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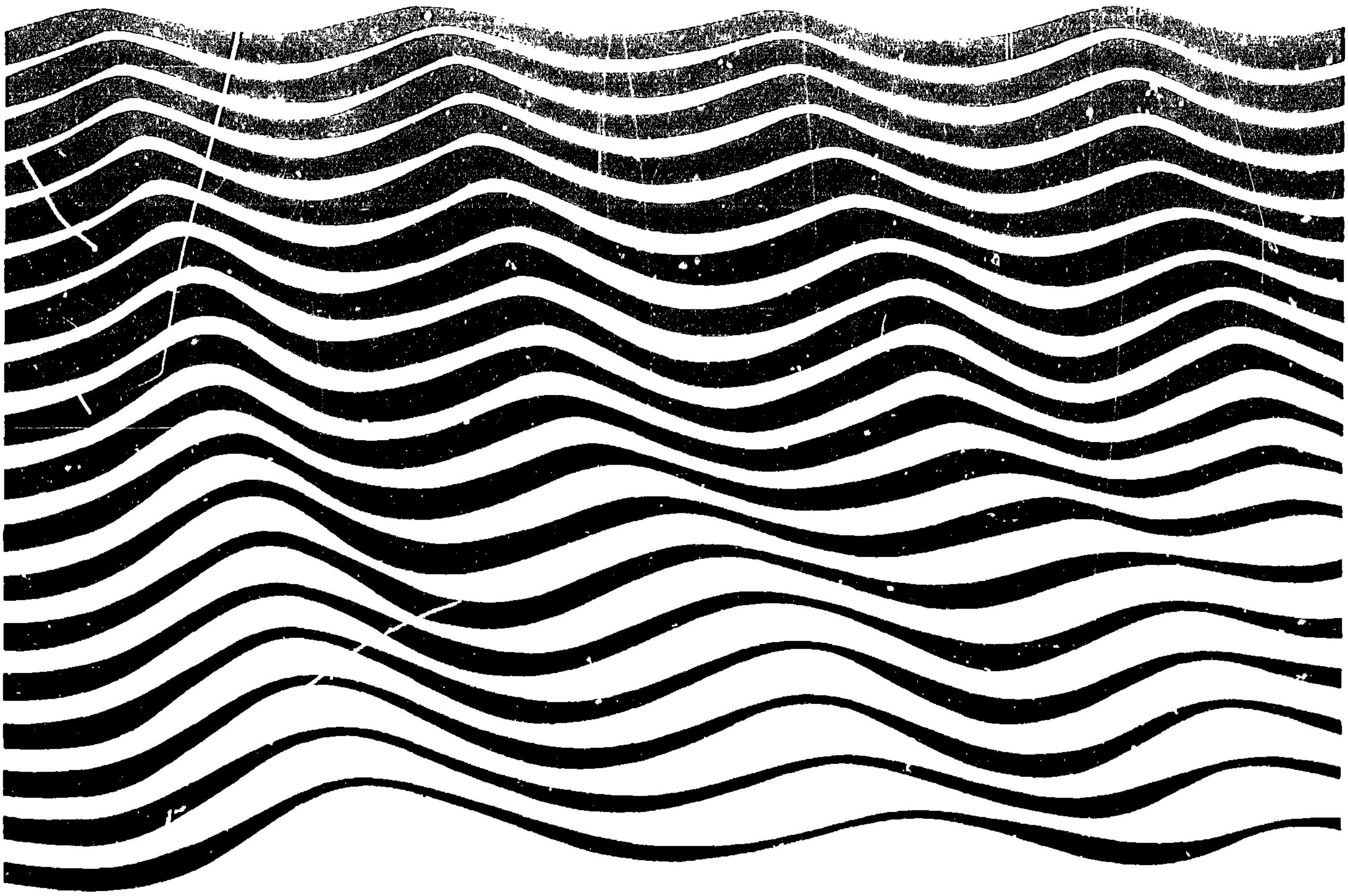
Intercomparison of total alkalinity and total inorganic carbon determinations in seawater

Recommended by
ICES Marine Chemistry Working Group and
SCOR Working Group 75
and endorsed by
SCOR/Unesco/ICES/IAPSO Joint Panel on
Oceanographic Tables and Standards



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Intercomparison of total alkalinity and total inorganic carbon determinations in seawater

by
Alain Poisson
Fred Culkin
Paul Ridout

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PREFACE

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INTRODUCTION

The aim of the intercomparison exercise was to assess the reliability of data for total alkalinity (TA), total dissolved inorganic carbon (TCO_2) and, if possible, pH and p(CO_2) in seawater, as determined by various laboratories engaged in programmes related to the CO_2 problem. This exercise was recommended by the ICES[1] Marine Chemistry Working Group and by SCOR[2] Working Group 75 on Methodology of Carbon Dioxide Measurements. The Sub-Panel on Standards for Carbon Dioxide Measurements of the SCOR/Unesco/ICES/IAPSO[3] Joint Panel on Oceanographic Tables and Standards (JPOTS) endorsed this recommendation during its first meeting in Vancouver, BC, Canada, in August 1987. In this report, we present (1) the results of preliminary tests on the preparation and storage of the samples and (2) the progress of the intercomparison exercise involving 12 laboratories and a comparison of their data.

A preliminary version of this report was discussed by the Sub-Panel on Standards for Carbon Dioxide Measurements during its second meeting in Acapulco, Mexico, in August 1988. The following members of the Sub-Panel attended the meeting:

- Dr. A. G. Dickson, Chairman, Marine Physical Laboratory, S-002, Scripps Institution of Oceanography, La Jolla, CA 92093, USA.
- Dr. F. Culkin, Institute of Oceanographic Sciences Deacon Laboratory, Brook Road, Wormley, Godalming, Surrey, GU8 5UB, UK.
- Prof. F. Millero, Rosenstiel School of Marine and Atmospheric Sciences, 4600 Rickenbacker Causeway, Miami, FL 33149, USA.
- Dr. S. Morcos, Unesco, Division of Marine Sciences, 7, place de Fontenoy, 75700 Paris, France.
- Dr. A. Poisson, Laboratoire de Physique et Chimie Marines (LPCM), Université Pierre et Marie Curie, 75252 Paris Cedex 05, France.
- Dr. C. S. Wong, Institute of Ocean Sciences, Sidney, BC, Canada.

STORAGE OF SAMPLES

An earlier investigation of the suitability of IAPSO Standard Seawater as a reference standard for alkalinity determinations showed significant variations in

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[1] International Council for the Exploration of the Sea

[2] Scientific Committee on Oceanic Research

[3] International Association for the Physical Sciences of the Ocean

alkalinity between batches (Goyet *et al.*, 1985). This was probably due to variations in composition in the North Atlantic surface water used to prepare standard seawater. Ampoules from a single batch showed more consistency in alkalinity but the standard deviation of the determinations (7 $\mu mol \cdot kg^{-1}$) was higher than that of the analytical method (3 $\mu mol \cdot kg^{-1}$).

