

# Chapter 3

## Quality assurance

### 1. Introduction

This chapter is intended to indicate some general principles of analytical quality assurance appropriate to the measurement of oceanic CO<sub>2</sub> parameters. Specific applications of analytical quality control are detailed as part of the individual standard operating procedures (Chapter 4).

Quality assurance constitutes the system by which an analytical laboratory can assure outside users that the analytical results they produce are of proven and known quality (Dux, 1990). In the past, the quality of most oceanic carbon data has depended on the skill and dedication of individual analysts. A formal quality assurance program is required for the development of a global ocean carbon data set, which depends on the consistency between measurements made by a variety of laboratories over an extended period of time<sup>1</sup>. Such a program was initiated during the World Ocean Circulation Experiment (WOCE) and Joint Global Ocean Flux Study (JGOFS) as described in the first (1994) edition of this manual. A quality assurance program consists of two separate related activities, quality control and quality assessment (Taylor, 1987):

*Quality control* — The overall system of activities whose purpose is to control the quality of a measurement so that it meets the needs of users. The aim is to ensure that data generated are of known accuracy to some stated, quantitative degree of probability, and thus provides quality that is satisfactory, dependable, and economic.

*Quality assessment* — The overall system of activities whose purpose is to provide assurance that quality control is being done effectively. It provides a continuing evaluation of the quality of the analyses and of the performance of the analytical system.

---

<sup>1</sup> An outline of how to go about establishing a formal quality assurance program for an analytical laboratory has been described by Dux (1990), additional useful information can be found in the book by Taylor (1987).

## 2. Quality control

The aim of quality control is to provide a stable measurement system whose properties can be treated statistically, *i.e.*, the measurement is “in control”. Anything that can influence the measurement process must be optimized and stabilized to the extent necessary and possible if reproducible measurements are to be obtained. Measurement quality can be influenced by a variety of factors that are classified into three main categories (Taylor and Oppermann, 1986): management practices, personnel training and technical operations.

Although emphasis on quality by laboratory management, together with competence and training of individual analysts, is essential to the production of data of high quality (see Taylor and Oppermann, 1986; Taylor, 1987; Vijverberg and Cofino, 1987; Dux, 1990), these aspects are not discussed further here. The emphasis in this Guide is on documenting various standard procedures so that all technical operations are carried out in a reliable and consistent manner.

The first requirement of quality control is for the use of suitable and properly maintained equipment and facilities. These are complemented by the use of documented Good Laboratory Practices (GLPs), Good Measurement Practices (GMPs) and Standard Operating Procedures (SOPs).

GLPs refer to general practices that relate to many of the measurements in a laboratory such as maintenance of equipment and facilities, records, sample management and handling, reagent control and storage, and cleaning of laboratory glassware. GMPs are essentially technique specific. Both GLPs and GMPs should be developed and documented by each laboratory so as to identify critical operations that can cause variance or bias.

SOPs describe the way specific operations or analytical methods should be carried out. They comprise written instructions which define completely the procedure to be adopted by an analyst to obtain the required result. Well written SOPs include tolerances for all critical parameters that must be observed to obtain results of a specified accuracy. This Guide contains a number of such SOPs, many of which have been in use since the early 1990s, and have been revised with accumulated experience and improved technology.

## 3. Quality assessment

A key part of any quality assurance program is the statistical evaluation of the quality of the data output (see SOPs 22 and 23). There are both internal and external techniques for quality assessment (Table 1). Most of these are self evident; some are discussed in more detail below.

**Table 1** Quality assessment techniques (after Taylor, 1987).

---

<b>Internal techniques</b>
Repetitive measurements
Internal test samples
Control charts
Interchange of operators
Interchange of equipment
Independent measurements
Measurements using a definitive method
Audits
<b>External techniques</b>
Collaborative tests
Exchange of samples
External reference materials
Certified reference materials
Audits

---

### 3.1 Internal techniques

Duplicate measurements of an appropriate number of samples provide an evaluation of precision that is needed while minimizing the level of pre-cruise preparation involved and eliminates all question of the appropriateness of the samples. At least 12 pairs distributed across the time and space scales of each measurement campaign (*i.e.*, each leg of a cruise) are needed to estimate a standard deviation with reasonable confidence. Ideally, if resources allow, one would like to collect and analyze duplicate samples from approximately 10% of the sample locations (*e.g.*, 3 sets of duplicates from a 36 position rosette). In cases where multiple instruments are used to increase sample throughput, replicate samples analyzed on each instrument provide useful cross-calibration documentation.

An internal test solution of reasonable stability can also be used to monitor precision (and bias, if the test solution value is known with sufficient accuracy). For example, the analysis of sub-samples from a large container of deep ocean water is frequently used to monitor the reproducibility of total alkalinity measurements. Historical data on a laboratory's own test solution can be used to develop a control chart and thus monitor and assess measurement precision<sup>2</sup>.

