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Carbon Dioxide Determination in Atmosphere by Non Dispersive Infrared Spectroscopy: a Possible approach towards the Comparability with Seawater CO₂ Measurement Results

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Abstract – The rising levels of carbon dioxide in the atmosphere are responsible for fundamental changes occurring in seawater carbonate chemistry. The partial pressure of oceanic CO₂ ($p\text{CO}_2$) is one of the four measurable parameters defining the marine carbon system. For this reason, the pressing need of assuring metrological traceability of $p\text{CO}_2$ measurement results has been recognized and pointed out by the oceanographic community. In order to achieve this fundamental goal, the lack of suitable reference materials has been identified as one of the most limiting factors. At INRIM several activities are carried out to establish the metrological traceability for carbon dioxide measurement results. The present paper describes two primary methods, the gravimetry and the dynamic dilution, used for the preparation of gaseous reference standards for composition which are fundamental to calibrate sensors and analytical instrumentation for carbon dioxide determination in atmosphere. Suitable procedures for the calibration and use of Non Dispersive Infrared Analysers (NDIR) are also presented and discussed. At present, feasibility studies are ongoing at INRIM to extend the use of these metrologically traceable mixtures to the calibration of sensors used for $p\text{CO}_2$ determination in seawater. An extensive work was carried out on a non-dispersive infrared analyser employed in air monitoring, to assess its robustness and stability, which are the major starting points to set up a calibration procedure to obtain comparable results in the atmospheric and marine compartments.

Keywords: carbon dioxide, metrological traceability, NDIR, primary reference gas mixtures

1. INTRODUCTION

Global warming is mainly caused by the increase of the concentration of carbon dioxide (CO₂) and other greenhouse gases in the atmosphere. The anthropic emission of these gases is among the main causes of their increasing concentration [1]. The rising levels of CO₂ in the atmosphere are also responsible for fundamental changes occurring in seawater carbonate chemistry. The oceans are absorbing more CO₂ from the atmosphere, which is decreasing seawater pH and leading to the acidification of marine waters, with important consequences for the global ecosystem [2]. The levels of CO₂ in seawater and atmosphere can change depending on the region of the oceans, as some regions tend to release CO₂ to the atmosphere (e.g. the Equatorial Pacific), whereas others (e.g. the North Atlantic) absorb it. In general, the values of the partial pressure of CO₂ ($p\text{CO}_2$) in seawater are slightly lower than the mole fractions of CO₂ in atmosphere, and this depends mainly on the temperature and relative humidity. For both the environmental compartments, i.e. air and water, there is a pressing need to assure metrological traceability thus obtaining comparable results on spatial and temporal scales. In addition it is necessary to reach measurement uncertainty small enough to discriminate observed variations due to natural fluctuations from those due to real trends. In this framework, the development and validation of proper analytical methods and measurement standards is of utmost importance. The set-up of reference measurement standards linking the results obtained for CO₂ determination in the two environmental compartments is necessary to assure their mutual comparability.

The importance of carrying out reliable and traceable CO₂ measurements in seawater is due to the fact that, at present, $p\text{CO}_2$ is one of the few variables of the marine carbon cycle directly measurable *in situ*. Despite a variety of *in-situ* sensors currently used to monitor CO₂ in marine environment, there are several problems to be faced, such as the differences in adopted calibration methodologies and non-validated procedures, the lack of metrological traceability and of operational harmonization for field measurements. 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 2016 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 by establishing a permanent working group for calibration activities. A main goal is the proposition of a future strategic plan towards a permanent, pan-European calibration grid to support the activities of marine observatories. The group has started its activities by focusing on pH, salinity, fluorescence and $p\text{CO}_2$.

At present there is a lack of suitable reference materials to calibrate instrumentation used for marine monitoring of CO_2 . A lot of effort has been paid to produce reference materials for CO_2 in seawater [4] and to extend their use in inter-laboratory comparisons to assess the quality of seawater CO_2 measurements [5]. However, the currently available seawater-based reference materials suffer from the instability of the matrix and on pH variations and are not certified for $p\text{CO}_2$ value. In addition, there is a high risk of CO_2 loss during the handling, particularly at high concentration levels. Clearly, there is a need for more reference materials, in order to rely on enough references both for calibration and for quality control checks, considering that whenever a reference material is used for calibration, it cannot be used for quality control.

