

Metrological traceability of carbon dioxide measurements in atmosphere and seawater

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Abstract. The accurate determination of gaseous pollutants is fundamental for the monitoring of the trends of these analytes in the environment and the application of the metrological concepts to this field is necessary to assure the reliability of the measurement results. In this work, an overview of the activity carried out at Istituto Nazionale di Ricerca Metrologica to establish the metrological traceability of the measurements of gaseous atmospheric pollutants, in particular of carbon dioxide (CO₂), is presented. Two primary methods, the gravimetry and the dynamic dilution, are used for the preparation of reference standards for composition which can be used to calibrate sensors and analytical instrumentation. At present, research is carried out to lower the measurement uncertainties of the primary gas mixtures and to extend their application to the oceanic field. The reason of such investigation is due to the evidence of the changes occurring in seawater carbonate chemistry, connected to the rising level of CO₂ in the atmosphere. The well established activity to assure the metrological traceability of CO₂ in the atmosphere will be applied to the determination of CO₂ in seawater, by developing suitable reference materials for calibration and control of the sensors during their routine use.

1. Introduction

The accurate and reliable determination of environmental gaseous pollutants is fundamental for the monitoring of the trends of these analytes in atmosphere and to obtain significant information about the current pollution levels and the future trends on a global scale. Hence, the application of the metrological concepts to this field is necessary to assure the reliability of the measurement results and to support the planning of suitable actions to reduce the negative effects on the environment and on the human beings.

In particular, the determination of carbon dioxide (CO₂) levels is important for the role of this gas in the greenhouse effect. CO₂, together with other gases such as water vapour and methane, absorbs the IR radiation and reflects part of it back to the terrestrial surface. This phenomenon contributes to the terrestrial warming, maintaining the temperature of the Earth at the value of 15 °C. Without the atmosphere and without the greenhouse effect the Earth would have a temperature of -15 °C [1] and would be covered in ice. During the last century, this positive effect has become responsible for an excessive global warming, due to the increasing levels of CO₂ and other greenhouse gases in atmosphere and, consequently, the temperature on the Earth's surface raised above 15 °C. Water vapour is responsible for two thirds of this effect, while CO₂ for one fourth.



In addition, the higher level of CO₂ absorbed by the oceans from the atmosphere causes an acidification of the marine waters, with fallouts on the global ecosystem. Although the natural absorption of CO₂ by the oceans helps to mitigate the climatic effects of anthropogenic emissions of CO₂, the resulting decrease in pH will have negative consequences primarily for oceanic calcifying organisms. Since the beginning of the industrial revolution, it has been estimated that surface ocean pH has fallen off by slightly more than 0.1 units on the logarithmic scale of pH. It is expected to drop by a further 0.3 to 0.5 pH units and these changes are predicted to be continuous and rapid as the oceans take up more anthropogenic CO₂ from the atmosphere than they can eliminate.

The choice of addressing the metrological traceability of CO₂ measurement results derives from CO₂ relevance for the World Meteorological Organisation (WMO), an intergovernmental organization that promotes observation of atmospheric environment. WMO operates with programmes as the “Global Atmosphere Watch” (GAW) which is divided into focal areas for different pollutant species. Suggestion of GAW in exposure limits can be implemented in international and national legislation, as in the European Directive 2008/50/EC [2] that is dedicated to ambient air quality and cleaner air in Europe.

As for the marine environment, the partial pressure of CO₂ ($p\text{CO}_2$) in seawater is an Essential Climate Variable which can be monitored in situ with networked sensors. At the European level, the Marine Strategy Framework Directive 2008/56/EC [3] asks for provisions for the adoption of methodological standards to assess the status of the marine environment, to implement its monitoring and to reach environmental targets. In addition, during the last year, a Joint Action called “European Marine Sensors Calibration Network” has been launched within the European Joint Programming Initiative “Healthy and Productive Seas and Oceans” (JPI Oceans - <http://www.jpi-oceans.eu/>) in order to bring together the competencies of various communities such as the oceanographic, metrological and sensor producers.

In this framework, there is a growing need of assessing the conformity of the instrumentation and the sensors necessary for the determination of CO₂ in atmosphere and seawater, in particular considering their measurement uncertainties.

