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Introduction

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Carbon dioxide (CO_2) is one of the key components in our life and without any doubt the most important chemical substance in the global climate system. It presents the feedstock for plant assimilation and for the growth of plants and phyto cells in the biological carbon cycle as well as buffer system in the blood of humans and animals, and hence, it is important for total life on Earth. On the other hand, CO_2 is the "waste" produced by the metabolism of most of the living creatures on our Earth and by combustion of fossil fuels using carbon stocks or biomass, and it is widely understood to be one of the crucial sources of the dangerous greenhouse effect. Observation of CO_2 in the atmosphere and in the oceans yields important signals for long-term predictions of the world's climate. Furthermore, in process technology, CO_2 is an important reagent for the manufacture of a variety of products. Monitoring of CO_2 in chemical as well as in biotechnological processes is a valuable tool to control the efficiency of the production processes. Since carbon dioxide in higher concentration can be lethal for human beings, CO_2 warning devices are needed. This short listing indicates the general importance of CO_2 and the need to determine it in gases as well as in liquids over a wide range of concentrations from ppm level up to 100% [1].

In publications and regulations the CO_2 concentration is indicated in different units. The general formula for converting the units vol ppm to $\mathrm{mg\,m^{-3}}$ and vice versa is:

$$c[\mathrm{mg\,m^{-3}}] = c[\mathrm{vol\,ppm}] \cdot M/V_\mathrm{m} \tag{1.1}$$

with M being the molar mass in $\mathrm{g\ mol^{-1}}$ (e.g. for CO_2 $M = 44\,\mathrm{g\,mol^{-1}}$) and V_m being the molar volume in $\mathrm{l\,mol^{-1}}$ (e.g. for ideal gases at 25 °C $V_\mathrm{m} = 24.5\,\mathrm{l\,mol^{-1}}$).

Table 1.1 is intended to simplify the conversion.

In medicine, the carbon dioxide partial pressure $p\mathrm{CO_2}$ is usually indicated in the unit mm Hg instead of in the SI unit Pa. The conversion is done according to Table 1.2.

Carbon Dioxide Sensing: Fundamentals, Principles, and Applications,
First Edition. Edited by Gerald Gerlach, Ulrich Guth, and Wolfram Oelßner.

Table 1.1 Conversion factors for CO_2 concentrations.

To convert from the units on the left to the units on top, multiply by		To		
		vol%	**vol ppm**	**mg m^{-3}**
From	vol%	1	10^4	1.8×10^4
	vol ppm	10^{-4}	1	1.8
	mg m^{-3}	5.56×10^{-5}	0.56	1

Table 1.2 Conversion factors for CO_2 partial pressures.

To convert from the units on the left to the units on top, multiply by		To		
		mm Hg	**Pa**	**bar**
From	mm Hg	1	133.32	1.33×10^{-3}
	Pa	7.50×10^{-3}	1	10^{-5}
	bar	750.06	10^5	1

This means that typical CO_2 partial pressures in the range pCO_2 = 35–45 mm Hg correspond to 4.6–6.0 kPa.

Depending on the medium in which CO_2 needs to be measured and the requirements for measuring range, accuracy, long-term stability, selectivity, and maintenance, different methods can be applied [1]:

a) Standard test methods for the analytical determination of total and dissolved carbon dioxide in water require the titration of test samples.
b) CO_2 sensors that are based on various chemical or physical measuring methods are more user-friendly and therefore preferably applied:

- Because of their simple set-up and the resulting low costs, membrane-covered electrochemical CO_2 sensors according to the Severinghaus principle have been manufactured and widely applied already for a long time. Unlike other types of CO_2 sensors, Severinghaus sensors can be applied not only in gases but also for direct measurements in liquid media.
- In comparison with these sensors with aqueous electrolytes, solid electrolyte CO_2 sensors operating at high temperatures have the advantages of a short response time and maintenance-free operation without calibration. They are used successfully in all cases of long-term measurements in air, in breath gas analysis, and in the process monitoring especially at higher temperatures.
- As an economic alternative to the electrochemical CO_2 sensors, detector tubes have been used in a broad range of applications, in particular for control of the concentration at the workplace.
- Nowadays IR, NDIR, opto-chemical, and acoustic CO_2 sensors, which use physical measuring methods, are being used increasingly.
- In several fields of application, a variety of other CO_2 sensor principles, based on conductometric, thermal conductivity, hydrogel expansion, and mass spectrometric measurements, have been tested and partly commercially applied.