In this framework, the development of appropriate reference standards in gas phase to be used to calibrate $p\text{CO}_2$ sensors might be a promising approach, due to the stability of the gas standards, and the applicability of Non Dispersive Infrared (NDIR) technique to $p\text{CO}_2$ measurement could be potentiated. This approach, however, is not straightforward and some issues must be taken into account. For example, when a NDIR analyser is calibrated with reference materials of CO_2 in gas phase and it is then used to measure CO_2 in seawater, a typical problem arising differences in its response is the detector drift. However, a regular calibration with certified reference gases, together with daily blank measurements may help in taking into account and correct for detector drift [6]. Another issue might be the NDIR CO_2 band broadening, an effect that can be minimized by drying the seawater-equilibrated gas, before entering the NDIR detector [6, 7]. Despite these problems, this procedure would be very useful to link the marine determination to the more consolidated atmospheric measurements, where the promotion of international comparability of measurement results has been in place since two decades. A strong cooperation is active, indeed, between the metrological community and the institutions involved in atmospheric measurement at global and remote level, like the World Meteorological Organization laboratories, the US National Oceanic and Atmospheric Administration (NOAA), the European network of Air Quality Reference Laboratories (AQUILA). In particular, NOAA Earth System Research Laboratory (ESRL) Global Monitoring Division (GMD) is the WMO Global Atmosphere Watch (GAW) Central Calibration Laboratory (CCL) for various greenhouse gases, responsible for maintaining and distributing the WMO mole fraction scale of such gases, among which CO_2 [8]. The proposed integrated approach could help in establishing a better comparability between the results of measurements carried out in the two different environmental compartments, which are unavoidably strongly linked. Examples of measurement campaigns which aim at comparing seawater measurements and atmospheric data collected from ships can be found in literature [7] and the measurement instruments used are calibrated in the range (200-450) ppm. An interesting example, reported in [7] shows the comparison between atmospheric values measured in Iceland and the record of flask data collected at the Icelandic Station of the NOAA/ESRL's GMD (Storhofdi, Vestmannaeyjar, Iceland): in this case, the measured atmospheric values were in agreement with the flask data to ± 0.8 ppm.

At INRIM several activities are carried out to establish the metrological traceability for CO_2 measurement results. Two primary methods, the gravimetry [9] and the dynamic dilution [10], are employed for the preparation of gaseous reference standards for composition which are used to calibrate sensors and analytical instrumentation for carbon dioxide determination in atmosphere. An extensive work was performed on a NDIR analyser used to monitor CO_2 in air at ambient level to assess its stability by means of repeated calibrations. The analyser showed to remain stable within two years, thus confirming the robustness of this kind of instruments, property which is a good starting point to extend their use to more challenging measurements, like the ones carried out in seawater. Some details on the preparation of the mixtures and on the associated uncertainty are presented in this work. Feasibility studies are ongoing to extend their use to the calibration of sensors for $p\text{CO}_2$ in seawater [11] by developing a possible approach to CO_2 sensor calibration to ensure comparability of measurements results in air and seawater.

2. MATERIALS AND METHODS

2.1 Measurement in atmosphere

The monitoring of CO_2 in atmosphere is mainly carried out by means of spectroscopic techniques. Several open path optical methods are applied to CO_2 emission monitoring [12], including Open Path Tunable Diode Laser (TDL) and Open Path Fourier Transform Infrared (FTIR) spectroscopy.

Another class of CO₂ analysers is represented by short closed-path infrared detectors, which involve the introduction of a gas sample into a chamber by means of a pump or diffusion and the quantification of a specific gas component by passing light across the chamber and through the sample. The principles are similar to open path laser techniques in terms of optical sources and detectors, but differ for the presence of the measurement chamber, which allows a greater portability and reduces interference. Although they may show lower sensitivity and a slower response time, due to their relatively low cost, flexibility and robustness, they are mainly employed in monitoring networks, including the ones devoted to background CO₂ levels in remote areas [13, 14]. There are two types of infrared detectors: non-dispersive (NDIR) and dispersive. In NDIR, all the light emitted by the source passes through the sample, after which it is filtered prior to detection. In a dispersive system a grating or prism is used prior to the sample to select a specific wavelength. In terms of atmospheric monitoring, NDIR analysers are the most commonly used detectors for field application. They can be easily calibrated by using proper reference gas mixtures. At INRIM, a NDIR URAS 14 (ABB, Switzerland) having a range from 0 to 1000 μmol/mol of CO₂ is used for CO₂ determination in ambient air. The analyser is also employed to carry out both the verification and the stability studies on the gravimetric primary mixtures produced at INRIM.

2.2 Measurement in seawater

In addition to *in-situ* sensors exploiting reagent-based colorimetry or solid-state detectors, NDIR is becoming a widespread technique also for CO₂ determination in water [6,7,15-21]. The operational principle is based on the equilibration of a carrier gas phase with a seawater sample and the subsequent determination of the CO₂ that diffuses through, by means of a NDIR detector. Equilibration of CO₂ between gas phase and seawater can be achieved either by direct contact between air and seawater (discrete or continuous), or by permeation of CO₂ through a membrane (continuous). Equilibration in discrete seawater samples is achieved either by pumping, using a closed loop, a known volume of air through a known volume of seawater in a flask, or by introducing a known small volume of air into a sealed sample bottle filled with seawater. Once equilibrium of CO₂ between the two phases is achieved, the molar fraction of CO₂ in the equilibrated air can then be measured by NDIR. The air used for equilibration needs to contain a known initial amount of CO₂ ideally close to the *p*CO₂ of the seawater sample, in order to minimise the perturbation in the CO₂ concentration in the sample. During the equilibration process, a constant known temperature and pressure within the closed circuit needs to be maintained [20]. NDIR sensors are beginning to be used more and more in different settings and under diverse conditions for marine CO₂ monitoring. The application of NDIR technique is very useful to link CO₂ measurements carried out in atmosphere and seawater. However, while the measurement uncertainty evaluation for the monitoring of CO₂ in gas phase is well established, there are no harmonized and standardized methods to evaluate the measurement uncertainty associated to the calibration of marine *p*CO₂ sensors.