An investigation was, therefore, carried out into the suitability of Pyrex bottles for the storage of intercalibration samples. A bulk sample of filtered seawater of salinity 35.013, to which was added 100 µl saturated mercuric chloride solution per litre of seawater, was prepared at the Institute of Oceanographic Sciences Deacon Laboratory, Wormley, UK. The water was transferred to one litre Pyrex bottles which were filled to overflowing and sealed with ground-glass stoppers greased with Apiezon H, and held in position by clips. Eleven samples were sent to the following investigators: Dr. P. Brewer (Woods Hole Oceanographic Institution), Dr. A. Poisson (LPCM, Paris) and Professor C.-T. Chen (Institute of Marine Geology, Taiwan). Determinations of total alkalinity (TA), total dissolved inorganic carbon (TCO_2) and pH were carried out by the three laboratories, but only C-T. Chen measured pH directly at 25 °C using two NBS buffers (4.004 and 7.415). Total alkalinity and total inorganic carbon were determined by the modified potentiometric titration previously published by Dyrssen (1965) and Bradshaw *et al.* (1981). The first two laboratories determined the pH from the initial measurement of potential of this titration.

Five sets of measurements were made, spread over fifteen months, the first in Woods Hole in August 1986, the second in Paris in December 1986, the third and fourth respectively in Paris and Taiwan in June 1987, and the last one in Taiwan in November 1987. Results are set out in Tables 1 through 5. The mean TA results obtained for the five sets of measurements (Table 6) are in good agreement. The mean of all the TA measurements is 2294.3 $\mu mol \cdot kg^{-1}$ with a standard deviation of 3.9 $\mu mol \cdot kg^{-1}$ and the overall mean of the mean TA values corresponding to the five sets of measurements is 2294.4 $\mu mol \cdot kg^{-1}$ with a standard deviation of 0.8 $\mu mol \cdot kg^{-1}$. These results show that the samples were sufficiently reproducible for TA between bottles, and stable over a period of more than one year, to be used in a TA intercomparison exercise.

For TCO_2 the scatter of the results from each laboratory is acceptable but the mean values from the various institutions disagree significantly. The standard deviation for all the data of the five sets of measurements is 15.9 $\mu mol \cdot kg^{-1}$, which is several times the individual standard deviation. These results indicate that the samples are sufficiently reproducible for TCO_2 between bottles but that discrepancies exist between the results of the various laboratories.

Brewer reported that a large number of bubbles were present in his samples during the titrations, which was not the case for the samples used by Poisson. This may be explained by the fact that Brewer made his measurements at 25°C and Poisson at 22°C. Within four sets of determinations, however, the standard deviation was less than 0.2% which is adequate for an intercomparison exercise.

The pH measurements showed a significant difference between those of Brewer, who obtained a mean value of 7.785 at 25 °C compared with 7.839 and 7.817 at 25 °C by Poisson, both on a sea water "total proton" scale (SWS), and with the mean values of 7.965 and 7.986 on the NBS scale obtained by Chen. The mean value of the three first sets is 7.814 ($s = 0.027$), compared with the mean of the two other sets, 7.976, which are on the NBS scale. The difference between the two mean values (0.162) is close to the one between the two scales determined by Bates (1982) in seawater of salinity 35 at 25 °C. However, these data are difficult to compare because only NBS data were directly measured relative to NBS buffers, the "total proton" scale data being calculated from the initial potential value measured at the beginning of a potentiometric titration of TA and TCO_2. The comparison between bottles of each set shows a reproducibility within one unit in the second decimal place.

The conclusion drawn from these preliminary tests was that seawater samples prepared and stored as described above are satisfactory for a TA and TCO_2 intercomparison exercise, but that the samples should be equilibrated with air at a temperature of at least 25°C during their preparation, to be adequate for pH and $p(CO_2)$ intercomparison.

Table 1. Results of preliminary measurements made by Dr. P. Brewer from 14 to 29 August 1986. TA and TCO_2 measurements are expressed in $\mu mol \cdot kg^{-1}$, pH measurements are on the "total proton" concentration scale.

Bottle	TA	$\overline{TA}$	s(TA)	TCO_2	$\overline{TCO_2}$	s(TCO_2)	pH (25°C)	$\overline{\text{pH (25°C)}}$	s(pH)
49	2299.3	2298.1	3.6	2125.0	2125.1	0.8	7.822	7.793	0.026
	2300.9			2124.4			7.787		
	2294.1			2125.9			7.771		
52	2294.2	2294.2	0.1	2119.5	2120.7	1.8	7.794	7.785	0.008
	2294.3			2122.8			7.782		
	2294.2			2119.8			7.778		
55	2292.3	2294.0	3.2	2120.1	2123.0	3.9	7.769	7.772	0.004
	2296.6			2121.4			7.777		
	2290.3			2121.9			7.773		
	2296.6			2128.7			7.769		
58	2290.8	2295.0	6.5	2118.7	2121.5	2.4	7.774	7.775	0.003
	2303.9			2122.8			7.772		
	2289.6			2120.6			7.774		
	2295.7			2124.0			7.779		
61	2289.5	2290.9	6.2	2116.2	2118.3	3.9	7.786	7.782	0.006
	2288.3			2116.7			7.783		
	2299.9			2124.1			7.786		
	2285.7			2116.0			7.774		
64	2289.7	2290.7	2.1	2117.4	2117.4	0.5	7.786	7.783	0.006
	2293.1			2117.9			7.786		
	2289.4			2117.0			7.776		
67	2289.9	2291.8	1.9	2115.0	2116.7	2.4	7.788	7.792	0.004
	2291.7			2115.7			7.796		
	2293.7			2119.4			7.791		
70	2294.9	2295.7	1.9	2117.3	2118.5	2.0	7.800	7.797	0.003
	2294.3			2117.5			7.795		
	2297.9			2120.8			7.795		
73	2291.5	2292.7	1.1	2115.2	2117.1	1.8	7.788	7.790	0.002
	2292.9			2117.4			7.791		
	2293.6			2118.8			7.791		
76	2292.8	2292.7	0.2	2115.1	2115.4	0.2	7.797	7.793	0.004
	2292.7			2115.5			7.790		
	2292.5			2115.5			7.793		
All bottles		**2293.5**	**3.9**		**2119.5**	**3.6**		**7.785**	**0.011**

Table 2. Results of preliminary measurements made by A. Poisson from 2 to 9 December 1986. TA and TCO_2 measurements are expressed in $\mu mol{\cdot}kg^{-1}$, pH are on the "total proton" concentration scale.

