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The quality control of oceanic carbon dioxide measurements: preparation and distribution of reference materials

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Goal

The goal of this project — together with that of a related project that was funded by National Science Foundation (OCE 9207265 and OCE 9521976) — was to provide a mechanism for the quality control of the oceanic carbon dioxide measurements that can ensure that measurements made as part of the JGOFS Global CO_2 Survey are comparable and accurate, although made by different laboratories at different times.

The strategy we chose to achieve this had four principal thrusts:

- The preparation, certification and distribution of reference materials that investigators can use to evaluate their shipboard data quality.
- The organization of collaborative studies to test various methods and to help the community in identifying improved analytical approaches.
- The preparation and distribution of well written Standard Operating Procedures describing the analysis of the oceanic carbon dioxide system
- Active participation in various committees and meetings to proselytize the need for a systematic approach to the quality control of oceanic chemical measurements.

Production, certification, and distribution of reference materials

As part of our initial NSF funded project (OCE 88-00474) we built an apparatus to sterilize sea water, to equilibrate it to a controlled level of carbon dioxide, and to deliver it for bottling. We have used this apparatus over the past eight years to prepare a series of batches of natural sea water which have excellent stability with respect to both total dissolved inorganic carbon and total alkalinity. (Some batches in 1991 were unstable as a result of contamination with mercury tolerant organisms. Improved cleaning procedures seem to have taken care of the problem.

Reference materials based on natural sea water are now produced regularly in our laboratory: about six batches per year. These batches of sea water have been certified for total dissolved inorganic carbon in Dr. Keeling's laboratory using the definitive extraction / manometry procedure (Table 1). A weighed sea water sample is acidified with phosphoric acid; the CO_2 evolved is then extracted under vacuum and condensed in a trap cooled by liquid nitrogen. The water and CO_2 are separated from one another by sublimation, and the CO_2 is transferred into a mercury column manometer. There its pressure, volume and temperature are measured; the amount of CO_2 separated is computed from an appropriate equation of state. This vacuum extraction/manometric technique constitutes a reference procedure for this measurement as it links the amount of carbon dioxide to fundamental measurements of temperature, pressure and volume. The pooled standard

Table 1. Reference material batch information certified results are expressed as mean ± std. dev. (number of analyses).

Batch Number	Bottling Date	Salinity	C_T / μmol kg^{-1}	A_T / μmol kg^{-1}
Batch 1	Jan 29, 1990	33.51	2020.15 ± 0.84 (12)	–[a]
Batch 2	Oct 1, 1990	33.36	1978.70 ± 0.90 (9)	2248.27 ± 0.94 (10)[b]
Batch 3	Jan 8, 1991		*batch not stable*	
Batch 4	Mar 20, 1991		*batch not stable*	
Batch 5	May 7, 1991		*batch not stable*	
Batch 6	May 22, 1991	38.43[c]	2304.64 ± 1.58 (9)	2375.61 ± 1.07 (9)[b]
Batch 7	Aug 8, 1991	37.12[c]	1926.63 ± 0.72 (6)	–[a]
Batch 8	Aug 26, 1991		*batch not stable*	
Batch 9	Sep 20, 1991		*batch not stable*	
Batch 10	Nov 15, 1991	34.57	1960.61 ± 0.39 (7)	2257.50 ± 0.69 (10)[b]
Batch 11	Jan 7, 1992	38.50[c]	2188.89 ± 0.53 (7)	–[a]
Batch 12	Feb 27, 1992	33.49	1984.26 ± 0.73 (7)	2226.56 ± 0.60 (10)[b]
Batch 13	Jun 25, 1992	32.86	2015.13 ± 0.58 (7)	2203.79 ± 0.47 (10)[b]
Batch 14	Jul 23, 1992		*not distributed as RM*[d]	
Batch 15	Nov 30, 1992	33.199	2031.65 ± 1.12 (11)	2202.38 ± 0.33 (10)[b]
Batch 16	Dec 4, 1992	33.203	2034.54 ± 0.91 (9)	2206.78 ± 0.54 (8)[b]
Batch 17	Apr 8, 1993	33.226	2044.54 ± 0.58 (9)	2219.15 ± 0.82 (11)[b]
Batch 18	Sep 10, 1993	35.298	2115.15 ± 1.00 (9)	2297.77 ± 0.72 (17)[b]
Batch 19	Sep 15, 1993	33.705	2004.08 ± 1.01 (17)	–[a]
Batch 20	Nov 23, 1993	33.145	1983.40 ± 1.59 (13)	2211.53 ± 1.04 (11)[b]
Batch 21	Jan 28, 1994	34.534	1991.98 ± 0.76 (10)	2258.36 ± 0.67 (6)[b]
Batch 22	Apr 1, 1994	33.561	1995.19 ± 0.71 (13)	2217.16 ± 1.51 (18)[b]
Batch 23	May 4, 1994	33.483	1993.10 ± 1.00 (12)	2212.71 ± 1.24 (18)[b]
Batch 24	Aug 26, 1994	33.264	1987.53 ± 1.34 (13)	2215.51 ± 0.57 (10)[b]
Batch 25	Nov 10, 1994	34.910	2127.21 ± 1.02 (9)	2299.79 ± 0.75 (12)[b]
Batch 26	Dec 13, 1994	33.258	1978.34 ± 0.67 (9)	2176.59 ±1.38 (17)[b]
Batch 27	Dec 21, 1994	33.209	1988.10 ± 0.60 (9)	2214.89 ± 1.53 (18)[b]
Batch 28	Feb 27, 1995	33.407	1994.64 ± 0.75 (10)	2223.47 ± 0.52 (13)[b]
Batch 29	Apr 19, 1995	33.701	1902.33 ± 1.06 (11)	2184.76 ± 1.08 (19)[b]
Batch 30	Jun 14, 1995	33.420	1988.78 ± 1.24 (10)	2201.88 ± 0.70 (28)[b]
Batch 31	Aug 16, 1995	32.899	1876.57 ± 1.27 (10)	2130.33 ± 0.79 (17)[b]
Batch 32	Oct 17, 1995	33.745	1997.57 ± 1.35 (10)	2221.48 ± 0.98 (22)[b]
Batch 33	Feb 27, 1996	33.781	2009.85 ± 0.85 (11)	2234.92 ± 0.44 (35)