Usually, these sensors are calibrated in a temperature stabilized water tank, but carrying out their calibration by means of dry standard gases can be easier and much faster [15,16] and eliminates the problems related to the instability of water-based standards. Calibration of sensors in a temperature stabilized environment can be done to reduce possible variations in the response of the sensors. However, when the sensors only experience a maximum temperature difference of 1 °C between all sensor zeroing and the maximum deployment depth is less than 15 m, both the temperature and the depth influence on the response time can be neglected, assuming a constant response time can for further processing [19]. The accuracy of the calibration gases is a critical factor in sensor accuracy, hence high quality gas standards with known and small uncertainty are preferable. In addition, the use of traceable standards can assure the metrological traceability of *p*CO₂ determination results, thus increasing their reliability and comparability.

2.3 Gas Reference Standards for CO₂

Reference gas mixtures prepared by primary methods, like gravimetry and dynamic dilution, can be used as reference measurement standards to assure metrological traceability to the results of CO₂ determination in air. As an alternative, they can be used to calibrate by comparison secondary gas standards.

Gravimetry is a weighing process based on subsequent steps in which the masses of gases introduced in a cylinder are accurately weighted; it gives direct traceability to mass standards and the purity of the parent gases [22]. Due to its intrinsic features, including its high accuracy, gravimetry is the most widely used technique to prepare reference gas standards. It is applicable to several classes of compounds and in wide amount of substance fraction ranges. It is particularly fit for preparing mixtures of non-reactive gases that can be easily stored in high pressure cylinders and may remain stable even for years. The cylinder in which the mixture is prepared 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 either in a pure gas or in a parent mixture 3) cylinder after the introduction of the matrix gas. At INRIM a facility to prepare gas mixtures by gravimetry is in place [9,11]. The high precision weighing steps are carried out by means of a mass comparator PR 10003 (Mettler

Toledo, Switzerland), having measurement range of (0.001-10010) g. The mixtures are prepared in cylinders of aluminium alloy (Luxfer, UK) having internal volume of 5 L. The comparability of these mixtures at international level is supported by the participation in the International Key-Comparison CCQM-K52 “Carbon dioxide in synthetic air” [23] organised in the framework of the Consultative Committee of Amount of Substance: Metrology in Chemistry and Biology (CCQM) of the International Committee for Weights and Measures (CIPM).

The dynamic dilution is a process in which two gases are mixed together by controlling their flows: a ready-to-use gas mixture at a desired molar fraction is generated, starting from a more concentrated gas mixture and a matrix gas. 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 unstable in high pressure cylinders. In addition, mixtures generated by dynamic dilutions can also be used to check and validate gas standards prepared by gravimetry. Its drawback is related to the fact that the mixtures are used at the same time they are prepared and cannot be stored. In addition, a more concentrated mixture, usually prepared by gravimetry, is generally needed as a starting parent gas. A dynamic dilution system might be obtained by using two or more Mass Flow Controllers (MFCs). A MFC is designed and calibrated to control a specific type of liquid or gas at a particular range of flow rates. At INRIM a dynamic dilution system composed of two MFCs and a mixing chamber is used. Two pairs of MFCs (MKS Instrument Inc., MA, USA) having full scale range (FSR) of 200 SCCM and 2000 SCCM or, alternatively, of FSR 500 SCCM and 2000 SCCM are employed depending on the mixtures to be prepared.

3. RESULTS AND DISCUSSION

For the gravimetric preparation of a gas mixture, a simplified model equation for the calculation of the molar fractions of a generic analyte, A, in a matrix component, B, starting from two pure gases 1 and 2, is the following (eq. 1):

$$\chi_A = \frac{n_A}{n_A + n_B} = \frac{n_{A,1} + n_{A,2}}{n_{A,1} + n_{A,2} + n_{B,1} + n_{B,2}} \quad (1)$$

where:

χ_A = molar fraction of the analyte gas A in the final mixture (mol/mol)

$n_{A,i}$ = moles of the analyte A in the i -th pure parent gas (mol)

$n_{B,i}$ = moles of the matrix B in the i -th pure parent gas (mol).

Figure 1 reports a cause and effect diagram which summarises the main uncertainty sources that contribute to the uncertainty on the molar fraction of the mixture.