In this work, an overview of the activity carried out at INRiM for the establishment of metrological traceability of the measurements of CO₂ and in particular for the preparation of primary reference gas standards for the molar fraction of CO₂, is presented. A focus on the uncertainty evaluation and on some applications for the atmospheric monitoring is given.

Metrological traceability is defined, in the International Vocabulary of Metrology [4], as “the property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty”. This definition highlights the necessity of the availability of suitable reference standards for the calibration of the instrumentation and for the development and validation of measurement procedures. INRiM, being the Italian National Metrological Institute, has among its duties to realise and maintain primary standards for the basic and derived units of the International System of Units (SI). In the gas analysis field, suitable primary reference materials are represented by gas mixtures prepared by means of primary methods, such as gravimetry and dynamic dilution. A primary method of measurement in the SI is defined as “a method having the highest metrological qualities whose model (mathematical equation) and realisation are completely described and understood in terms of SI units” [5].

2. Reference gas standards

2.1. Gravimetry

Gravimetry is a primary method which can be used for the preparation of primary reference standards and it can be applied to the preparation of primary gas mixtures in high pressure

cylinders. Gravimetry gives direct traceability to mass standards and the purity of the parent gases. The preparation procedure followed at INRiM is divided in two steps: 1) the conditioning and 2) the weighing. During the conditioning step the gas cylinder is evacuated and heated for some hours, then is filled with matrix gas (usually nitrogen or synthetic air). The conditioning cycle is generally repeated for three times. The conditioning step aims to desorb contaminants from internal cylinder walls as the presence of contaminants would lead to fast degradation of the gas mixture. During the second part of the procedure the mass of the gas cylinder is compared with the mass of an empty reference cylinder, and calibrated mass standards are arranged on the top of the lighter cylinder to maintain the difference between the gas cylinder and the reference gas cylinder within 1 g, thus optimising the mass comparator performance. The use of calibrated mass standards also assures the metrological traceability of the mass measurement (Figs. 1(a) and 1(b)). The reference cylinder and the gas cylinder are alternatively weighed according to the double substitution scheme (A-B-B-A), where A represents the sample cylinder and B the empty cylinder used as reference. This comparison is carried out to minimise the correction for the buoyancy effect due to the shape of the cylinder. This correction is calculated taking into account the air density during the weighing process. The sample cylinder is weighted prior and after the addition of each component of the final gas mixture. For a bi-component mixture the weighing procedure would be: 1) empty cylinder, 2) cylinder after the introduction of the analyte gas, which can be present in a pure gas or in a parent gas mixture, 3) cylinder after the introduction of the matrix gas. The mass of the gas introduced inside the cylinder is related to the gas concentration [6–8]. The simplified model equation for the calculation of the molar fraction of a generic analyte in a bi-component mixture starting from a parent gas mixture is the following:

$$\chi_{\text{fin}} = \chi_{\text{in}} \frac{m_2 - m_1}{m_3 - m_1} \quad (1)$$

where:

χ_{fin} = molar fraction of the analyte gas in the final mixture ($\mu\text{mol}/\text{mol}$)

χ_{in} = molar fraction of the analyte gas in the parent gas mixture to be diluted ($\mu\text{mol}/\text{mol}$)

m_i = mass (g) of the gas determined in each of the three weighing steps (1: tare, 2: tare + parent mixture, 3: tare + parent gas mixture + matrix gas).



Figure 1. a) Primary gravimetric gas mixtures produced at INRiM; b) Detail of the INRiM facility for the weighing of a primary gas mixture, with calibrated mass standards.

