFs may result in a bias in the assignment of the molar fraction of dynamic mixtures. The present paper deals with the calculation carried out at INRIM of the GCF in the generation of dynamic mixtures of carbon dioxide in synthetic air at ambient level. The results obtained without using the GCFs are compared with those obtained by application of the correction, showing the presence of a systematic non-negligible bias.

1. Introduction

The need for accurate and reliable measurement results is an essential aspect when monitoring environmental pollutants. Metrological traceability of measurement results [1], which is a fundamental feature in every measurement field, becomes crucial when dealing with the environmental chemistry. In this field, the application of metrological concepts is not straightforward, as primary methods are often not available in routine measurements and comparison methods with dedicated analysers are commonly employed. These analysers need to be calibrated with suitable traceable reference materials and, for the determination of gaseous pollutants in atmosphere, the calibration procedure is carried out by using proper certified reference gas mixtures. These certified standards can be prepared directly by primary methods, like gravimetry [2], or certified by comparison with other independent reference standards [3]. In this framework, the application of dynamic dilution is assuming an important role, since it allows the generation of the required gas mixtures (which can be employed either to calibrate the analysers or to validate gas mixtures contained in high pressure cylinders) on the fly or, even more important, on the spot, thus allowing a much higher level of transportability of the references and

² To whom any correspondence should be addressed.



consequently the possibility to calibrate the instruments in the field. Dynamic dilution is carried out by mixing two or more gases on the fly; in the simplest case of a binary mixture, a parent mixture, containing the desired analyte at high molar fraction, is diluted by a pure gas. The dynamic dilution is often achieved by using Mass Flow Controllers (MFCs) due to their ease of use and good level of reliability. In order to guarantee the metrological traceability of the mixtures produced by dynamic dilution, certified parent mixtures and pure gases with assessed purity must be used, together with calibrated MFCs. The MFC sensors are based on heat exchange equations, therefore the response of these instruments is sensitive to the nature of the flowing gas. Calibration of MFCs is usually carried out using dry, pure gases, and often a single calibration in nitrogen is performed for reasons of costs. The different response can be taken into account through a so-called Gas Correction Factor (GCF), which can be computed when the gas properties are known. Although the importance of using the GCF is well known when a pure gas different from that used to calibrate the MFCs is employed [4], less attention has been paid so far to diluted mixtures of an analyte gas in nitrogen or air. Though, the presence of the analyte may change the overall gas properties, and therefore the MFC response, by a measurable amount. Consequently, neglecting the use of proper GCFs may result in a bias in the assignment of the molar fraction of dynamic mixtures. The present paper deals with the calculation carried out at the Istituto Nazionale di Ricerca Metrologica (INRIM) of the GCF to be applied in the generation of dynamic mixtures of carbon dioxide (CO₂) in synthetic air, with nominal molar fractions in the range of (750-950) $\mu\text{mol mol}^{-1}$, starting from a parent mixture having CO₂ at nominal concentration of about 5000 $\mu\text{mol mol}^{-1}$. Such mixtures were used to calibrate a non-dispersive infrared (NDIR) analyser for CO₂, which was then employed to analyse the molar fraction of mixtures of CO₂ in synthetic air gravimetrically prepared at INRIM, having known molar fractions in the range of (800-920) $\mu\text{mol mol}^{-1}$. The results obtained without using the GCFs are compared with those obtained by application of the correction, showing the presence of a systematic non-negligible bias.

2. Materials and methods

A facility for dynamic dilution was assembled by employing two MFCs (MKS, US) with full scale range (FSR) of 200 and 2000 SCCM, respectively, and a mixing chamber. SCCM, Standard Cubic Centimeters per minute is the flow rate unit usually employed for MFCs; it is used because it allows to refer to a well-defined amount of gas, i.e. to the gas volume at specific conditions of temperature and pressure – usually 0° C and 1 atm. The MFCs had been previously calibrated at INRIM using dry nitrogen. The MFC having 200 SCCM FSR was used for regulating the flow of the parent mixture of CO₂ in synthetic air, gravimetrically prepared at INRIM and having molar fraction of 4983.5 $\mu\text{mol mol}^{-1}$ and associated expanded uncertainty ($k = 2$) of 1.1 $\mu\text{mol mol}^{-1}$, while the 2000 SCCM MFC was employed for the diluent gas synthetic air (Air Liquide, France) having certified purity of 99,9997 %. Five dynamic mixtures were generated and used to calibrate a CO₂ NDIR Analyser URAS 14 (ABB, Switzerland) in the ranges (750-850) $\mu\text{mol mol}^{-1}$ and (850-950) $\mu\text{mol mol}^{-1}$. The calibrated analyser was then employed to assess by analysis the CO₂ molar fraction of two primary gas mixtures at ambient level gravimetrically prepared at INRIM (indicated here with codes 1 and 2), whose gravimetric values, reported in table 1, are centred in the two calibration ranges of the NDIR analyser.