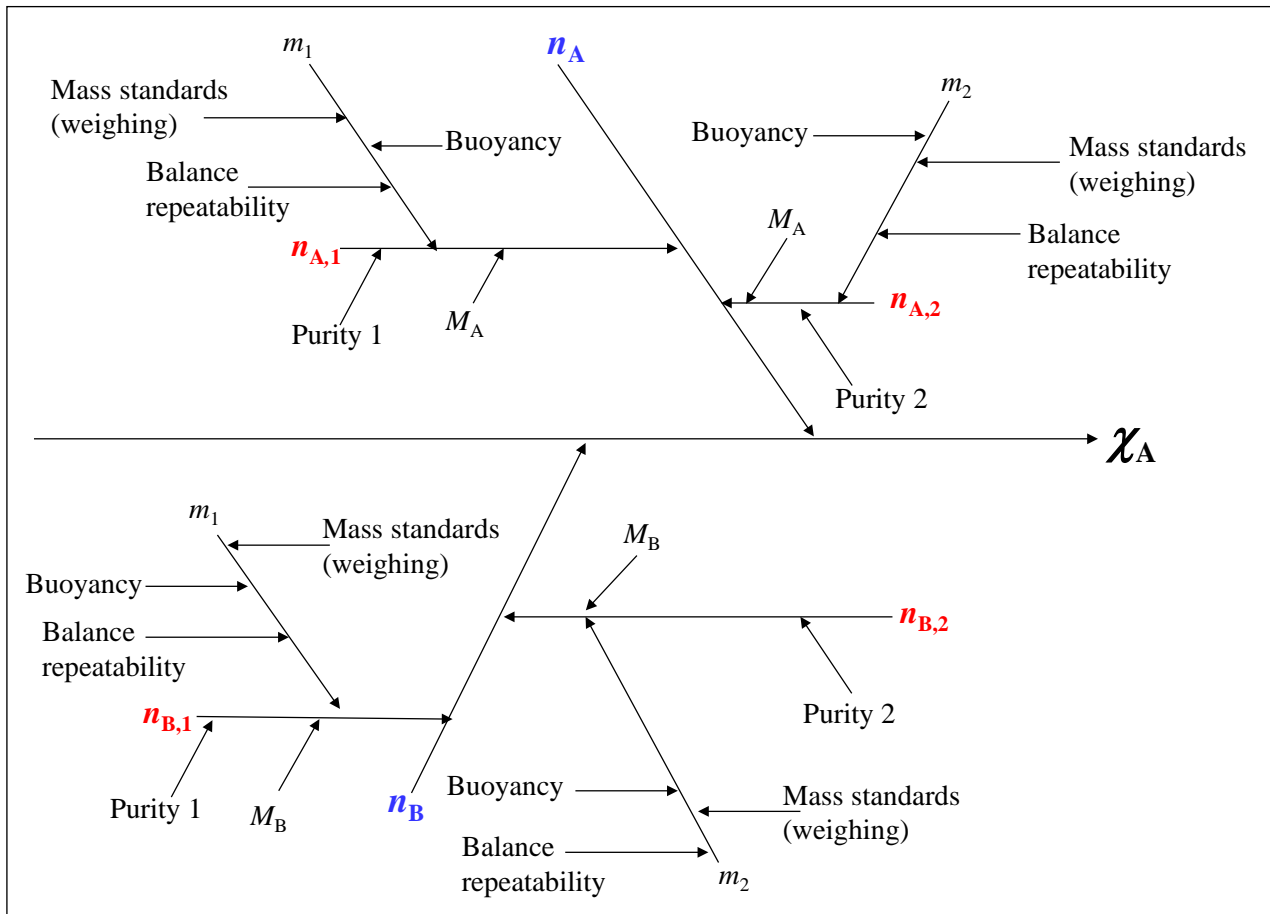


Figure 1. Cause and effect diagram summarising the main uncertainty sources for a gravimetric reference gas mixture, where “m” are the weighted masses of gases 1 and 2 and “M” are the molar masses of compounds A and B.

Equation 2 represents a simplified model equation to calculate the molar fraction of a generic gas mixture obtained by dilution with two MFCs:

$$\chi_A = \frac{(\chi_{A,1} \cdot Q_1 + \chi_{A,2} \cdot Q_2)}{(Q_1 + Q_2)} \quad (2)$$

where:

Q_1 : is the flow of the MFC used for the gas 1 that has to be diluted (SCCM= cm^3/min),

Q_2 : is the flow of the MFC used for the diluting gas 2 (SCCM= cm^3/min),

$\chi_{A,1}$: molar fraction of the analyte A in gas 1 to be diluted (mol/mol),

$\chi_{A,2}$: molar fraction of the analyte A present as impurity in the diluting gas 2 (mol/mol).

Figure 2 reports a cause and effect diagram which summarises the main uncertainty sources that contribute to the uncertainty on the molar fraction of the mixture.

