



FASTER, BETTER, CHEAPER?

**ENSURING QUALITY IN OA
MEASUREMENTS**

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Photograph by David Liitschwager

FASTER, BETTER, CHEAPER

In 1992, NASA Administrator Daniel Goldin began the agency's "Faster, Better, Cheaper" initiative.

The popular consensus on "Faster, Better, Cheaper" is often expressed in the supposedly self-evident saying: "faster, better, cheaper – pick two."

Is this necessarily true for seawater carbonate system measurements?

We clearly understand the meanings of "faster" and "cheaper", but how should we define "better"?

A RELEVANT QUOTATION?

It's unwise to pay too much, but it's worse to pay too little. When you pay too much, you lose a little money – that is all. When you pay too little, you sometimes lose everything, because the thing you bought was incapable of doing the thing it was bought to do.

Widely attributed to John Ruskin (1819–1900)

ANALYTICAL PARAMETERS OF THE SEAWATER CO₂ SYSTEM

- Total dissolved inorganic carbon

$$C_T = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

- Total hydrogen ion concentration (pH)

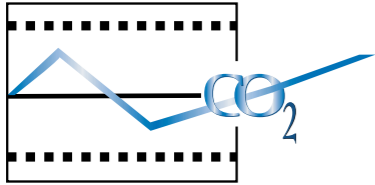
$$\text{pH} = -\lg [\text{H}^+]$$

- Partial pressure of CO₂ (in air in equilibrium with sea water)

$$p(\text{CO}_2) = x(\text{CO}_2)p = [\text{CO}_2] / K_0$$

- Total alkalinity

$$A_T = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] - [\text{H}^+]$$



Advantages

Disadvantages

C_T

T, p independent
 Unambiguous interpretation of changes

Needs care with sample handling

No autonomous system available

pH

Autonomous systems available

Master variable?

Function of T, p

Needs care with sample handling

Interpretation problems

$p(\text{CO}_2)$

Autonomous systems available

Function of T, p

Changes not easy to interpret

A_T

T, p independent

Often possible to interpret changes

No autonomous system available

Harder to interpret in some systems

APPROACHES?

A. Discrete sampling and subsequent analysis in the laboratory

$C_T, \text{pH}, p(\text{CO}_2), A_T$

B. Discrete sampling and immediate on-site analysis

$C_T, \text{pH}, p(\text{CO}_2), A_T$

C. In-line analytical system

$C_T, \text{pH}, p(\text{CO}_2), A_T$

D. In-line sensor system

$C_T, \text{pH}, p(\text{CO}_2), A_T$

ESTIMATED UNCERTAINTIES FOR MEASUREMENT TECHNIQUES ON DISCRETE SAMPLES[†]

Parameter	State-of-the-art laboratory	State-of-the-art at-sea (suitable RMs)	Other techniques (suitable RMs)	Techniques not using RMs
Total alkalinity	1.2 $\mu\text{mol kg}^{-1}$	2–3 $\mu\text{mol kg}^{-1}$	4–10 $\mu\text{mol kg}^{-1}$?
Total carbon	1.0 $\mu\text{mol kg}^{-1}$	2–3 $\mu\text{mol kg}^{-1}$	4–10 $\mu\text{mol kg}^{-1}$?
pH	0.003	~0.005	0.01–0.02	?
$p(\text{CO}_2)$	1.0 μatm	~2 μatm	5–10 μatm	?