Bottle	TA	TCO_2	pH (25°C)
45	2299.0	2096.0	7.844
	2294.0	2096.5	7.840
48	2300.0	2096.5	7.859
	2297.0	2096.5	7.845
	2291.0	2097.0	7.840
51	2290.0	2100.0	7.836
	2295.0	2092.5	7.836
54	2312.0	2094.5	7.841
	2305.0	2096.5	7.842
57	2289.0	2094.5	7.835
	2289.0	2096.5	7.822
	2291.0	2094.0	7.839
60	2293.0	2088.0	7.843
	2287.0	2096.5	7.829

Table 3. Results of preliminary measurements made by A. Poisson from 12 to 15 June 1987. TA and TCO_2 measurements are expressed in $\mu mol{\cdot}kg^{-1}$, pH are on the "total proton" concentration scale.

Bottle	TA	TCO_2	pH (25°C)
	2289.3	2103.4	7.798
63	2291.5	2100.1	7.816
	2297.0	2103.2	7.826
	2296.5	2103.7	7.819
66	2294.8	2107.6	7.815
	2298.3	2111.8	7.823
	2298.9	2115.1	7.822
69	2293.8	2107.4	7.817
	2296.8	2109.1	7.821
	2292.4	2107.4	7.819
72	2287.1	2102.6	7.802
	2287.9	2103.9	7.813
	2298.4	2098.7	7.835
75	2298.8	2110.1	7.819

Table 4. Results of preliminary measurements made by C.–T. Chen in June 1987. TA and TCO_2 measurements are expressed in $\mu mol{\cdot}kg^{-1}$, pH are on NBS scale

Bottle	TA	TCO_2	pH (25°C)
47	2299	2095	7.971
50	2290	2086	7.966
53	2295	2078	7.970
56	2293	2082	7.950
62	2293	2079	7.972

Table 5. Results of preliminary measurements made by C.–T. Chen in November 1987. TA and TCO_2 measurements are expressed in $\mu mol{\cdot}kg^{-1}$, pH are on NBS scale

Bottle	TA	TCO_2	pH (25°C)
65	2292	2079	7.983
68	2298	2079	7.987
71	2298	2078	7.983
74	2297	2081	7.986
77	2291	2082	7.991

Table 6. Mean results of preliminary measurements made by the three Laboratories. TA and TCO_2 measurements are expressed in $\mu mol{\cdot}kg^{-1}$, pH are on "total proton" concentration scale (SWS) or NBS scale.

Lab	date	$\overline{TA}$	$\overline{TCO_2}$	$\overline{pH}$(25 °C)
WHOI	8/86	2293.4 s = 3.8 (10)	2119.4 s = 3.8 (10)	7.785 s = 0.011 (10)
LPCM	12/86	2295.1 s = 6.7 (6)	2095 s = 2.6 (6)	7.839 s = 0.008 (6)
LPCM	6/87	2294.4 s = 4.0 (5)	2105 s = 3.8 (5)	7.817 s = 0.009 (5)
IMG	6/87	2293.8 s = 3.0 (6)	2083.3 s = 6.4 (6)	7.965 s = 0.008 (6)
IMG	11/87	2295.2 s = 3.4 (5)	2079.8 s = 1.6 (5)	7.986 s = 0.003 (5)
all	8/86 to 11/87	2294.3 s = 3.9 (32)	2099.5 s = 15.9 (32)	7.813 (SWS) s = 0.026 (21) 7.974 (NBS) s = 0.013 (11)

INTERCOMPARISON EXERCISE

Thirty-five letters were sent to various laboratories and institutions in nine countries and an announcement of the exercise was published in the International Marine Science (IMS) Newsletter and American Geophysical Union EOS Transactions. Twenty-four laboratories expressed interest in the exercise, nineteen ordered the samples but only twelve sent in their results. The laboratories which effectively participated in the exercise were the following:

- Bregant, D., Istituto Tallasografico di Trieste, Italy.
- Carlberg, S. R., Swedish Meteorological and Hydrological Institute, Oceanographical Laboratory, Göteborg, Sweden.
- Chen, C.-T., National Sun Yat-Sen University, Institute of Marine Geology Kaohsiung, Taïwan, Republic of China.
- Chipman, D. W., Lamont-Doherty Geological Observatory of Columbia University, Geochemistry Division, Palisades, New York, USA.
- Copin-Montegut, C., Centre d'Etudes et de Recherches Océanographiques de Villefranche-sur-Mer, Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, Villefranche-sur-Mer, France.
- Jones, E. P., Bedford Institute of Oceanography, Dartmouth, Nova Scotia, Canada.
- Keeling, C. D., Scripps Institution of Oceanography, La Jolla, California, USA.
- Oudot, C., Institut Français de Recherche Scientifique pour le Développement en Coopération, Dakar, Senegal.
- Perez, F. F., Instituto de Investigaciones Marinas, Vigo, Spain.
- Poisson, A., Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, Paris, France.
- Robinson, C., University College of North Wales, School of Ocean Sciences, Marine Science Laboratories, Gwynedd, Wales, UK.
- Wong, C. S., Institute of Ocean Sciences, Sidney, B.C., Canada.

Preparation of samples

Four bulk samples of seawater, of salinities *ca* 8, 30, 35, and 38, each equilibrated with air at 26 °C, were prepared at the Institute of Oceanographic Sciences Deacon Laboratory, UK and transferred to 1 liter Pyrex bottles as described on page 2.

Results and discussion

Total alkalinity

The individual data from all the participating laboratories are in Table 7. The columns are the following:

Bottle/run = bottle number/individual measurement number. The analysts from Laboratory B processed their data using a curve fitting programme (CF) and the Alkfini programme (AF) based on modified Gran functions. In Laboratory C, two analysts (A1 and A2) made the measurements on the same samples.

Salinity = conductivity salinity measured by the participants.

TA = total alkalinity ($\mu mol \cdot kg^{-1}$).

$\overline{TA}$ = mean total alkalinity ($\mu mol \cdot kg^{-1}$) of the bottle.

range = range of values of TA for the bottle.

Date = year/month.

Ref = publication on which the technique of measurement is based. The references at the end of the text.

$\overline{TA}$ norm = mean TA normalized to SSWS salinity. SSWS salinity is the salinity measured by the Standard Seawater Service during the preparation of the four samples:

\X\TO(TA) norm = \F(\X\TO(TA) x SSWS salinity, Salinity)

The data obtained by potentiometric titration were calculated for a seawater without silicate and phosphate.

Individual measurements are shown on Figs. 1, 2, 3 and 4a for samples of salinity *ca* 8, 30, 35, 38. The analysis number is a "fictive" number corresponding to increments of one for each individual measurement to give an indication of the scatter of the individual TA measurements of the various bottles. The individual laboratories, designated from A to M, are represented by the marks specified to the right of the figures.

Mean values of TA for the bottles are plotted versus both the bottle number (Figs. 1, 2, 3 and 4b) and the date of the measurements (Figs. 1, 2, 3 and 4c) to test whether a shift exists with either the order of filling of the bottles or with the storage time.