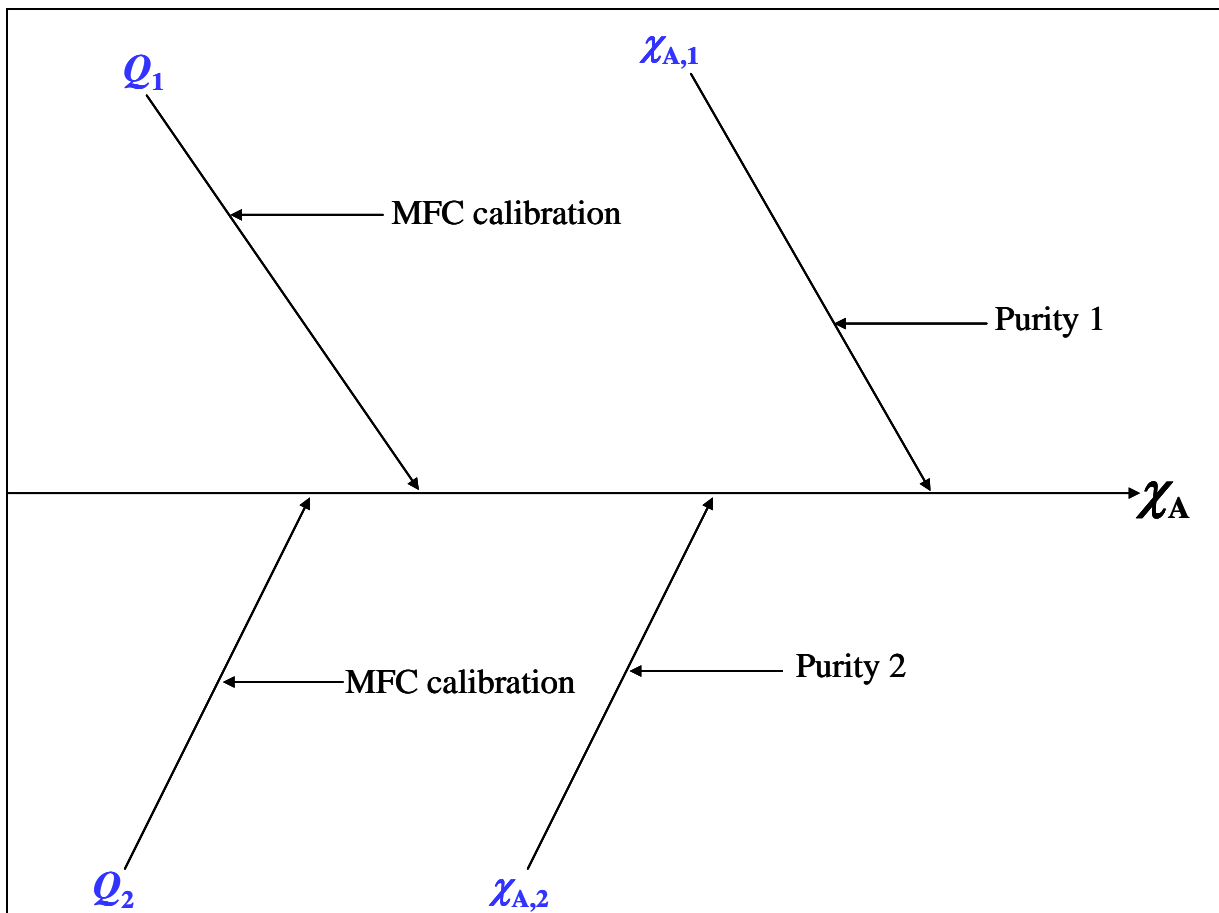


Figure 2. Cause and effect diagram summarising the main uncertainty sources for a reference gas mixture prepared by dynamic dilution

Primary reference mixtures of CO₂ in nitrogen or synthetic air matrices are prepared in INRIM by gravimetry in high pressure cylinders of aluminum alloy, having an internal volume of 5 L and also by applying a dynamic dilution system. The CO₂ mixtures cover the molar fraction range (50-1000) μmol/mol. The relative standard uncertainty associated to these mixtures decreases with increasing molar fraction and is in the range (0.5 - 0.01) % for both methods, being the purity of parent gases the major uncertainty source for gravimetry, and MFCs repeatability for dynamic dilution.

Currently, one of the major challenges is the preparation of gas mixtures having uncertainties small enough to satisfy the requirements prescribed by the World Meteorological Organization (WMO), which recommends for CO₂ measurement in the Northern hemisphere a compatibility goal of ± 0.1 μmol/mol (at 1-σ level) for a CO₂ range of [380-450] μmol/mol, value that goes down to ± 0.05 μmol/mol in the Southern hemisphere [24]. In this context, as previously reported, one of the major issues is represented by the purity of the parent gases that needs to be carefully investigated, but this is beyond the scope of the present paper.

At INRIM the performance of NDIR analysers have been studied for various years. An internal procedure to calibrate NDIR analysers for CO₂ at atmospheric level was developed [25]. According to the procedure, the analyser is calibrated by using reference gas mixtures of CO₂ either in nitrogen or in air and a correction curve of the analyser is determined, together with the uncertainty associated to the correction in the whole calibration range. The NDIR ABB URAS 14 CO₂ analyser is periodically calibrated and verified in the range (200-900) μmol/mol of CO₂. It shows to be robust either in the medium term (Figure 3) and in the long term (Figure 4). Figure 3 shows two correction curves determined within two months: it can be seen that the two analyser response curves are totally comparable in the whole calibration range.