Table 1. Gravimetric values of the two INRIM mixtures of CO₂ in air at ambient level.

Mixture	CO ₂ molar fraction $\mu\text{mol mol}^{-1}$	U ($k = 2$) $\mu\text{mol mol}^{-1}$
1	800.50	0.40
2	916.70	0.40

3. Results and discussion

Mixtures 1 and 2 were analysed by means of the calibrated NDIR analyser and the CO₂ amount fraction and its associated uncertainty were calculated. As previously said, when gases different by nitrogen are employed with MFCs, a proper GCF has to be considered. Such correction is defined as a function of specific heat, density and molecular structure of the gas. Synthetic air can be assumed equivalent to nitrogen, hence it does not require any correction. For the parent mixture of CO₂ at 4983.5 μmol mol⁻¹ in synthetic air, instead, a relevant GCF was calculated according to eq. 1 [5]:

$$\text{GCF}_m = \frac{0.316 \times (a_1 s_1 + a_2 s_2 + \dots + a_n s_n)}{a_1 \rho_1 c p_1 + a_2 \rho_2 c p_2 + \dots + a_n \rho_n c p_n}$$

where:

GCF_m is the gas correction factor for a gas mixture m

0.316 is the standard density of nitrogen

a_i is the fractional gas flow of the i -th gas in the mixture

s_i is the molecular structure correction factor for the i -th gas in the mixture

ρ_i is the standard density for the i -th gas in the mixture, expressed in g L⁻¹ at standard conditions (0°C and 1 atm)

$c p_i$ is the specific heat of the i -th gas in the mixture, expressed in cal g⁻¹ °C⁻¹.

The CO₂ amount fraction and its associated uncertainty analytically obtained by NDIR analysis for mixtures 1 and 2 were re-determined taking into account the GCF_m. Figure 1 reports the comparison of the analytical data and the gravimetric value for mixture 1, while Fig. 2 reports corresponding data for mixture 2.

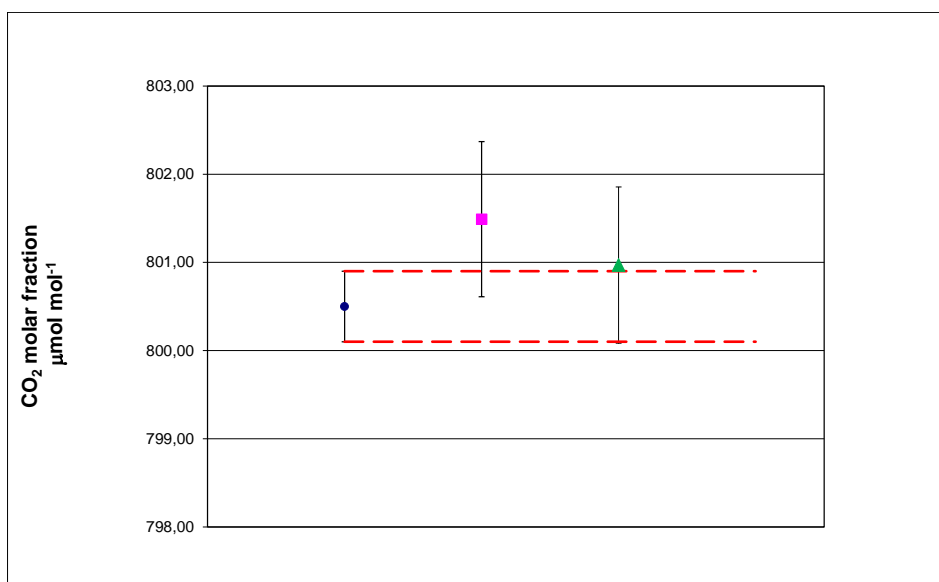


Figure 1. CO₂ molar fractions for mixture 1 having gravimetric value of 800.50 μmol mol⁻¹ and expanded uncertainty ($k = 2$) of 0.40 μmol mol⁻¹. ●: gravimetric value; ■: analytical value without GCF correction; ▲: analytical value with GCF correction. The indicated error bars correspond to the expanded uncertainty ($k = 2$).