Table 1. Reference material batch information certified results are expressed as mean ± std. dev. (number of analyses).

Batch Number	Bottling Date	Salinity	C_T / µmol kg^{-1}	A_T / µmol kg^{-1}
Batch 34	Apr 23, 1996	34.514	2061.52 ± 1.62 (15)	2284.35 ± 0.86 (34)
Batch 35	Aug 6, 1996	35.661	2111.62 ± 0.82 (11)	2354.05 ± 0.50 (34)
Batch 36	Nov 7, 1996	35.368	2050.21 ± 0.72 (10)	2283.83 ± 0.77 (25)
Batch 37	Apr 2, 1997	34.983	2044.15 ± 1.04 (11)	2314.11 ± 0.63 (16)
Batch 38	May 8, 1997	34.932	2089.99 ± 1.16 (15)	2300.89 ± 0.76 (51)
Batch 39	Jul 24, 1997		*batch not stable*	
Batch 40	Sep 16, 1997	33.383	1985.76 ± 0.72 (10)	2196.41 ± 0.61 (24)
Batch 41	Oct 31, 1997	33.368	1977.71 ± 0.51 (11)	2195.78 ± 0.38 (21)
Batch 42	Dec 16, 1997	33.364	1985.10 ± 1.14 (11)	2210.54 ± 0.62 (22)

a. Total alkalinity not known as archived samples were not available; however, it is expected to have been stable.

b. These total alkalinity values were not measured when the batch was originally certified; they are based on measurements performed on archived samples of the batch in question.

c. Batches 6, 7 and 11 were synthetic solutions of sodium chloride and sodium bicarbonate in deionized water. The salinity value is a value that will give the appropriate density at 20 °C.

d. Batch 14 was used as the basis of a collaborative study for the analysis of total dissolved inorganic carbon by coulometry.

