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Carbon Dioxide Determination in Atmosphere and Seawater: Approaches for the Comparability of 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. For both air and water, there is a pressing need to assure metrological traceability thus obtaining comparable measurement results on spatial and temporal scales. At INRIM several activities are carried out to establish the metrological traceability for carbon dioxide measurement results. 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 for carbon dioxide determination both in atmosphere and seawater. An overview of possible approaches is given.**

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

I. INTRODUCTION

Global warming is mainly caused by the increase of the concentration of carbon dioxide (CO_2) 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 CO_2 in the atmosphere are also responsible for fundamental changes occurring in seawater carbonate chemistry. The oceans are absorbing more CO_2 from the atmosphere, which is decreasing seawater pH and leading to the acidification of marine waters, with important consequences for the global ecosystem [2]. 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 outmost importance. The set-up of reference measurement standards linking the results obtained for CO_2 determination in the two environmental compartments is necessary to assure their mutual comparability.

At INRIM activities are carried out to establish the metrological traceability for CO_2 measurement results. Two primary methods, the gravimetry [3] and the dynamic dilution [4], are used for the preparation of reference standards for composition which can be used to calibrate sensors and analytical instrumentation.

II. MEASUREMENT METHODS FOR CO_2 QUANTIFICATION

A. 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 [5], including Open Path Tunable Laser (TDL) and Open Path Fourier Transform Infrared (FTIR) spectroscopy.

Another class of CO_2 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 CO_2 levels in remote areas [6, 7]. 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 (see section III).

B. Measurement in seawater

The importance of carrying out reliable and traceable CO_2 measurements in seawater is due to the fact that, at present, the partial pressure of CO_2 (pCO_2) is one of the few directly measurable variables of the marine carbon cycle. Despite a variety of *in-situ* sensors currently used to monitor CO_2 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 [8] 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 to *in-situ* sensors exploiting reagent-based colorimetry or solid-state detectors, NDIR is becoming a widespread technique for CO_2 determination in water. The operational principle is based on the equilibration of a carrier gas phase with a seawater sample and the subsequent determination of the CO_2 that diffuses through, by means of a NDIR detector. Such sensors are beginning to be used more and more in different settings and under diverse conditions for marine CO_2 monitoring.

The application of NDIR technique is very useful to link CO_2 measurements carried out in atmosphere and seawater. In addition, while the measurement uncertainty evaluation for the monitoring of CO_2 in gas phase is well established, there are no harmonized and standardized methods to evaluate the measurement uncertainty associated to the calibration of marine pCO_2 sensors.

III. REFERENCE MEASUREMENT STANDARDS FOR CO_2 QUANTIFICATION

A. Measurement in atmosphere

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 CO_2 determination in air.

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 [9]. 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.

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):

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

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.

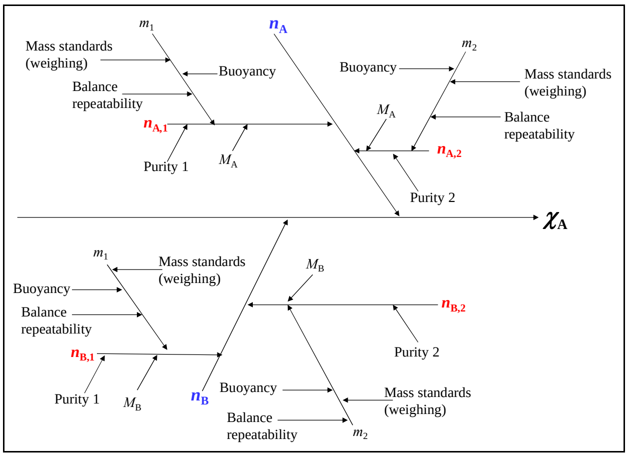

Figure 1. Cause and effect diagram summarising the main uncertainty sources for a gravimetric reference gas mixture, where "m" are the weighted masses of gases 1 and 2 and "M" are the molar masses of compounds A and B.

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. A dynamic dilution system might be obtained by using two or more Mass Flow Controllers (MFCs). Equation 2 represents a simplified model equation to calculate the molar fraction of a generic gas mixture obtained by dilution with two MFCs:

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

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),

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

$\chi_{\mathrm{A},2}$: 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.

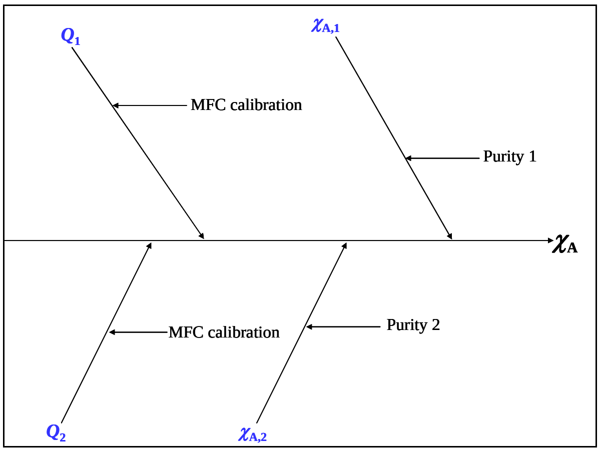

Figure 2. Cause and effect diagram summarising the main uncertainty sources for a reference gas mixture prepared by dynamic dilution

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). In this context, 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.

Primary reference mixtures of CO_2 in nitrogen or synthetic air matrices are prepared in INRIM by gravimetry in high pressure cylinders of aluminium alloy, having an internal volume of 5 L and also by applying a dynamic dilution system. The CO_2 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.

B. Measurement in seawater

There is a lot of concern both in the oceanographic and metrological communities to address the issue of seawater measurements. 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, and fluorescence, but the need of addressing also $p\mathrm{CO}_2$ has been recognized.

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 [10] and to extend their use in inter-laboratory comparisons to assess the quality of seawater CO_2 measurements [11]. However, the currently available seawater-based reference materials suffer from the instability of the matrix and on pH variations. 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 $p\mathrm{CO}_2$ sensors might be a promising approach, due to the stability of the gas standards. In addition, this would be very useful to link the marine determination to the more consolidated atmospheric measurements. Such 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.

IV. CONCLUSIONS

The rising levels of CO_2 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 CO_2 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 CO_2 in seawater, by developing suitable reference materials for calibration and control of the sensors during their routine use and linking the CO_2

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 CO_2 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.

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