TA normalized to the SSWS salinity are plotted versus the bottle numbers (Figs. 1, 2, 3 and 4d) to test if leakage occured during the storage. Normalized values were calculated using the salinity measured by the laboratories:

No shift appears with storage time or filling order, showing that the differences between the data of the various participants are due to the measurements. If data from Laboratory C, which used a manual titration

(Gripenberg, 1972), are not taken into account, the maximum scatter of the individual data is 16 µmol·kg^{-1} for the sample of salinity 8, 82 µmol·kg^{-1} for salinity 30, 66 µmol·kg^{-1} for salinity 35, and 70 µmol·kg^{-1} for salinity 38. If data from Laboratory F are not taken into account either, these scatters are reduced to 28, 30 and 28 µmol·kg^{-1} for salinities of 30, 35 and 38 respectively . The maximum differences between the mean TA values of the various bottles (excluding data from Laboratories C and F) are respectively 14, 22, 29 and 26 µmol·kg^{-1} for salinities 8, 30, 35 and 38. This corresponds to 2.7%, 1.1%, 1.3% and 1% of the measured values, which is about 5 or 10 times greater than the reproducibility of the individual laboratories.

Total dissolved inorganic carbon

The individual data for all the participating laboratories are shown in Table 8. The columns are the following:

Bottle/Run = bottle number/individual measurement number. Method used: gas chromatography (GC); coulometry (C); manometry (M); potentiometry (P, or nothing)

Salinity = conductivity salinity measured by the participants.

TCO_2 (p) = Total dissolved inorganic carbon measured by potentiometric titration.

TCO_2 (e) = Total dissolved inorganic carbon determined by an extraction technique (gas chromatography, coulometry, manometry).

$\overline{TCO_2}$ (p/e) = mean value ot TCO_2 for the bottle (potentiometry/extraction).

range = range of measured TCO_2 values for the bottle.

Date = year/month

Ref = reference paper on which the technique of measurement is based. The references are at the end of the text.

$\overline{TCO_2}$ (p/e) norm = mean TCO_2 normalized to SSWS salinity. SSWS salinity is the salinity measured by the Standard Seawater Service during the preparation of the four samples:

\X\TO(TCO_2) norm = \F(\X\TO(TCO_2) x SSWS salinity, Salinity)

The individual measurements are plotted on Figs. 5, 6, 7 and 8 for samples of salinity *ca* 8, 30, 35 and 38. Data obtained with a potentiometric titration are on figures "a" and those obtained by a technique of extraction by acidification of the sample are on figures "b". Potentiometric TCO_2 data are systematically higher than the extraction TCO_2 data. The differences between the mean values are 9, 27, 28 and 28 µmol·kg^{-1} for samples of salinity 8, 30, 35 and 38. They are reduced to

10, 18 and 21 $\mu mol \cdot kg^{-1}$ at salinity 30, 35 and 38 when the data far from the mean (Laboratories F and L) are not taken into account.

Measurements of TCO_2 on 12 bottles of salinity 35 by the same laboratory (Fig. 7c) show that only small differences in TCO_2 exist between the various bottles ($s = 2.5\ \mu mol \cdot kg^{-1}$). The scatter which exists between the various laboratory data (Figs. 5, 6, 7, 8c, 8d, 8e, 8f) is certainly due to standardization problems. It is also apparent from these figures that the scatter of the data obtained by potentiometry is of the same order as that of the data obtained by extraction and even a little greater. It is thus the technique of measurement itself — manometry, gas chromatography, coulometry — which introduces these differences.

It is apparent that the scatter of the mean TCO_2 data when normalized to SSWS salinity (Figs. 5, 6, 7, 8g, 8h) is no smaller than that of the unnormalised mean data. This demonstrates that no leakage occurred during the storage of the samples. The scatter of the measured salinity is due to problems with salinity measurements, and does not result from variation of the salinity of the samples during the storage.

pH

Several laboratories either measured the pH either directly using "tris" or NBS buffers, or determined it indirectly from the first measurement of the potential of the samples during the potentiometric titration of TA and TCO_2. Measurements using "tris" buffers or from the first measured potential are on a "total proton" or sea water scale (SWS). The results are shown in Table 9. The columns are:

Bottle/Run	=	bottle number /individual measurement number
Scale	=	pH Scale used (NBS or SWS)
t (°C)	=	temperature of measurement
pH (t)	=	pH measured at temperature t °C
pH (25 °C)	=	measured pH, corrected to the temperature 25°C, using Gieskes's formula (1969):

$$pH\ (25\ °C) = pH\ (t) + 0.0114\ (t - 25)$$

The mean values of pH at 25 °C are in Table 10. At salinity 35, one laboratory determined the pH on 12 bottles. The standard deviation of these results is 0.005, which demonstrates that the variation from one bottle to another is small. Even if the storage conditions were different for the samples of the various laboratories, it is obvious that the differences which exist between the data (standard deviation greater than 0.1 for the direct measurements) is due either to problems of standardization or to unrecognized liquid junction errors.

The pH (25 °C) data are plotted versus the analysis number (same meaning as in previous figures) to show the scatter of the individual measurements (Figs. 9, 10, 11, 12a).

Plots of mean values of pH (25 °C)for the bottles versus the bottle number (Figs. 9, 10, 11, 12b) and versus the date of the measurement (Figs. 9, 10, 11, 12c) show no evidence of CO_2 contamination of the samples during the filling of the bottles or during their storage.

The scatter of the NBS data, whatever the salinity, is of the order of 0.3. Values from Laboratories A and C are greater than others for all the salinities. The scatter decreases if the data of these two laboratories are not taken into account, but it remains high: 0.10 for salinity 30; 0.02 for salinity 35, and 0.02 for salinity 38. The scatter of data obtained on 12 bottles in the same laboratory (Fig. 11b) is smaller (s = 0.005) than the scatter between the various laboratories. The scatter of SWS data is 0.03 for salinity 30; 0.04 for salinity 35, and 0.02 for salinity 38. The NBS data are all measured directly, whereas SWS data are either calculated during the potentiometric titration or measured directly using "tris" buffers. It is not easy to draw a conclusion from these results because of the restricted number of measurements, except that the discrepancy between the various laboratories is greater than the reproducibility of a single laboratory.

p(CO_2)

Only three laboratories measured p(CO_2) directly. The maximum difference between the mean p(CO_2) at 25°C of the three laboratories are 50, 25, 10 and 15 µatm for salinities 8, 30, 35 and 38 respectively. It is noticeable that for the four sets of data, the mean data of two laboratories are always very close (2.5 µatm at salinity 8, 0.1 µatm at salinity 30, 3.2 µatm at salinity 35 and 2.5 µatm at salinity 38). But in each case the two laboratories are different: A and E for S = 8, E and G for S = 30 and 38, A and G for S = 35.