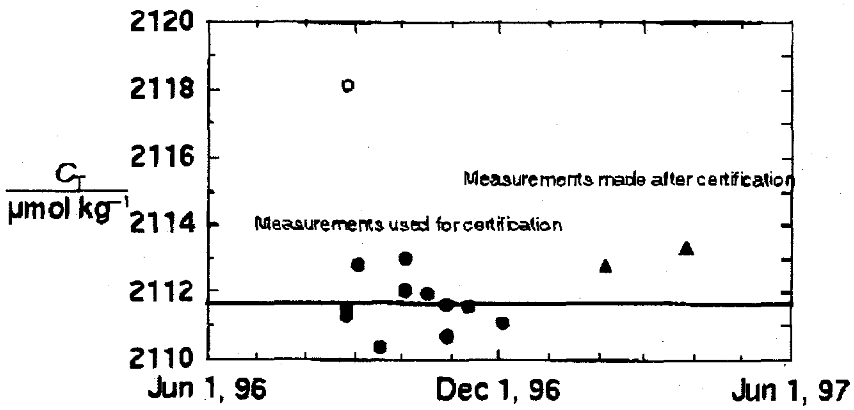

Figure 1. Stability of Batch 19: C_T = 2004.08 ± 1.01 (17) µmol·kg^{-1}.

deviation for this procedure, obtained from the measurements made on reference materials (Table 1), is about 1.0 µmol kg^{-1}. This value is probably equivalent to a long-term reproducibility (see *e.g.* Fig. 1). The accuracy is somewhat harder to assess but all the tests carried out to date indicate it is of the same order as the precision.

We have also developed a definitive procedure for the determination of total alkalinity in which the total alkalinity is assayed by a two-stage, potentiometric, open-cell titration using coulometrically analyzed hydrochloric acid. A weighed sample of reference material is acidified to a pH between 3.5 and 4.0 with an aliquot of titrant. The solution is stirred for a period of time to allow the evolved carbon dioxide to escape. The titration is then continued to a pH of about 3.0 and the equivalence point evaluated from titration points in the pH region 3.0 - 3.5 using a modified Gran procedure that corrects for the reactions with sulfate and fluoride ions.

The pooled standard deviation of this procedure, obtained from the measurements made on reference materials from Batch 33 onwards (Table 1), *i.e.* not including measurements made on archived samples, is 0.68 μmol kg^{-1}. This is a reasonable estimate of the long term reproducibility of the procedure (see *e.g.* Fig. 2). The accuracy is within 2 μmol kg^{-1} (see Table 2).

Table 2. Results from total alkalinity measurements on synthetic solutions. Results are presented as mean ± standard deviation (number of analyses).

	Coulometric Back-titration[a]	**Open-cell titration**	**Calculated Value**[b]
NIST SRM 723 ("tris")	2191.00 ± 0.57 (4)	2190.25 ± 0.81 (4)	2189.5
NIST SRM 413 (Na_2CO_3)	2172.48 ± 0.88 (4)	2172.21 ± 0.51 (4)	2172.0
$Na_2B_4O_7.10H_2O$	2001.01 ± 0.22 (3)	1998.58 ± 0.44 (3)	2000.5
natural sea water[c]	2278.52 ± 0.85 (3)	2279.15 ± 0.37 (9)	–

a. These procedures are described in Dickson et al. (1998).

b. The calculated alkalinities assume a zero background alkalinity due to the NaCl.

c. The sea water was sterilized by filtration through a 0.1 μm filter. Presence of mercuric ion prevents accurate coulometric analysis as it is preferentially reduced at the electrode.

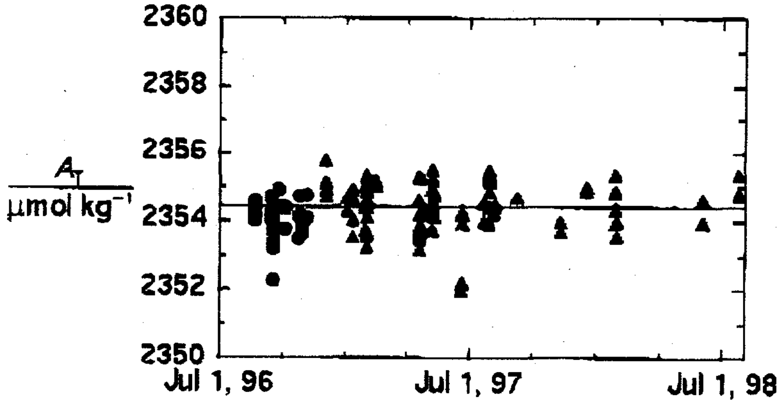

Figure 2. Results obtained for the total alkalinity of Batch 35. The early measurements (filled circles) were used to certify this batch (certified value: 2354.05 ± 0.50 μmol kg^{-1}). The later measurements (filled triangles) were used to monitor the stability of our measurement process. The overall mean and standard deviation of all the results are 2354.34 ± 0.66 (127) μmol kg^{-1}.