---

<sup>2</sup> Considerable confusion exists between the terms *precision* and *accuracy*. Precision is a measure of how *reproducible* a particular experimental procedure is. It can refer either to a particular stage of the procedure, *e.g.*, the final analysis, or to the entire procedure including sampling and sample handling. It is estimated by performing replicate measurements and estimating a mean and standard deviation from the results obtained. Accuracy, however, is a measure of the degree of agreement of a measured value with the "true" value. An accurate method provides unbiased results. It is a much more difficult quantity to estimate and can only be inferred by careful attention to possible sources of systematic error.

A laboratory should also conduct regular audits to ensure that its quality assurance program is indeed being carried out appropriately and that the necessary documentation is being maintained.

### 3.2 External techniques

External evidence for the quality of the measurement process is important for several reasons. First, it provides the most straightforward approach for assuring the compatibility of the measurements with other laboratories. Second, errors can arise over time that internal evaluations can not detect. External quality assessment techniques, however, should supplement, but not replace, a laboratory's ongoing internal quality assessment program.

Collaborative test exercises provide the opportunity to compare an individual laboratory's performance with that of others. If the results for the test samples are known accurately, biases can be evaluated. Such exercises were organized as part of the WOCE/JGOFS CO<sub>2</sub> survey and provided a useful tool for estimating overall data quality (Dickson, 2001; Feely *et al.*, 2001). Exchange of samples, or of internal test solutions with other laboratories can provide similar evidence of the level of agreement or possible biases in particular laboratories.

The use of reference materials to evaluate measurement capability is the procedure of choice whenever suitable reference materials are available. Reference materials are stable substances for which one or more properties are established sufficiently well to calibrate a chemical analyzer, or to validate a measurement process (Taylor, 1987). Ideally, such materials are based on a matrix similar to that of the samples of interest, in this case, sea water. The most useful reference materials are those for which one or more properties have been *certified* as accurate, preferably by the use of a definitive method in the hands of two or more analysts. Reference materials test the full measurement process (though not the sampling).

The U.S. National Science Foundation funded the development of certified reference materials (CRMs) for the measurement of oceanic CO<sub>2</sub> parameters (Dickson, 2001); the U.S. Department of Energy promoted the widespread use of CRMs by providing to participants (both from the U.S. and from other nations) in the WOCE/JGOFS CO<sub>2</sub> survey, the time-series stations at Hawaii and Bermuda and to other JGOFS investigations (Feely *et al.*, 2001). The Scripps Institution of Oceanography CRMs have proven to be a valuable quality assessment tool over the last decade and are currently widely used by the international ocean carbon community<sup>3</sup>. We recommend their use in the individual SOPs (see Table 2 for their certification status). Ideally, CRMs should be analyzed on each instrument any time a component of the system is changed (*e.g.*, with each new coulometer cell for C<sub>T</sub>) or at least once per day. If resources are limited, a minimum of 12 CRMs, spread evenly over the timeframe of the expedition, should be analyzed to give reasonable confidence in the average value.

---

<sup>3</sup> Available from Dr. Andrew G. Dickson, Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, U.S.A. (fax: 1-858-822-2919; e-mail: [co2crms@ucsd.edu](mailto:co2crms@ucsd.edu); <http://andrew.ucsd.edu/co2qc/>).

**Table 2** Present status (2007) of certified reference materials for the quality control of oceanic carbon dioxide measurements.

Analytical Measurement	Desired Accuracy <sup>a</sup>	Certification
total dissolved inorganic carbon	$\pm 1 \mu\text{mol kg}^{-1}$	since 1991
total alkalinity	$\pm 1 \mu\text{mol kg}^{-1}$	since 1996 <sup>b</sup>
pH	$\pm 0.002$	— <sup>c</sup>
$f(\text{CO}_2)$	$\pm 0.05 \text{ Pa (} 0.5 \mu\text{atm)}$	— <sup>d</sup>

<sup>a</sup> Based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the  $\text{CO}_2$  content of sea water that allow the increases due to the burning of fossil fuels to be observed.

<sup>b</sup> Representative samples of earlier batches were also certified for alkalinity at that time.

<sup>c</sup> The pH of a reference material can be calculated from the measurements of total dissolved inorganic carbon and total alkalinity. Also, buffer solutions based on TRIS in synthetic sea water can be certified for pH, but—as yet—this is not done regularly.

<sup>d</sup>  $\text{CO}_2$  in air reference materials are presently available through a variety of sources. However, it is desirable to use a sterilized sea water sample as a reference material for a discrete  $f(\text{CO}_2)$  measurement. Although the thermodynamics of the sea water system suggest that, since the CRMs are certified stable for  $C_T$ ,  $A_T$ , and pH, they should be stable for  $f(\text{CO}_2)$ , a reliable technique for independently determining  $f(\text{CO}_2)$  to allow proper certification has not yet been developed.