The data of all the individual measurements are shown in Table 11 for samples of salinity 8, 30, 35 and 38. The columns are the following:

$p(CO_2)$ = partial pressure of CO_2 in equilibrium with the sample, measured at temperature t (°C).

$p(CO_2)$ (25°C) = partial pressure of CO_2 corrected to 25°C. The corrections were calculated using the thermodynamic relations between TA, TCO_2 and $p(CO_2)$ for seawater of salinity S at temperature t and the dissociation constants of carbonic acid recommended by the Joint Panel on Oceanographic Tables and Standards (Unesco, 1983). The $p(CO_2)$ was calculated, for the four batches, using the SSWS salinity, the mean total alkalinity and the mean total inorganic carbon for the temperatures of measurements 18, 25 and 26.

$\overline{p(CO_2)}$ (25°C) = The mean data for pCO_2 corrected to 25°C for each bottle are shown in this column .

Individual $p(CO_2)$ (25 °C) values are plotted on Figs. 13, 14, 15 and 16a versus the analysis number. Mean data are plotted versus the bottle number and the data of analysis on Figs. 13, 14, 15, 16b and 16c.

As was observed for pH, there is no clear evidence in Figs. 13b, 14b, 15b and 16b of either contamination or of loss of CO_2 from the samples during the filling of the bottles or during their storage.

CONCLUSIONS

The present intercomparison has shown that the probable accuracy of the measurement of TA, TCO_2, pH and $p(CO_2)$ is considerably lower than the reproducibility obtained by an individual laboratory.

For TA, the maximum differences between the mean values of the various bottles (excluding data from laboratories C and F) are 14, 22, 29 and 26 $\mu mol \cdot kg^{-1}$ for batches of salinity 8, 30, 35 and 38 respectively. Even for salinity 35, the difference is greater than 1% of the measured values while the "accuracy" claimed by most of the laboratories is 0.1% or 0.2%. Furthermore, the desired accuracy for standards for JGOFS[1] and WOCE[2] programmes is 1 $\mu mol \cdot kg^{-1}$ which is equivalent to about 0.05% of the measured value. Thus, there is a great need for standards for TA measurements of sea water, which should improve the precision and accuracy of the data.

For TCO_2, this intercomparison has demonstrated that the method used for the preparation of the samples — a method used for several years at sea by C.D.

[1] Joint Global Ocean Flux Study

[2] World Ocean Circulation Experiment

Keeling (Scripps Institution of Oceanography) — was adequate for this purpose. The scatter between the mean data for the various laboratories is due to the measurements themselves. It is noticeable that the scatter of mean data for potentiometric titration is no greater than that of extraction techniques (gas chromatography, manometry and coulometry), and that the first data are systematically higher than the second ones for the four salinity batches.

The scatter of normalized mean TCO_2 (= $\overline{TCO_2}$ x SSWS salinity/Salinity) is no smaller and is sometimes greater than that of mean TCO_2 because salinity measured by the various laboratories shows a discrepancy which is not negligible. As with TA, TCO_2 measurements also need suitable standards to reduce the discrepancy between the various laboratories.

In the pH data, about the same trend occurs as for the preliminary tests: the NBS values are greater than those on SWS by 0.21 if all the NBS data are used, but this difference decreases to about 0.12 when data from Laboratories A and C are not taken into account. The scatter of individual laboratory measurements is smaller than the one between the various laboratories. This is due to standardization problems with the buffers used, and probably also to unrecognized liquid junction errors.

For $p(CO_2)$, surprisingly, pairs of values were reported which are closer than 3 µatm, but the pairs do not correspond to the same laboratories for each of the four salinities. It seems that the problem with these $p(CO_2)$ results is not a problem of reference, but one which lies in the techniques of measurement of $p(CO_2)$ in a gas, or in the equilibration between seawater and the gas of measurement, or perhaps also in corrections used for the temperature variation.

In conclusion, it is obvious that the availability of suitable certified reference materials would increase the accuracy for TA, TCO_2 and pH measurements, but for $p(CO_2)$ it would also be necessary for the different laboratories that engage in the $p(CO_2)$ measurements to make an intercomparison on board a ship to improve the $p(CO_2)$ techniques of measurement. It would also be desirable to improve the accuracy and precision of at-sea pH measurements.

REFERENCES

1. Barron, J. L., Dyrssen, D., Jones, E. P. and Wedborg, M. (1983) A comparison of computer methods for seawater alkalinity titrations. *Deep-Sea Res.*, **30**, 441–8.

2. Bates, R. G. (1982) pH measurements in the marine environment. *Pure Appl. Chem.*, **54**, 229–32.

3. Bradshaw, A. L., Brewer, P. G., Shafer, D. K. and Williams, R. T. (1981) Measurements of total carbon dioxide and alkalinity by potentiometric titration in the Geosecs programme. *Earth Planet. Science Letter*, **55**, 99–115.

4. Dyrssen, D. (1965) A Gran titration of sea water on board Sagitta. *Acta Chemica Scandinavica*, **19**, 1265.

5. Gieskes, J. M. (1969) Effect of temperature on the pH of seawater. *Limnol. Oceanogr.*, **14**, 679–85.

6. Goyet, C., Poisson, A., Brunet, C. and Culkin, F. (1985) IAPSO standard seawater as a reference standard for alkalinity determinations. *Deep-Sea Res.*, **32**, 1437–43.

7. Gripenberg, S. (1972) *New Baltic Manual.*, (unpublished report).

8. Hansson, I. (1973) A new set of pH-scales and standard buffers for seawater. *Deep-Sea Res.*, **20**, 479–91.

9. Hansson, I. and Jagner, D. (1973) Evaluation of the accuracy of Gran plots by means of computer calculations. Application to the potentiometric titration of the total alkalinity and carbonate content in seawater. *Anal. Chim. Acta*, **65**, 363–73.

10. Johnson, K. M., King, A. E. and Sieburth, J. McN. (1985) Coulometric TCO_2 analysis for marine studies; an introduction. *Mar. Chem.*, **16**, 61–82.

11. Johnson, K. M., Sieburth, J. McN., Williams, P. J. LeB. and Brandstrom, L. (1987) Coulometric total carbon dioxide analysis for marine studies: automation and calibration. *Mar. Chem.*, **21**, 117–33.

12. Millero, F. J. (1979) The thermodynamics of the carbonate system in seawater. *Geochim. Cosmochim. Acta*, **43**, 1651–61.

13. Oudot, C. and Wauthy, B. (1978) Adaptation d'un chromatographe en phase gazeuse pour le dosage en mer des gaz dissous: azote, oxygène et gaz carbonique total. *Cah. ORSTOM, Sér. Océanogr.*, **16**, 89–102.

14. Perez, F. F. and Fraga, F. (1987) A precise and rapid analytical procedure for alkalinity determination. *Mar. Chem.*, **21**, 169–82.