During the period of this grant, reference materials have been distributed to a wide variety of laboratories both within the US and abroad. They are used extensively to confirm that instruments are performing properly and to ensure measurement compatibility. The scale of the operation is indicated in Fig. 3 which shows that in the period from January 1990 to July 1998, we have bottled almost 24.000 bottles and have certified and distributed about 20,000 bottles to other laboratories for use in the quality control of their measurements.

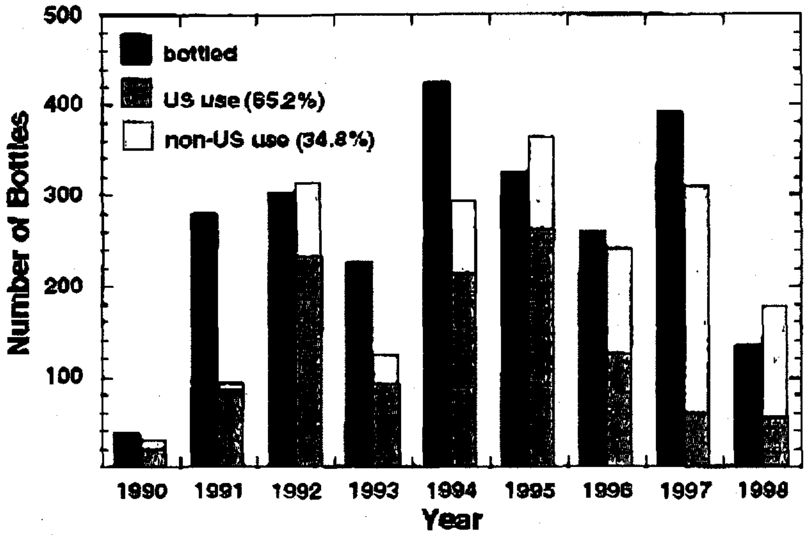

Figure 3. Production and shipping of reference materials Jan 1990 – Jul 1998.

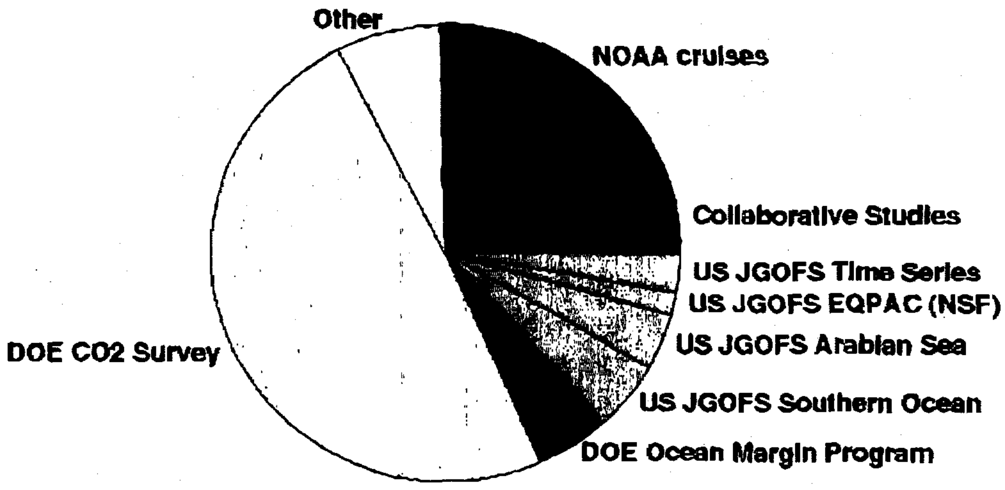

Figure 4. Distribution of reference materials for use by US programs.