[†] Based on measuring surface oceanic CO_2 levels

DEVELOPMENT STATE OF CO₂ MEASUREMENT SYSTEMS

Level 0 – No working system available

Level 1 – Prototype system available in single lab

Level 2 – 2nd generation prototype in use

Level 3 – Home-built systems in a number of labs

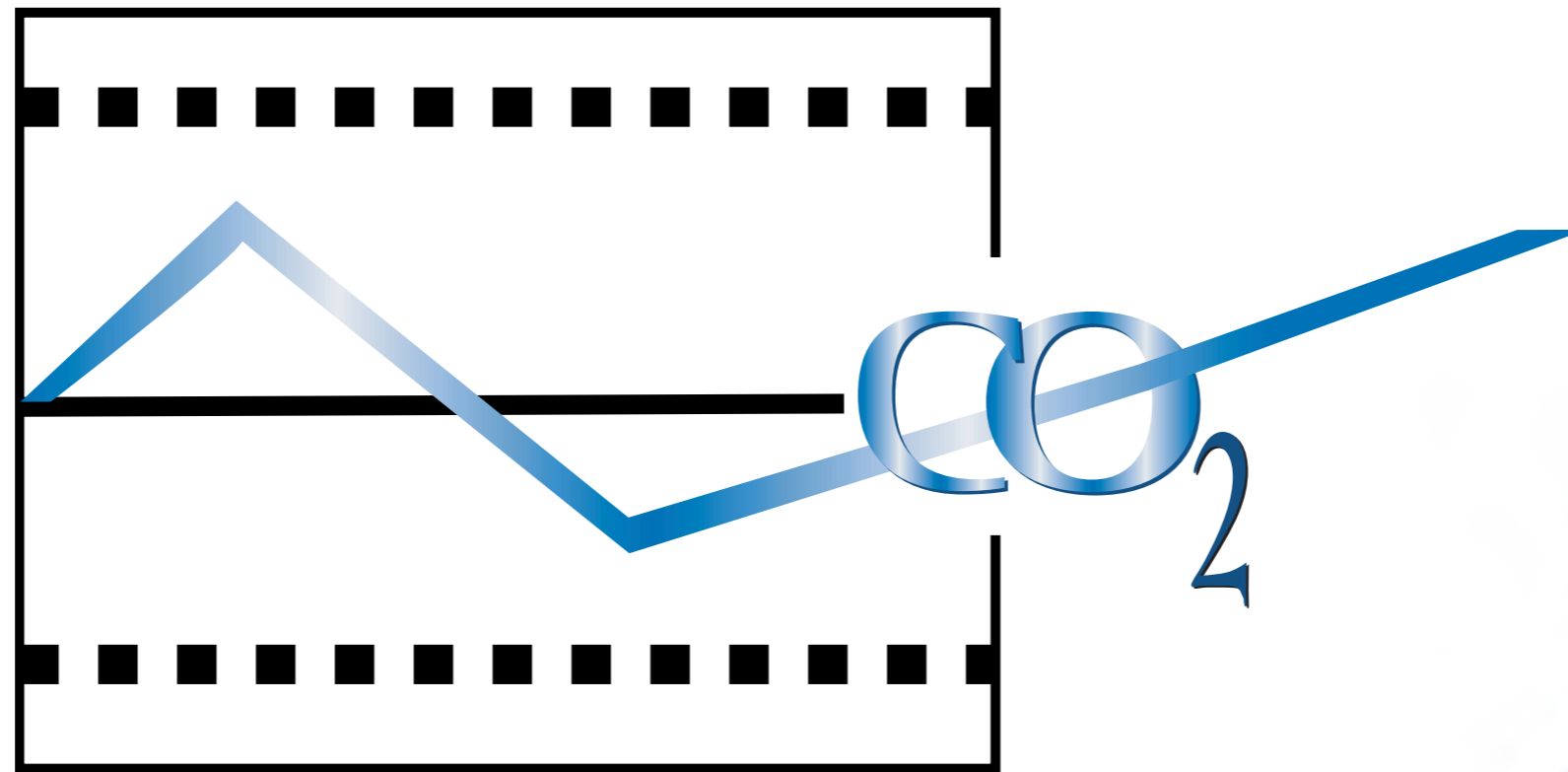
Level 4 – Can be purchased commercially

Level 5 – Commercially available, reliable, and fully supported

DEVELOPMENT STATE OF CO₂ MEASUREMENT SYSTEMS

	Discrete samples	Autonomous sampling & analysis	Profiling instrument	Remote instruments in ocean
C _T	3/4	1/2	0	0/1
pH	3	2	1/2	3/4
p(CO ₂)	2	3/4	1	3/4/5
A _T	3/4	1	0	0/1

DESIRE FOR HIGH-QUALITY MEASUREMENTS



WHAT IS QUALITY?

Quality is fitness for purpose.

Fitness for purpose: the property of data produced by a measurement process that enables a user of the data to make technically correct decisions for a stated purpose.

Fitness for purpose therefore refers to the magnitude of the uncertainty associated with a measurement in relation to the needs of the application area.

Can have implications for the level of resources needed!

SO, WHEN ASSESSING “BETTER”, UNCERTAINTY IS NOT THE ONLY MEASURE!

YOU SHOULD CONSIDER:

1. Overall uncertainty required
2. Cost of measurement(s)
 - a. Cost of equipment (purchase / maintenance)
 - b. Cost of training
 - c. Cost of analysis (time & materials)
3. Convenience of measurement
 - a. Availability of equipment (purchase / maintenance)
 - b. Sample size required
 - c. Time until results are available
4. Cost of making a wrong measurement.

**These procedures are aimed at scientists
making open ocean measurements**

Best Practices for
CO₂ Measurements
SPECIAL PUBLICATION 3
OCCP REPORT No. 8



http://cdiac.ornl.gov/oceans/Handbook_2007.html

FOR OPEN-OCEAN MEASUREMENTS

YOU SHOULD CONSIDER:

1. Overall uncertainty required **AS GOOD AS POSSIBLE!**
2. Cost of measurement(s) **MONEY NO OBJECT!**
 - a. Cost of equipment (purchase / maintenance)
 - b. Cost of training
 - c. Cost of analysis (time & materials)
3. Convenience of measurement **WOULD BE NICE!**
 - a. Availability of equipment (purchase / maintenance)
 - b. Sample size required
 - c. Time until results are available
4. Cost of making a wrong measurement. **PERCEIVED AS HIGH!**

FOR OCEAN ACIDIFICATION NETWORK MEASUREMENTS

YOU SHOULD CONSIDER:

1. Overall uncertainty required STILL NEEDS THOUGHT
2. Cost of measurement(s) BE NICE IT IT WERE CHEAP!
 - a. Cost of equipment (purchase / maintenance)
 - b. Cost of training
 - c. Cost of analysis (time & materials)
3. Convenience of measurement PLEASE!!
 - a. Availability of equipment (purchase / maintenance)
 - b. Sample size required
 - c. Time until results are available
4. Cost of making a wrong measurement. NEEDS THOUGHT?

CAN USE ANY TWO (OR MORE) OF THESE PARAMETERS TO DESCRIBE THE CO₂ SYSTEM IN A SEAWATER SAMPLE

Mathematically, all choices should be equivalent.

In practice that is not the case. Every one of these terms is an experimental quantity with an associated uncertainty. These uncertainties propagate through the calculations resulting in uncertainties in the various calculated values.

In addition to uncertainties in the measured CO₂ parameters, there are also uncertainties in the various equilibrium constants, and in the total concentrations of other acid-base systems such as boron, *etc.*
(Also, the expression used for alkalinity may be incomplete.)

WHAT DO WE NEED TO DO?

- To articulate the necessary measurement quality (in terms of particular goals for the proposed network)
- To agree on a subset of possible measurement techniques that C-CAN will work to support
- To articulate what form that support will/can take
 - e.g. testing / evaluation of instrumentation
 - development of appropriate training in measurements
 - development of appropriate QC/QA strategy

THINK!



**THERE MIGHT BE
A *BETTER* WAY**