15. Perez, F. F. and Fraga, F. (1987) The pH measurements in seawater on the NBS scale. *Mar. Chem.*, **21**, 315–27.

16. Swinnerton, J. W., Linnebom, V. J. and Cheek, C. H. (1962) Determination of dissolved gases in solution by gas chromatography. *Anal. Chem.*, **34**, 483–85.

17. Takahashi, T., Chipman, D., Schechtman, N., Goddard, J. and Wanninkof, R. (1982) Measurements of the partial pressure of CO_2 in discrete water samples during the North Atlantic Expedition, the Transient Tracers of Oceans project. Technical Report, Lamont-Doherty Geol. Obs., Palisades, New York, 9 pp. plus data table.

18. Unesco (1983) Carbon dioxide sub-group of the joint panel on oceanographic tables and standards. Report of a meeting, Miami, Florida, 21–23 September 1981. *Unesco Tech. Pap. Mar. Science*, **42**, 30 pp.

19. Weiss, R. F. and Craig, H. (1973) Precise shipboard determination of dissolved nitrogen, argon and total inorganic carbon by gas chromatography. *Deep-Sea Res.*, **20**, 291–303.

20. Wong, C. S. (1970) Quantitative analysis of total carbon dioxide in seawater: a new extraction method. *Deep-Sea Res.*, **17**, 9–17.

Table 7. Measured total alkalinity (μmol/kg). Note: [Si] = [PO_4] = 0.

Lab	Bottle/run	Salinity	TA	$\overline{TA}$	Range	Date	Ref.	TA norm
Nominal salinity 7.950 (as determined by the Standard Sea Water Service).*								
B	208-1-CF	7.969	520.0			3/88	1	
B	208-2-CF	7.969	518.0			3/88		
B	208-3-CF	7.969	520.0	519		3/88		518
B	208-1-AF	7.969	521.0			3/88	1	
B	208-2-AF	7.969	519.0			3/88		
B	208-3-AF	7.969	522.0	521	4	3/88		520
B	239-1-CF	7.968	522.0			3/88	1	
B	239-2-CF	7.968	523.0			3/88		
B	239-3-CF	7.968	522.0	522		3/88		521
B	239-1-AF	7.968	524.0			3/88	1	
B	239-2-AF	7.968	525.0			3/88		
B	239-3-AF	7.968	524.0	524	3	3/88		523
C	210-1-A1	7.926	536.0			3/88	7	
C	210-2-A1	7.926	541.0			3/88		
C	210-3-A1	7.926	538.0			3/88		
C	210-4-A1	7.926	548.0			3/88		
C	210-5-A1	7.926	544.0	541	12	3/88		543
C	210-6-A2	7.926	542.0			4/88	7	
C	210-7-A2	7.926	527.0			4/88		
C	210-8-A2	7.926	530.0			4/88		
C	210-9-A2	7.926	538.0			4/88		
C	210-10-A2	7.926	542.0			4/88		
C	210-11-A2	7.926	538.0	536	15	4/88		538
C	248-1-A1	7.987	596.0			3/88	7	
C	248-2-A1	7.987	556.0			3/88		
C	248-3-A1	7.987	581.0			3/88		
C	248-4-A1	7.987	586.0			3/88		
C	248-5-A1	7.987	571.0	578	40	3/88		575
C	248-6-A2	7.987	547.0			4/88	7	
C	248-7-A2	7.987	554.0			4/88		
C	248-8-A2	7.987	549.0			4/88		
C	248-9-A2	7.987	547.0			4/88		
C	248-10-A2	7.987	542.0			4/88		
C	248-11-A2	7.987	540.0	546	14	4/88		544
D	207-1	8.000	529.0			5/88	3	
D	207-2	8.000	533.0	531	4	5/88		528
D	241-1	8.000	530.0			5/88	3	
D	241-2	8.000	530.0	530	0	5/88		527
J	212-1	8.200	519.8			6/88	15	
J	212-2	8.200	517.6			6/88		
J	212-3	8.200	517.3			6/88		
J	212-4	8.200	517.7	518	2.5	6/88		502

* No data were received for samples with S = 7.950 from labs A, E, F, G, H, K, L, and M.

Table 7 (cont.).

Lab	Bottle/run	Salinity	TA	$\overline{TA}$	Range	Date	Ref.	TA norm
J	234-1	8.200	517.1			6/88	15	
J	234-2	8.200	518.0			6/88		
J	234-3	8.200	516.8			6/88		
J	234-4	8.200	516.8	517	1.2	6/88		501
Nominal salinity 29.974 (as determined by the Standard Sea Water Service).*								
B	156-1-CF	29.989	1922			3/88	1	
B	156-2-CF	29.989	1922			3/88		
B	156-3-CF	29.989	1917	1920		3/88		1919
B	156-1-AF	29.989	1925			3/88	1	
B	156-2-AF	29.989	1926			3/88		
B	156-3-AF	29.989	1921	1924	9	3/88		1923
B	179-1-CF	29.987	1927			3/88	1	
B	179-2-CF	29.987	1925			3/88		
B	179-3-CF	29.987	1920	1924		3/88		1923
B	179-1-AF	29.987	1929			3/88	1	
B	179-2-AF	29.987	1929			3/88		
B	179-3-AF	29.987	1924	1927	9	3/88		1926
C	148-1-A1	29.854	1942			3/88	7	
C	148-2-A1	29.854	1967			3/88		
C	148-3-A1	29.854	1928			3/88		
C	148-4-A1	29.854	1940			3/88		
C	148-5-A1	29.854	1945	1944	39	3/88		1952
C	148-6-A2	29.854	1850			4/88	7	
C	148-7-A2	29.854	1848			4/88		
C	148-8-A2	29.854	1850			4/88		
C	148-9-A2	29.854	1850			4/88		
C	148-10-A2	29.854	1857			4/88		
C	148-11-A2	29.854	1862	1853	14	4/88		1860
C	192-1-A1	29.878	1967			3/88	7	
C	192-2-A1	29.878	1952			3/88		
C	192-3-A1	29.878	1938			3/88		
C	192-4-A1	29.878	1938			3/88		
C	192-5-A1	29.878	1942	1947	29	3/88		1953
C	192-6-A2	29.878	1850			4/88	7	
C	192-7-A2	29.878	1848			4/88		
C	192-8-A2	29.878	1852			4/88		
C	192-9-A2	29.878	1850			4/88		
C	192-10-A2	29.878	1855			4/88		
C	192-11-A2	29.878	1848	1850	7	4/88		1866

* No data were received for samples with S = 29.974 from labs A, E, G, K, and L.

Table 7 (cont.).