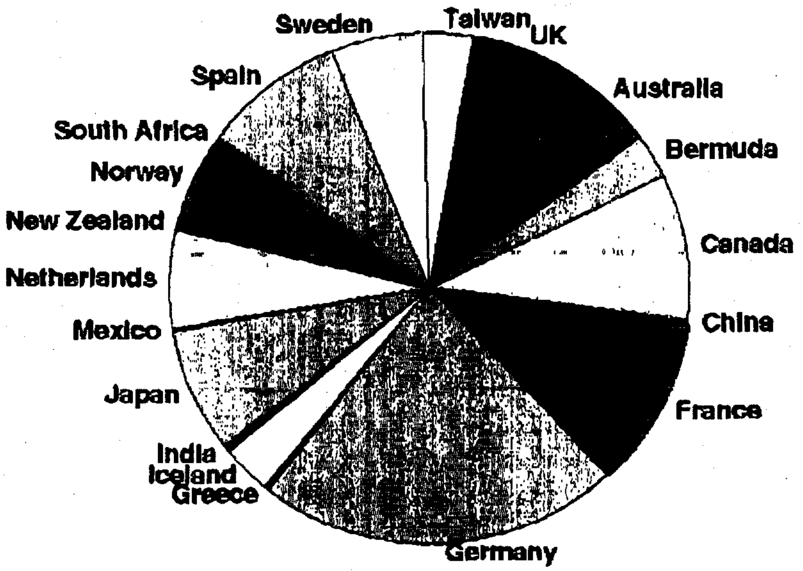

Figure 5. Distribution of reference materials for use by non-US programs.

The majority of bottles of reference material have been used by US scientists; the distribution between the various programs is shown in Fig. 4. The remaining bottles were used to support CO_2 measurement activities in other countries (Fig. 5). Many of the major non-US users — Australia. Bermuda, Canada, France, Germany, the Netherlands and the United Kingdom — have also been heavily involved in JGOFS related measurements.

At least half of the reference materials that we have produced over the past few years were distributed for use as part of the US JGOFS Global CO_2 survey that was funded by the US Department of Energy (and which this grant was explicitly in support of). These cruises were organized as part of the WOCE Hydrographic Program and provided a unique opportunity to combine high quality CO_2 data together with state-of-the-art hydrographic measurements. Reference materials were analyzed regularly on board ship — for both total dissolved inorganic carbon and for total alkalinity — to confirm that the ship-board analytical systems were working correctly and to provide assurance of the quality of the results obtained (DOE, 1994; Johnson *et al.*, 1998; Millero *et al.*, 1998).

Organization of collaborative studies

During the course of this work a number of international and national collaborative studies of CO_2 analytical methodology have been carried out. In these, we have typically used our reference materials as the study material.

Total dissolved inorganic carbon
1990 International study involving 14 groups
1992 International study involving 12 groups

Total alkalinity
1993 Limited study involving 10 DOE and NOAA funded investigators.

P(CO_2)

1994 International inter-laboratory comparison / workshop (involving 13 groups) organized at the Scripps Institution of Oceanography.

Carbon-13 in sea water

1996 International inter-laboratory study involving 11 groups

Preparation and distribution of Standard Operating Procedures

A set of Standard Operating Procedures was written as part of the related project funded by the Department of Energy. These are available in printed form from CDIAC at the Oak Ridge National Laboratory. A more up to date set of these procedures is being maintained as part of this project as a set of Adobe Acrobat files on my web site:

`http://www-mpl.ucsd.edu/people/adickson/CO2_QC/`

Participation in committees, scientific meetings, etc.

During the course of this project I have taken an active role in presenting this work and proselytizing the benefits of using reference materials to a variety of audiences. This has involved me on a number of committees either as a member or as an invited guest:

- The WOCE Hydrographic Program Planning Committee (1991–1994)
- GESREM (Group of Experts on Standards and Reference Materials)
- US JGOFS Steering Committee (1994–1997)
- NRC Committee on Oceanic Carbon (1993–1995)
- Joint IOC-JGOFS Carbon Dioxide Panel (1991–)

Scientific meeting presentations involving work supported by this grant

3/93	Pittsburg Conference
7/93	5th International Congress on the history of Oceanography
9/93	4th CO_2 conference, Carqueiranne
10/93	Alex '93, San Francisco
4/94	BERM-6, Kona
11/94	World Ocean Circulation Experiment Workshop, Kaohsiung, ROC
11/94	Japanese IGBP meeting, Sapporo, Japan (invited speaker)
1/95	NOPACCS symposium. Osaka, Japan (invited speaker)
3/95	Pittcon 95, New Orleans
5/95	JGOFS meeting, Villefranche-sur-mer, France
1/96	ICES 95, Trivandrum, India (invited speaker)
1/96	CO_2 in the Oceans, Puerto Rico (plenary lecture)
3/96	ACS Meeting, New Orleans

Publications supported by this project (in conjunction with the related NSF grants)

A. G. Dickson (1992) The determination of total dissolved inorganic carbon in sea water using extraction/coulometry: the first stage of a collaborative study. U. S. Department of Energy Report No. DOE/RL/01830T–H14

A. G. Dickson (1992) JGOFS: measuring CO_2 in the ocean. *EOS, Transactions, Am. Geophys. Union* 73, 546.

A. G. Dickson (1992) CO_2 panel proposes comparison of methods for determining pCO2 in sea water. *U. S. JGOFS News* 4(2), 6.