2.2. Dynamic dilution

A dynamic dilution system can mix in real time two or more gas mixtures to generate a new gas mixture. Two gases can be mixed together in order to reach the desired molar fraction, starting from a more concentrated gas mixture and a matrix gas. The reference gases obtained by dynamic dilution can be used for instrumental calibration or validation of calibration curves by changing the parent gases. With respect to gravimetry, dynamic dilution has the advantage that a gas mixture can be diluted in real time on a range of different concentrations and can be more easily used also for reactive gases that are instable in high pressure cylinders. In addition, mixtures generated by dynamic dilutions can also be used to check and validate gas standards prepared by gravimetry. At INRiM a dynamic dilution system composed of two Mass Flow Controllers (MFCs) and a mixing chamber is used (Figs. 2(a) and 2(b)). MFCs are calibrated at the INRiM micro-gas station, which is one of the Italian gas flow rate primary standards. Three different MFCs having full scale range (FSR) of 200 sccm, 500 sccm and 2000 sccm can be used [9]. Two pairs of MFCs of FSR 200 sccm and 2000 sccm or, alternatively, of FSR 500 sccm and 2000 sccm are employed depending on the mixtures to be prepared. A polynomial regression curve was obtained from the calibration results of the MFCs: the regression curve gives a correction for the nominal flow displayed by the MFCs. The molar fraction of a generic gas mixture obtained by dilution with two MFCs [10] is calculated according to the following equation:

$$\chi_{a_out} = \frac{\chi_{1a}Q_1 + \chi_{2a}Q_2}{Q_1 + Q_2} \quad (2)$$

where:

χ_{a_out} = molar fraction of the analyte gas in the final mixture ($\mu\text{mol/mol}$),
 Q_1 = flow of the MFC used for the analyte gas that has to be diluted ($\text{sccm}=\text{cm}^3/\text{min}$),
 Q_2 = flow of the MFC used for the diluting matrix gas ($\text{sccm}=\text{cm}^3/\text{min}$),
 χ_{1a} = molar fraction of the analyte gas to be diluted ($\mu\text{mol/mol}$),
 χ_{2a} = molar fraction of the analyte in the diluting gas matrix ($\mu\text{mol/mol}$).

The uncertainties of Q_1 and Q_2 are obtained during the calibration, while uncertainties of the concentrations χ_{1a} and χ_{2a} are certified by the gas mixture producers.

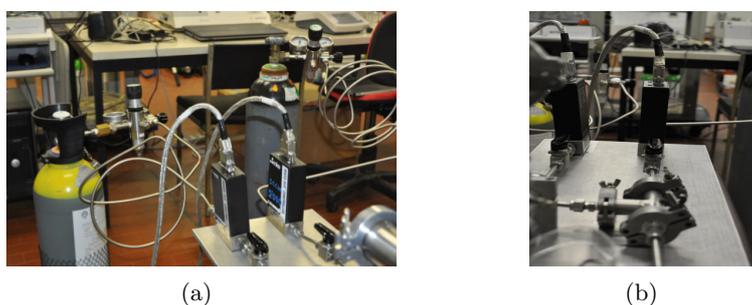


Figure 2. INRiM dynamic dilution system: a) MFCs connected to gas cylinders; b) MFCs and mixing chamber.

3. CO₂ mixtures produced at INRiM

At INRiM, a facility for the production of primary CO₂ standards by gravimetry has been used since 2004. Due to the huge amount of gas mixtures that are needed to cover different ranges

of concentration during the calibration of instrumentation, a new system for dynamic dilution was recently set up. In both cases, reference gas mixtures are produced paying particular attention to the traceability of the gas standard, hence primary methods are used for this purpose. Primary reference mixtures of CO₂ in nitrogen or synthetic air matrices are prepared by gravimetry in high pressure cylinders of aluminum alloy, having an internal volume of 5 L. The CO₂ mixtures cover the molar fraction range (50-1000) μmol/mol. The relative gravimetric standard uncertainty associated with these mixtures decreases with increasing molar fraction and is in the range (0.5-0.01)%. The gravimetric uncertainty depends on:

- uncertainty on the molar mass of the parent gases;
- uncertainty on the parent gas mixture composition;
- uncertainty of the weighing process.

For the dynamic dilution, the same molar fraction range and uncertainties can be obtained. The main sources of uncertainty contributing to the uncertainty of the preparation of dynamic mixtures are:

- uncertainty of the parent gas mixture composition;
- uncertainty of the flow rates;
- uncertainty of the purity of the parent gases.

The main uncertainty contribution is related to the parent gas mixture composition for both the preparation techniques. Due to the wide range of concentrations that can be obtained by mixing two gas mixtures, the dilution system results in a powerful tool for situations that request the use of many gas mixtures. For this reason, the dynamic dilution can be employed to calibrate CO₂ analysers and sensors, to validate calibration curves and to assign analytical values in the stability study of CO₂ gas mixtures prepared by gravimetry in high pressure cylinders. The dynamic dilution proved not to introduce any additional contribution to the uncertainty budget, maintaining an uncertainty comparable with the uncertainty of the parent gas mixture to be diluted.