Lab	Bottle/run	Salinity	TA	$\overline{TA}$	Range	Date	Ref.	TA norm
D	155-1	30.010	1931			5/88	3	
D	155-2	30.010	1931	1931	0	5/88		1929
D	199-1	30.000	1930			5/88	3	
D	199-2	30.000	1929	1930	1	5/88		1928
F	159-1	29.990	1986			5/88	9	
F	159-2	29.990	1969			5/88		
F	159-3	29.990	1974	1976	17	5/88		1975
F	181-1	29.990	1977			5/88	9	
F	181-2	29.990	1968			5/88		
F	181-3	29.990	1971	1972	9	5/88		1971
H	153-1		1911	1911		7/88	3	
H	197-1		1909	1909		7/88	3	
J	120-1	30.000	1923			6/88	15	
J	120-2	30.000	1923			6/88		
J	120-3	30.000	1922	1923	0.9	6/88		1921
J	158-1	30.000	1915			6/88	15	
J	158-2	30.000	1915			6/88		
J	158-3	30.000	1914			6/88		
J	158-4	30.000	1914	1914	1	6/88		1912
M	149-1	30.005	1903	1903		10/88	3	1901
M	149-1	30.006	1914	1914		11/88	3	1912
Nominal salinity 35.380 (as determined by the Standard Sea Water Service)*								
B	57-1-CF	35.393	2287			3/88	1	
B	57-2-CF	35.393	2287			3/88		
B	57-3-CF	35.393	2286	2287		3/88		2286
B	57-1-AF	35.393	2288			3/88	1	
B	57-2-AF	35.393	2289			3/88		
B	57-3-AF	35.393	2286	2288	3	3/88		2287
B	63-1-CF	35.391	2286			3/88	1	
B	63-2-CF	35.391	2287			3/88		
B	63-3-CF	35.391	2286	2286		3/88		2285
B	63-1-AF	35.391	2288			3/88	1	
B	63-2-AF	35.391	2288			3/88		
B	63-3-AF	35.391	2288	2288	2	3/88		2287
C	1-1-A1	35.266	2259			3/88	7	
C	1-2-A1	35.266	2247			3/88		
C	1-3-A1	35.266	2264			3/88		
C	1-4-A1	35.266	2269			3/88		
C	1-5-A1	35.266	2257	2259	22	3/88		2256

* No data were received for samples with S = 35.380 from labs A, E, G, K, and L.

Table 7 (cont.).

Lab	Bottle/run	Salinity	TA	$\overline{TA}$	Range	Date	Ref.	TA norm
C	1-6-A2	35.266	2186			4/88	7	
C	1-7-A2	35.266	2196			4/88		
C	1-8-A2	35.266	2189			4/88		
C	1-9-A2	35.266	2181			4/88		
C	1-10-A2	35.266	2189			4/88		
C	1-11-A2	35.266	2191	2189	15	4/88		2196
C	92-1-A1	35.268	2274			3/88	7	
C	92-2-A1	35.268	2254			3/88		
C	92-3-A1	35.268	2274			3/88		
C	92-4-A1	35.268	2269			3/88		
C	92-5-A1	35.268	2262	2267	20	3/88		2274
C	92-6-A2	35.268	2222			4/88	7	
C	92-7-A2	35.268	2212			4/88		
C	92-8-A2	35.268	2222			4/88		
C	92-9-A2	35.268	2208			4/88		
C	92-10-A2	35.268	2215			4/88		
C	92-11-A2	35.268	2208	2214	14	4/88		2221
D	9-1	35.400	2297			5/88	3	
D	9-2	35.400	2296	2296	1	5/88		2295
D	11-1	35.390	2299			5/88	3	
D	11-2	35.390	2297	2298	2	5/88		2297
D	13-1		2300			5/88	3	
D	13-2		2297	2298	3	5/88		
D	29-1	35.390	2299			5/88	3	
D	29-2	35.390	2298	2298	1	5/88		2297
D	33-1	35.400	2298			5/88	3	
D	33-2	35.400	2294	2296	4	5/88		2295
D	36-1	35.390	2297			5/88	3	
D	36-2	35.390	2296	2296	1	5/88		2295
D	55-1	35.400	2294			5/88	3	
D	55-2	35.400	2294	2294	0	5/88		2293
D	65-1	35.400	2298			5/88	3	
D	65-2	35.400	2295	2296	3	5/88		2295
D	70-1	35.400	2300			5/88	3	
D	70-2	35.400	2300	2300	0	5/88		2299
D	76-1	35.410	2296			5/88	3	
D	76-2	35.410	2297	2296	1	5/88		2294
D	80-1		2301			5/88	3	
D	80-2		2301	2301	0	5/88		

Table 7 (cont.).

Lab	Bottle/run	Salinity	TA	$\overline{TA}$	Range	Date	Ref.	TA norm
D	88-1	35.390	2294			5/88	3	
D	88-2	35.390	2295	2294	1	5/88		2293
F	15-1	35.390	2335			5/88	9	
F	15-2	35.390	2334			5/88		
F	15-3	35.390	2334	2334	1	5/88		2333
F	60-1	35.390	2334			5/88	9	
F	60-2	35.390	2321			5/88		
F	60-3	35.390	2334	2330	13	5/88		2329
H	8-1	35.380	2282			3/88	3	
H	8-2	35.380	2282	2282	0.02	3/88		2282
H	10-1	35.382	2281			3/88	3	
H	10-2	35.382	2278	2279	3.27	3/88		2279
H	21-1	35.384	2282			3/88	3	
H	21-2	35.384	2280	2281	1.87	3/88		2281
H	31-1		2275			5/88	3	
H	46-1	35.397	2282	2282		4/88	3	2281
J	25-1	35.300	2272			6/88	15	
J	25-2	35.300	2272			6/88		
J	25-3	35.300	2271			6/88		
J	25-4	35.300	2272	2272	0.7	6/88		2277
J	47-1	35.300	2279			6/88	15	
J	47-2	35.300	2281			6/88		
J	47-3	35.300	2280			6/88		
J	47-4	35.300	2277	2279	3.9	6/88		2284
M	2-1	35.391	2281	2281		10/88	3	2280
M	90-1	35.398	2270	2270		11/88	3	2269
Nominal salinity 38.254 (as determined by the Standard Sea Water Service).*								
B	103-1-CF	38.269	2471			3/88	1	
B	103-2-CF	38.269	2469			3/88		
B	103-3-CF	38.269	2469	2470		3/88		2469
B	103-1-AF	38.269	2472			3/88	1	
B	103-2-AF	38.269	2469			3/88		
B	103-3-AF	38.269	2470	2470	3	3/88		2469
B	140-1-CF	38.270	2471			3/88	1	
B	140-2-CF	38.270	2470			3/88		
B	140-3-CF	38.270	2467	2469		3/88		2468
B	140-1-AF	38.270	2471			3/88	1	
B	140-2-AF	38.270	2471			3/88		
B	140-3-AF	38.270	2468	2470	4	3/88		2469

* No data were received for samples with S = 38.254 from labs A, E, G, K, and L.

