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_2 parameters for a global survey of CO_2 in the oceans. 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 much oceanic carbon data has depended on the skill and dedication of individual analysts and typically a formal quality assurance program has been lacking. Clearly the collection of a global data set for oceanic carbon, depending as it will on the consistency between measurements made by a variety of laboratories over an extended period of time, demands more attention to such matters.*

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 to provide quality that is satisfactory, dependable and economic.

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

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* 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 & 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 & Oppermann, 1986; Taylor, 1987; Vijverberg & Cofino, 1987; Dux, 1990), these aspects are not discussed further here. The emphasis in this Handbook 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 cleaning of laboratory glassware. GMPs are essentially technique specific. Both GLPs and GMPs should be developed and documented by each participating laboratory in such a fashion as to identify those critical operations which can be identified as assignable causes of variance or bias.

SOPs describe the way specific operations or analytical methods are to 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 Handbook contains a number of such SOPs which are in use by members of the DOE CO_2 survey science team.

3. Quality assessment

A key part of any quality assurance program is the monitoring of the effectiveness of the quality control program and 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)

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

Internal techniques

Duplicate measurement of an appropriate number of test samples provides much of the evaluation of precision that is needed while minimizing the work involved and eliminates all question of the appropriateness of the samples. At least 12 pairs are needed to estimate a standard deviation with reasonable confidence, such as is needed to establish control chart limits (the recommended way to use such data).

An internal test sample of reasonable stability—*e.g.* the use of deep ocean water to monitor the stability of measurements of total alkalinity—can also be used to monitor precision (and bias, if its value is known with sufficient accuracy). Historical data on a laboratory's own test sample can be used to develop a control chart and thus monitor and assess measurement precision.*

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.

External techniques

External evidence for the quality of the measurement process is important for several reasons. First, it is the easiest approach in that it can minimize much of the effort required for internal evaluation. Second, it minimizes the danger of error due to introspection. It must however be emphasized that the attainment of acceptable precision, based on a laboratory's internal quality assessment program, is a prerequisite for participation in any external quality assessment activity.

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 with accuracy, bias can be evaluated. Such exercises are being organized as part of the DOE CO_2 survey in collaboration with other JGOFS scientists and the results will be reported as they become available. Exchange of samples, or of internal calibration standards, with other laboratories can provide similar evidence of agreement or disagreement, and this can be used to make inferences about bias or the lack thereof.

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

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* 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 experiments 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 is one capable of providing precise and 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.

case sea water.The most useful reference materials are those for which one or more properties have been *certified* on the basis of their accuracy, preferably by the use of a definitive method in the hands of two or more analysts. Reference materials have the advantage of the ability to test the whole measurement process

The U. S. National Science Foundation has funded the development of reference materials for the measurement of oceanic CO_2 parameters; the U. S. Department of Energy has agreed to provide for the distribution of such reference materials to participants (both from the U. S. and from other nations) in the CO_2 survey being conducted as part of the WOCE Hydrographic Program; as well as to the JGOFS time-series stations at Hawaii and Bermuda. We recommend their use in the individual SOPs where appropriate (see Table 2 for their availability).

Table 2. Present status (1994) of reference materials for the quality control of oceanic carbon dioxide measurements.

analytical measurement	desired accuracy [a]	availability[b]
total dissolved inorganic carbon	± 1 μmol·kg^{-1}	since May 1991[c]
total alkalinity	± 1 μmol·kg^{-1}	projected for September1994
pH (–log [H^+])	± 0.002	since January 1994
$f(CO_2)$	± 0.05 Pa (0.5 μatm)	—[d]

a. Based on considerations outlined in the report of SCOR Working Group 75 (SCOR, 1985). They reflect the desire to measure changes in the CO_2 content of sea water that will allow the increases due to the burning of fossil fuels to be observed.

b. Available from Dr. Andrew G. Dickson, Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0902, U.S.A. (telefax 1-619-456-9079).

c. Work is also currently in progress at the Institute of Ocean Sciences, Canada to develop such a reference material.

d. 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 $f(CO_2)$ measurement. The feasibility of doing this is currently being examined at the Scripps Institution of Oceanography in collaboration with Dr. Chipman of the Lamont-Doherty Earth Observatory of Columbia University.

4. 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:

- What is measured
- Who measured it
- How measurements are made
  i.e. Equipment, Calibration, Methodology
- Data obtained
- Calculations
- Quality assurance support
- Reports

Although good analysts have historically kept such documentation, typically in bound laboratory notebooks, a quality assurance program should address in detail the way that such documentation is to be maintained.

5. References

Dux, J. P. (1990) *Handbook of quality assurance for the analytical chemistry laboratory.* 2nd edn. Van Nostrand Reinhold, New York, 203 pp.

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Unesco (1991) Reference materials for oceanic carbon dioxide measurements. *Unesco Technical Papers in Marine Science No. 60.*

Vijverberg F. A. J. M. & W. P. Cofino (1987) *Control procedures: good laboratory practice and quality assurance.* ICES Techniques in Marine Science No. 6.