Compared to spectrometric (FTIR, UV-VIS), mass spectrometric (MS) and chromatographic techniques (GC, HPLC), electrochemical sensors (Severinghaus and solid electrolyte sensors) are simple in their set-up as well as in the electronic equipment necessary for operation and for data acquisition. The effort for maintenance and calibration is low. Since sensor signals are obtained directly (*in situ*), real-time information for process control is delivered. Therefore, they are preferred tools for screenings in field application. On the other hand, electrochemical sensors cannot completely replace the standard methods in laboratories in terms of precision, detection limit, etc.

The current development activities in CO_2 sensor technology and application are focused on [1]:

- Miniaturization of electrochemical sensors based on the Severinghaus principle, e.g. for measurement in liquid biological systems, cell cultures, cell tissues, and living organisms;
- Development of sterilizable and even CIP (cleaning in process)-resistant sensors for measurement of dissolved CO_2 in biotechnological processes and foodstuff production;
- Extension of the measuring ranges to higher or lower concentrations, as required;
- Extension of the sensor service lifetime and the calibration intervals;
- Application of thin-film and thick-film manufacturing technologies for the mass production of low-cost sensors;
- Development of solid electrolyte CO_2 sensors with short response time for *in situ* breath analysis;
- Miniaturization and improvement of selectivity and sensitivity of IR sensors; and
- Utilization of ultrasonic sensors for breath gas analysis in medical and sportive applications.

Depending on the special field of application and the goals of the investigation, the measuring conditions and technical requirements on the sensors can be very different. Each application has its own scientific background without which the results of measurement cannot be interpreted. A detailed knowledge of the basic detection principles and the frames for their applications is necessary to find an appropriate decision on the technology to be applied for measuring dissolved CO_2. Especially the pH value and the composition of the analyte matrix may exert important influence on the results of the measurements, and sampling of liquids in which CO_2 is dissolved is often a source of errors. Sensors for safety control should be mechanically robust and long-term stable and have low maintenance, whereas for measurements in boreholes or in the deep sea, challenging demands on pressure resistance and compensation of rapid temperature changes have to be fulfilled. In biology and medicine often small dimensions and short response times are required. In biotechnology precise, real-time data on CO_2 concentration fosters the understanding of critical fermentation and cell culture processes and can help in gaining insight into cell metabolism, cell culture productivity, and other processes within bioreactors. But in this case the sensor must be sterilizable. When being applied online in food industry, it is required that the sensor is non-breakable and even survives the rigorous CIP cleaning procedures [1].

After a general consideration on the CO_2 cycle, the book gives an overview of the different chemical and physical measuring methods and sensors for the determination of CO_2 in liquids and gases and their manifold applications in environmental control, biotechnology, biology, food industry, and medicine to a certain extent without claiming to cover completely the whole phenomenon. The wide variety of applications is illustrated by some typical and also somewhat original examples ranging from measurements in the higher atmosphere to the depth of the ocean. The advantages and drawbacks of the different sensor principles will be outlined with the main focus directed on electrochemical sensors, which means on devices that can be applied directly (*in situ*) without sampling. There is no CO_2 sensor available to date that meets these partly contrary requirements all at the same time. For this reason, the book should not only be a source of information about CO_2 measurement, but it is also intended to be an invitation to the reader to accept the challenge to continue developing and improving CO_2 sensors and to be a motivation to open up new areas for their application.

Reference

1 Zosel, J., Oelßner, W., Decker, M. et al. (2011). The measurement of dissolved and gaseous carbon dioxide concentration. *Meas. Sci. Technol.* 22: 072001. https://doi.org/10.1088/0957-0233/22/7/072001.