A. G. Dickson (1993) pH buffers for sea water media based on the total hydrogen ion concentration scale. *Deep-Sea Res.* **40**, 107–118.

A. G. Dickson (1993) The analytical chemistry of the oceanic carbon dioxide system. In *Proceedings of the International Symposium on Global Change (IGBP), Tokyo, Japan, March 27–29, 1992.* Secretariat of International Symposium on Global Change. pp. 183–192.

A. G. Dickson (1993) The measurement of sea water pH. *Mar. Chem.* **44**, 131–142.

A. G. Dickson (1994) The plastic menagerie: CO_2 teams compare seagoing systems. *U. S. JGOFS News* **5**(4), 5.

DOE (1994) Handbook of methods for the analysis of the various parameters of the carbon dioxide system in sea water. (Version 2), A. G. Dickson & C. Goyet, eds. ORNL/CDIAC-74.

A. G. Dickson (1995) The measurement of sea water pH. In *Global fluxes of carbon and its related substances in the coastal sea-ocean-atmosphere system.* Proceedings of the 1994 Sapporo IGBP Symposium, 14–17 September, 1994. Hokkaido University, Sapporo, Hokkaido, Japan.

C. D. Winn & A. G. Dickson (1995) Global survey continues to yield high-quality CO_2 data from Indian Ocean. *US JGOFS News* **6(4)**, 6.

A. G. Dickson (1995) Determination of dissolved oxygen in sea water by Winkler titration. WOCE Operations Manual. Part 3.1.3 Operations & Methods. WHP Office Report WHPO 91-1.

A. G. Dickson (1997) The development and use of reference materials for the quality control of oceanic CO_2 measurements. In *Advances in Environmental Science* (C. S. P. Iyer, ed.), pp. 31–42, Educational Book Publishers & Distributors, New Delhi, India.

T. A. DelValls & A. G. Dickson (1998) The pH of buffers based on 2-amino-2-hydroxymethyl-1,3-propanediol ("tris") in synthetic sea water. *Deep-Sea Res.* **45**, 1541–1554.

F. J. Millero, A. G. Dickson, G. Eischeid, C. Goyet, P. Guenther, K. M. Johnson, R. M. Key, K. Lee, D. Purkerson, C. L. Sabine, R. G. Schottle, D. R. W. Wallace, E. Lewis & C. D. Winn (1998) Total alkalinity measurements in the Indian Ocean during the WOCE Hydrographic Program CO_2 Survey Cruises 1994–1996. *Mar. Chem.* **63**, 9–20.

K. M. Johnson, A. G. Dickson, G. Eischeid, C. Goyet, P. Guenther, R. M. Key, F. J. Millero, D. Purkerson, C. L. Sabine, R. G. Schottle, D. R. W. Wallace, R. J. Wilke & C. D. Winn (1998) Coulometric total carbon dioxide analysis for marine studies: assessment of the quality of total inorganic carbon measurements made during the US Indian Ocean CO_2 survey 1994–1996. *Mar. Chem.* **63**, 21–37.

Additonal work in preparation

A. G. Dickson & G. C. Anderson, Sea water based reference materials for CO_2 analysis: 1. Preparation and distribution. *(in preparation)*

A. G. Dickson, J. Afghan & G. C. Anderson, Sea water based reference materials for CO_2 analysis: 2. A method for the certification of total alkalinity. *(in preparation)*

C. D. Keeling, P. R. Guenther, G. Emanuele, T. J. Leuker and A. G. Dickson, Sea water based reference materials for CO_2 analysis: 3. A method for the certification of total dissolved inorganic carbon. (*in preparation*)

A. G. Dickson & G. C. Anderson, Purification of sodium chloride to reduce protolytic impurities. *(in preparation)*.

Publication database

I am also in the process of compiling a database of publications describing studies that used our CO_2 reference materials as the basis of their quality control. These citations have been provided by the various investigators that have used our reference materials. To date, this database has 130 entries: about two thirds of these are to a variety of technical and cruise reports, the remainder to peer-reviewed publications. I plan to make this bibliography available on our web site in the next few weeks.