#### 4. Calibration of temperature measurements

The accurate measurement of temperature is central to many of the SOPs included in this Guide, yet, on a number of occasions, it has been apparent that the calibration of the various temperature probes that have been used has not received the attention it should. To be accurate, all temperature sensors must be calibrated against a known standard. However, only short-term stability is checked during calibration. Long-term stability should be monitored and determined by the user through periodic regular comparisons with standards of higher accuracy. The frequency of such checks should be governed by experience, recognizing the potential fragility of many temperature probes.

The official temperature scale presently in use is the International Temperature Scale of 1990 (ITS-90)<sup>4</sup>. Although this is intended to represent closely *thermodynamic temperature* over a wide range of temperatures, it is first and foremost a temperature scale that can be realized in practice. It achieves this by assigning temperatures to particular fixed points such as the triple point of water: 273.16 K (0.01°C), or the triple point of gallium: 302.9146 K (29.7646°C), as well as defining appropriate interpolating equations based (for the oceanographic temperature range) on the properties of a standard platinum resistance thermometer.

Typically, working thermometer probes<sup>5</sup> are calibrated (at a number of different temperatures over the desired range of use) by placing them in a stable

<sup>4</sup> For additional information, see <http://www.its-90.com>.

<sup>5</sup> For high-quality measurements it is appropriate to recognize that what is typically needed is not just a calibration of the thermometer probe, but rather of the entire temperature measuring system (probe and readout).

temperature environment (*e.g.*, a temperature-controlled water bath) where their reading can be compared with the temperature value obtained using a reference thermometer whose own calibration is traceable to ITS-90. A good rule-of-thumb is that the uncertainty of this reference thermometer should be about 4 times smaller than the uncertainty desired for the thermometer being calibrated. Usually the reference thermometer is itself calibrated annually at an accredited calibration facility. The stability of a probe can be ascertained by monitoring its performance at a single temperature. (As is noted in the next section, it is important—for quality assurance purposes—to document the calibration of any thermometer used in the measurements described in this Guide.)

## 5. Documentation

One aspect of quality assurance that merits emphasis is that of documentation. All data must be technically sound and supported by evidence of unquestionable reliability. While the correct use of tested and reliable procedures such as those described in Chapter 4 is, without doubt, the most important part of quality control, inadequate documentation can cast doubt on the technical merits and defensibility of the results produced. Accordingly, adequate and accurate records must be kept of:

- when the measurement was made (date and time of taking the sample as well as date and time of processing the sample; in special cases, geological age of sample);
- where the measurement was made (latitude, longitude of the sampling from the official station list);
- what was measured (variables/parameters, units);
- how the measurement was made (equipment, calibration, methodology *etc.*, with references to literature, if available);
- who measured it (name and institution of the Principal Investigator);
- publications associated (in preparation or submitted);
- data obtained;
- calculations;
- quality assurance support;
- relevant data reports.

Although good analysts have historically kept such documentation, typically in bound laboratory notebooks, current practices of data sharing and archiving of data at national and world data centers require that this documentation (known as metadata) be maintained in electronic format with the data. Without an accompanying electronic version of the metadata to document methods and QA/QC protocols, archived data are of limited use. The challenge of documenting changes in the Earth system that have been ongoing since before any measurements were done makes it particularly important that data collected at different times and places be comparable, and that archived data be sufficiently well documented to be usable for decades or longer.

## 6. Bibliography

- Dickson, A.G. 2001. Reference materials for oceanic CO<sub>2</sub> measurements. *Oceanography* **14**: 21–22.
- Dickson, A.G., Afghan, J.D. and Anderson, G.C. 2003. Reference materials for oceanic CO<sub>2</sub> analysis: a method for the certification of total alkalinity. *Mar. Chem.* **80**: 185–197.
- Dux, J.P. 1990. Handbook of Quality Assurance for the Analytical Chemistry Laboratory, 2nd edition, Van Nostrand Reinhold, New York, 203 pp.
- Feely, R.A., Sabine, C.L., Takahashi, T. and Wanninkhof, R. 2001. Uptake and storage of carbon dioxide in the ocean: The global CO<sub>2</sub> survey. *Oceanography* **14**: 18–32.
- SCOR. 1985. Oceanic CO<sub>2</sub> measurements. Report of the third meeting of the Working Group 75, Les Houches, France, October 1985.
- Taylor, J.K. (1987) Quality Assurance of Chemical Measurements. Lewis Publishers, Chelsea, 328 pp.
- Taylor J.K. and Oppermann, H.V. 1986. Handbook for the quality assurance of metrological measurements. National Bureau of Standards Handbook 145.
- UNESCO. 1991. Reference materials for oceanic carbon dioxide measurements. UNESCO Tech. Papers Mar. Sci. No. 60.
- Vijverberg F.A.J.M. and Cofino, W.P. 1987. Control procedures: good laboratory practice and quality assurance. ICES Techniques in Marine Science No. 6.