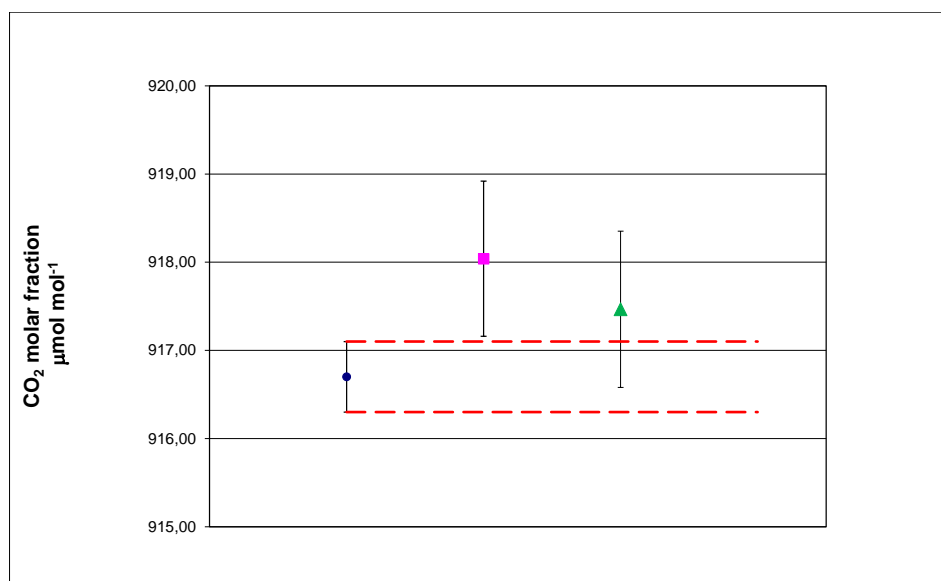


Figure 2. CO₂ molar fractions for mixture 2 having gravimetric value of 916.70 $\mu\text{mol mol}^{-1}$ and expanded uncertainty ($k = 2$) of 0.40 $\mu\text{mol mol}^{-1}$. ●: gravimetric value; ■: analytical value without GCF correction; ▲ analytical value with GCF correction. The indicated error bars correspond to the expanded uncertainty ($k = 2$).

From the data in Fig. 1 and 2 it can be seen that ignoring the GCF leads to systematic effects of overestimation of the CO₂ molar fraction. The analytical value obtained by NDIR analysis for mixture 2 is even not compatible with the gravimetric value. The corresponding values obtained taking into account the GCF, on the other hand, showed to be compatible with the gravimetric value within the stated uncertainties for both mixtures 1 and 2. The uncertainties in the analytical values are the same in the two cases since the uncertainty contribution associated with the GCF is considered negligible. The comparison between Fig. 1 and Fig. 2 shows that the bias increases when the amount fraction of the mixture is higher. This can be explained by the fact that larger flows of parent mixture are needed to obtain calibration gas mixtures at higher CO₂ molar fraction by dynamic dilution, hence the effect of neglecting the correction becomes more visible.

4. Conclusions

Dynamic dilution by means of MFCs allows the generation of ready-to-use gas mixtures which can be employed either to calibrate the analysers or to validate gas mixtures contained in high pressure cylinders. When MFCs are used with gases different from the gas used to calibrate them, usually nitrogen, a proper GCF should be calculated and applied. The results shown in the present work for mixtures of CO₂ in synthetic air at ambient level clearly demonstrate the occurrence of a systematic bias when GCF is not applied. More work needs to be done to further reduce the discrepancies that still remain between gravimetric and analytical data.

5. References

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