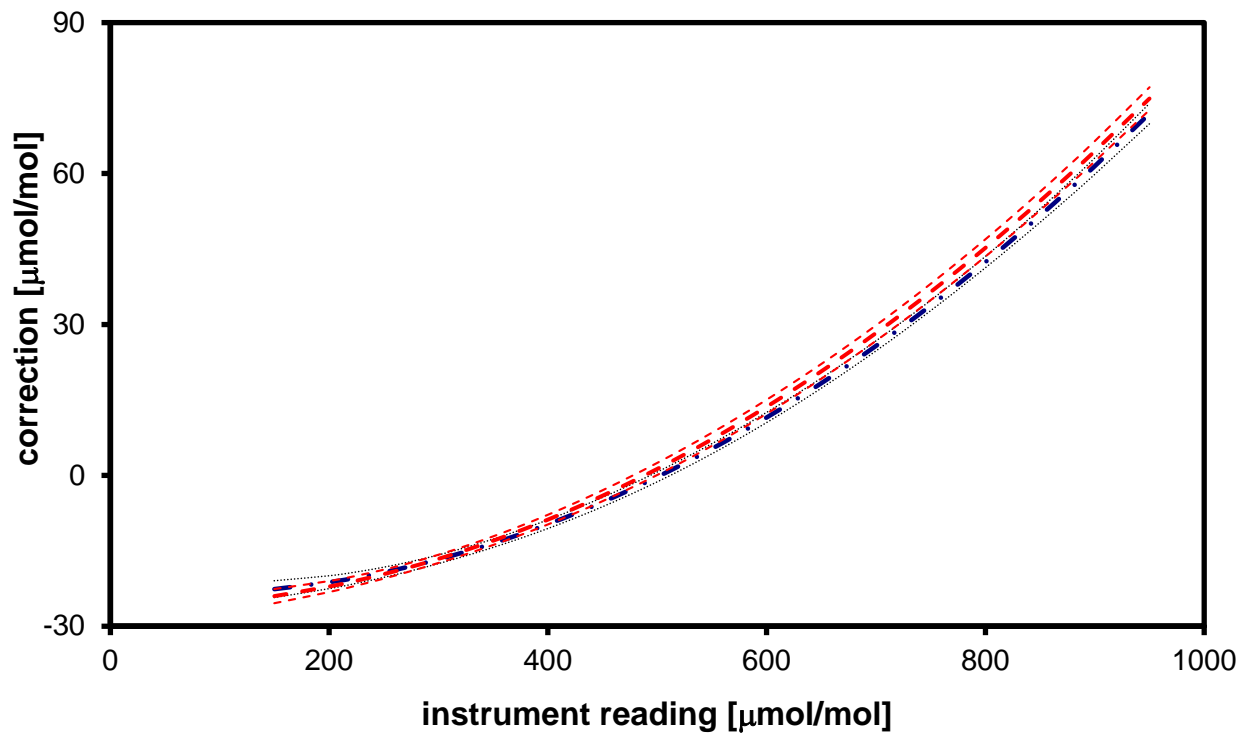


Figure 3: Mid-term stability of a NDIR ABB URAS 14 analyser for CO₂: comparison between two correction curves (- - -, - . - .-) together with their expanded uncertainty bands (red dashed and blue dotted lines, respectively) corresponding to 95% confidence level ($k = 2$), obtained within two months.

Figure 4 compares a correction curve (- - -) with a second one obtained 2 years later (- . - .-). In this case, a good comparability is also observed; in particular, the two curves are totally comparable in the range (200-700) µmol/mol of CO₂. Furthermore, the NDIR principle is a non-destructive one, hence different analysers can be simultaneously calibrated by connecting them in series and using the same calibration gas mixtures.