4. Applications for atmospheric monitoring

Different analytical techniques can be used for the monitoring of atmospheric pollutants. Non Dispersive Infrared spectroscopy (NDIR) is suggested as a detection method by the WMO, being a robust and selective technique, easily applicable to portable instruments. As NDIR is selective to CO₂, it cannot be applied to the determination of degradation products and impurities. On the other hand, Fourier Transform Infrared spectroscopy (FTIR) is sensitive to all molecules having a net change in their dipole moment. For this reason, FTIR is used at INRiM to identify the presence of impurities and degradation products inside the gas mixtures which might affect the nominal concentration of the mixtures, their stability and also the response of the analysers. FTIR is a powerful tool also for the identification of the presence of different isotopes of carbon in CO₂ mixtures, an important aspect considering that the determination of the ratio ¹³CO₂/¹²CO₂ ($\delta^{13}\text{C}$) helps to understand the global carbon cycle. Typically, the NDIR analysers use narrow band path filters to determine ¹²CO₂ in all CO₂ molecules and can ignore the measurement of ¹³CO₂ partially or totally. However, if the carbon isotopic abundances of CO₂ samples deviate from those in CO₂ gas standard, the NDIR measurement will be affected by a bias. The discrimination of ¹³CO₂ from ¹²CO₂ is extremely important not only for obtaining a correction to be used for analytical responses. Carbon isotope fractionation is associated with photosynthesis and the plants, depending on their metabolism, prefer ¹²C. This fractionation results in lowering the $\delta^{13}\text{C}$ by about 20 per thousand for land plants and 10 per thousand for marine plants [11–13]. Moreover when organic carbon is buried, more ¹²C is locked out of the

system in sediments. During summer, the atmosphere contains relatively more ^{13}C , as plants consume $^{12}\text{CO}_2$, while in winter plant respiration dominates and atmospheric $^{12}\text{CO}_2$ increases while $\delta^{13}\text{C}$ decreases. In addition, fossil fuels (originally plants) contain relatively more ^{12}C , so that, as fossil fuels are burned, atmospheric $^{12}\text{CO}_2$ increases while $\delta^{13}\text{C}$ decreases and the addition of $^{12}\text{CO}_2$ by the fossil fuel combustion is more than the amount of $^{12}\text{CO}_2$ removed by the terrestrial biosphere and the oceans. Measuring these isotopic tracers helps to understand the global carbon cycle and to assess how the human activity contributes to the increase of CO_2 .

5. Conclusions and future perspectives

In this work the activity carried out at INRiM for assuring metrological traceability to the measurement of carbon dioxide (CO_2), included in the group of greenhouse gases, was presented. The aspects related to the metrological traceability are mainly addressed by producing reference gas mixtures by using primary methods, namely gravimetry and dynamic dilution. Gravimetry is a weighing process based on subsequent steps in which the masses of gases introduced in a cylinder are accurately weighted and it gives direct traceability to mass standards and the purity of the parent gases. In order to guarantee the metrological traceability, the weighing process is carried out by comparison with traceable mass standards. The dynamic dilution is a process in which two gases are mixed together by controlling their flows. At this purpose, calibrated Mass Flow Controllers are used, after calibration by the gas flow rate primary standard of INRiM. Future activity will regard the application of the expertise obtained in the preparation of primary reference mixtures and in the establishment of metrological traceability to the calibration of sensors for the monitoring of CO_2 in seawater. Typical sensors for CO_2 measurement in water are based on spectroscopic techniques such as NDIR. The partial pressure of CO_2 in seawater is a variable that can be monitored in situ with networked sensors and there is a growing need of assessing the conformity of these sensors to the user requirements, in particular considering their measurement uncertainties. Establishing metrological traceability for CO_2 in seawater, by developing suitable reference materials for calibration and control of the sensors during their routine use, is a goal to achieve for a better monitoring of the trends of CO_2 in the marine environment and for the comprehension of the global carbon cycle.

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