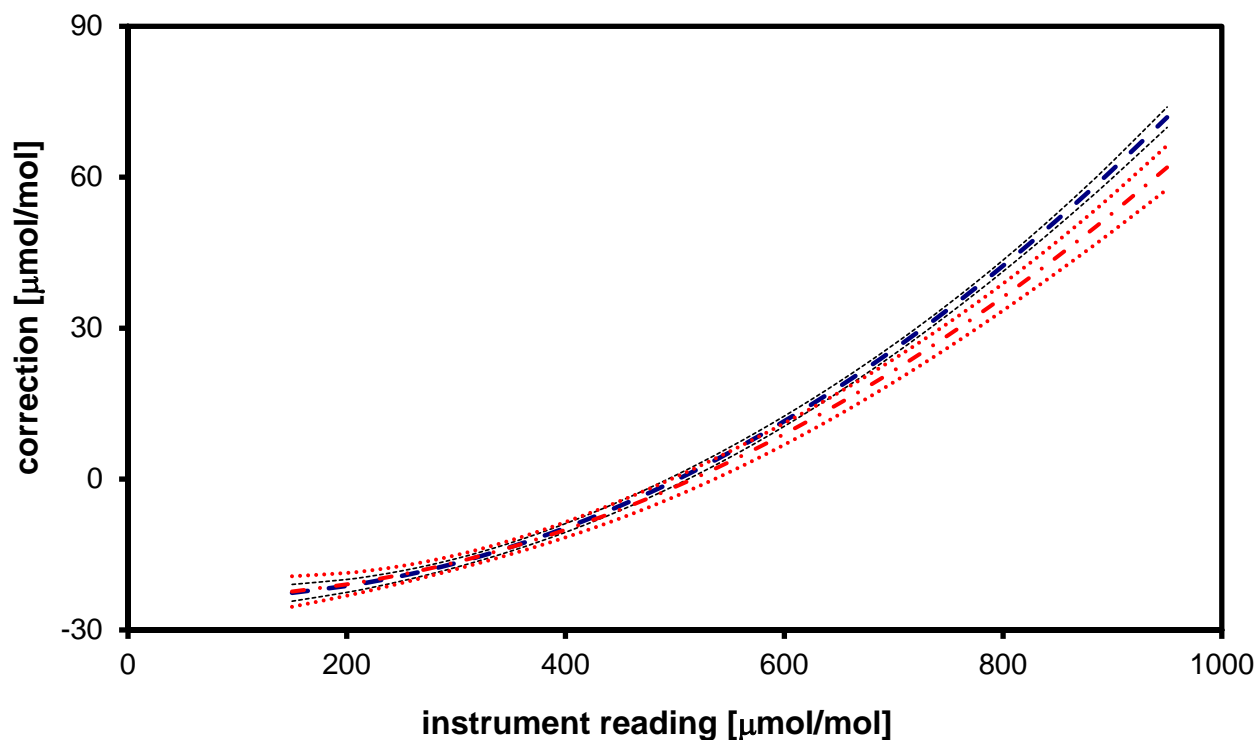


Figure 4: Long-term stability of a NDIR ABB URAS 14 analyser for CO₂: comparison between two correction curves (-, - . - .) together with their expanded uncertainty bands (blue dashed and red dotted lines, respectively) corresponding to 95% confidence level ($k = 2$), obtained within two years.

Considering both the intrinsic and well documented stability of NDIR analysers and the possibility of calibrating two or more of them simultaneously, it is possible to keep in the laboratory a regularly checked reference instrument and use it to compare the performance of NDIR analysers after *in-situ* campaign, in order to implement the comprehension of their behavior and the efficiency of their maintenance. The use of traceable reference gas mixtures in the calibration and verification processes can also guarantee the metrological traceability of the measurement results. In addition, using the same set of gas mixtures to calibrate NDIR analysers for both atmospheric and seawater CO₂ determination and following the same calibration procedure can allow to compare the results obtained in the two different environmental compartments. With respect to atmospheric monitoring, a NDIR analyser used for measurements in seawater could be subjected to major signal drift, because of the harsh environmental conditions typical of seawater. However, several methods are available to correct for drift effects, such as dual-beam setup or regular zero gas measurements realized automatically within the sensor, which can mitigate the effect of instrumental drift during seawater measurements [18]. The accuracy of a NDIR analyser and its uncertainty depends, as underlined in [16], on the uncertainty of the mixtures used for its calibration. In [16] it is stated that at least a manufacturer has already started to use traceable gas standards at high accuracy to carry out the factory calibrations. This approach should be extended also to regular calibrations of the analysers. Figure 5 compares two correction curves obtained in INRIM for the NDIR analyser by using calibration mixtures having the same nominal concentration of CO₂, expressed in μmol/mol, but different standard uncertainties: a series of calibration mixtures has relative standard uncertainty of 1% and the other one has relative standard uncertainty of 0.1%.

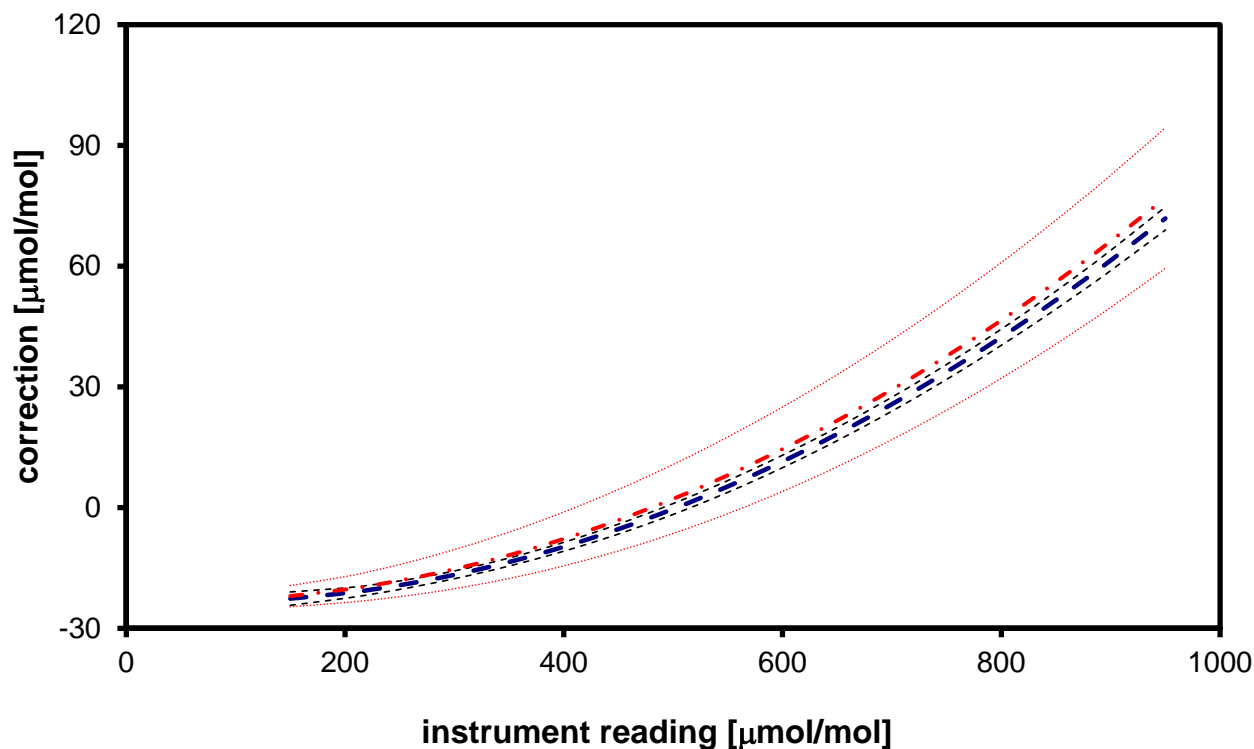


Figure 5: Comparison between two correction curves of a NDIR ABB URAS 14 analyser for CO₂ obtained by calibrating the analyser with reference gas mixtures having standard uncertainties of 0.1% relative (- - -) and 1 % relative (- . - .). The graph shows also the expanded uncertainty bands (blue dashed and red dotted lines, respectively) corresponding to 95% confidence level ($k = 2$).

From the curves reported in Figure 5, it can be seen that using calibration gas mixtures having standard uncertainties of one order of magnitude higher (1 % relative) a response curve is obtained that shows higher correction values and, moreover, higher uncertainties associated to the corrections, which can be from twice to ten times higher with respect to the ones obtained with mixtures having relative standard uncertainties of 0.1 %. It is clear that the use of standard gas mixtures having low uncertainties, like the ones prepared by gravimetry or dynamic dilution, not only in the factory calibration tests but also in the routine calibration, together with the establishment of proper calibration procedures, can effectively improve the performances of the NDIR analysers.

4. CONCLUSIONS

The rising levels of CO₂ in the atmosphere are not only responsible for the greenhouse effect, but also for fundamental changes occurring in seawater carbonate chemistry. The accurate determination of CO₂ both in atmosphere and seawater is fundamental to monitor its trends in both compartments and the application of the metrological concepts is necessary to assure the reliability of the measurement results. Establishing metrological traceability for CO₂ in seawater, by developing suitable reference materials for calibration and control of the sensors during their routine use and linking the CO₂ measurements carried out in atmosphere and seawater, is a goal to achieve to better understand the terrestrial carbon cycle and to monitor the trends of CO₂ in the atmosphere and the oceans. The process is at its early stage, but the acknowledgment of the need of bringing together competencies from different fields to fill this gap is a crucial starting point. The present paper describes two primary methods to prepare primary CO₂ gas mixtures currently used to calibrate CO₂ sensor for atmospheric monitoring. The performance evaluation of a NDIR analyser employed in air monitoring showed that it remained stable within two years, thus confirming the robustness of this kind of instruments, property which can support their use for more challenging measurements, like the ones carried out in seawater. At INRIM, feasibility studies are ongoing to extend the use of metrologically traceable gas mixtures to the calibration of NDIR sensors used for *p*CO₂ determination in seawater. Few examples of this approach were found in literature, showing that the calibration of NDIR analysers by means of reference gas mixtures is a good approach to be followed also for

seawater $p\text{CO}_2$ measurements, but it needs to be improved, starting from the cooperation of the metrological and oceanographic communities. For these reasons, INRIM has started collaborations with Institutions working on seawater measurements both at the national and international level, to help transferring the experience in the gas measurement field to the seawater community. These collaborations are fundamental to clarify the needs of the oceanographic community in terms of calibration of the sensors and, in particular, to highlight the main problematics for the calibration and use of the sensors *in situ*. A starting point will be the set-up of calibration procedures for the $p\text{CO}_2$ NDIR analysers in laboratory, also simulating *in situ* challenging conditions. Some difficulties related to the establishment of metrological traceability for $p\text{CO}_2$ in seawater can arise also from the transportation of gas mixtures for calibration, issue that can be mitigated by using reference mixtures in small cylinders, easily transportable and stored, or by developing dynamic dilution systems. The expenses connected to metrological traceability establishment, mainly linked to the costs of the primary reference standards, can be also reduced by using less expensive working standards, whose traceability is verified against primary mixtures, for checking the performances of *in situ* sensors, between regular calibrations, and this choice can sensibly reduce the costs for the end users of these sensors.

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