Table 7 (cont.).

Lab	Bottle/run	Salinity	TA	$\overline{TA}$	Range	Date	Ref.	TA norm
C	95-1-A1	38.122	2470			3/88	7	
C	95-2-A1	38.122	2460			3/88		
C	95-3-A1	38.122	2456			3/88		
C	95-4-A1	38.122	2505			3/88		
C	95-5-A1	38.122	2468	2472	49	3/88		2481
C	95-6-A2	38.122	2313			4/88	7	
C	95-7-A2	38.122	2310			4/88		
C	95-8-A2	38.122	2320			4/88		
C	95-9-A2	38.122	2325			4/88		
C	95-10-A2	38.122	2313			4/88		
C	95-11-A2	38.122	2313	2316	15	4/88		2324
C	143-1-A1	38.127	2495			3/88	7	
C	143-2-A1	38.127	2446			3/88		
C	143-3-A1	38.127	2460			3/88		
C	143-4-A1	38.127	2470			3/88		
C	143-5-A1	38.127	2475	2469	49	3/88		2477
C	143-6-A2	38.127	2325			4/88	7	
C	143-7-A2	38.127	2327			4/88		
C	143-8-A2	38.127	2322			4/88		
C	143-9-A2	38.127	2325			4/88		
C	143-10-A2	38.127	2325			4/88		
C	143-11-A2	38.127	2327	2325	5	4/88		2333
D	101-1	38.260	2480			5/88	3	
D	101-2	38.260	2479	2480	1	5/88		2480
D	139-1	38.260	2484			5/88	3	
D	139-2	38.260	2484	2484	0	5/88		2484
F	106-1	38.250	2522			5/88	9	
F	106-2	38.250	2522			5/88		
F	106-3	38.250	2520	2521	2	5/88		2521
F	136-1	38.250	2524			5/88	9	
F	136-2	38.250	2521			5/88		
F	136-3	38.250	2526	2524	5	5/88		2524
H	104-1		2462	2462		5/88	3	
H	138-1		2463	2463		7/88	3	
J	135-1	38.200	2458			6/88	15	
J	135-2	38.200	2458			6/88		
J	135-3	38.200	2458	2458	0.4	6/88		2462
J	108-1	38.200	2458			6/88	15	
J	108-2	38.200	2459			6/88		
J	108-3	38.200	2457			6/88		
J	108-4	38.200	2459	2458	1.7	6/88		2462
M	96-1	38.257	2458	2458		10/88	3	2458
M	144-1	38.273	2459	2459		11/88	3	2458

Table 8. Measured total inorganic carbon (µmol/kg)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	$\overline{TCO_2}$ (p) norm	$\overline{TCO_2}$ (e) norm
Nominal salinity 7.950 (as determined by the Standard Sea Water Service).*											
A	206-1	7.915		502				3/88	13,19		
A	206-2	7.915		505				3/88			
A	206-3	7.915		504		504	3	3/88			506
A	242-1	7.919		504				3/88	13,19		
A	242-2	7.919		506				3/88			
A	242-3	7.919		504		505	2	3/88			507
B	208-1-CF	7.969	508					3/88	1		
B	208-2-CF	7.969	510					3/88			
B	208-3-CF	7.969	512		510			3/88		509	
B	208-1-AF	7.969	513					3/88			
B	208-2-AF	7.969	515					3/88			
B	208-3-AF	7.969	519		516		11	3/88		515	
B	239-1-CF	7.968	511					3/88	1		
B	239-2-CF	7.968	510					3/88			
B	239-3-CF	7.968	510		510			3/88		509	
B	239-1-AF	7.968	516					3/88			
B	239-2-AF	7.968	517					3/88			
B	239-3-AF	7.968	517		517		7	3/88		516	
D	207	8.000	510					5/88	3		
D	207	8.000	514		512		4	5/88		509	
D	241	8.000	511					5/88	3		
D	241	8.000	513		512		2	5/88		509	
E	213-1-GC			501		501		5/88	19		
E	219-1-C	7.952		503				5/88	10,11,20		
E	219-2-C	7.952		502				5/88			
E	219-3-C	7.952		502				5/88			
E	219-4-C	7.952		502				5/88			
E	219-5-C	7.952		503				5/88			
E	219-6-C	7.952		504		503	1.5	5/88			503
E	222-1-C			505				5/88	10,11,20		
E	222-2-C			503				5/88			
E	222-3-C			502				5/88			
E	222-4-C			500		502	4.7	5/88			
G	215-1-C	7.992		504				7/88	10,11		
G	215-2-C	7.989		503		503	0.3	7/88			501
G	235-1-C			502				7/88	10,11		
G	235-2-C			502				7/88			
G	235-3-C			501		502	0.5	7/88			

* No data were received for samples with S = 7.950 from labs C, F, H, J, K, and M.

Table 8 (cont.)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	TCO_2 (p) norm	TCO_2 (e) norm
L	220-1-C	7.980		508				6/88			
L	220-2-C	7.980		508				6/88			
L	220-3-C	7.980		509				6/88			
L	220-4-C	7.980		507				6/88			
L	220-5-C	7.980		506				6/88			
L	220-6-C	7.980		507				6/88			
L	220-7-C	7.980		508		508	3.3	6/88			2226
L	229-1-C	7.970		505				6/88			
L	229-2-C	7.970		507				6/88			
L	229-3-C	7.970		505				6/88			
L	229-4-C	7.970		506				6/88			
L	229-5-C	7.970		507				6/88			
L	229-6-C	7.970		507				6/88			
L	229-7-C	7.970		507		506	2.5	6/88			2223
Nominal salinity 29.974 (as determined by the Standard Sea Water Service).*											
A	154-1	29.979		1768				3/88	13,19		
A	154-2	29.979		1767				3/88			
A	154-3	29.979		1754		1763	14	3/88			1763
A	198-1	29.985		1757				3/88	13,19		
A	198-2	29.985		1760				3/88			
A	198-3	29.985		1763		1760	6	3/88			1759
B	156-1-CF	29.989	1774					3/88	1		
B	156-2-CF	29.989	1776					3/88			
B	156-3-CF	29.989	1773		1774			3/88		1773	
B	156-1-AF	29.989	1773					3/88			
B	156-2-AF	29.989	1775					3/88			
B	156-3-AF	29.989	1773		1774		3	3/88		1773	
B	179-1-CF	29.987	1781					3/88	1		
B	179-2-CF	29.987	1774					3/88			
B	179-3-CF	29.987	1774		1776			3/88		1775	
B	179-1-AF	29.987	1780					3/88			
B	179-2-AF	29.987	1774					3/88			
B	179-3-AF	29.987	1773		1776		8	3/88		1775	
D	155-1	30.010	1762					5/88	3		
D	155-2	30.010	1762		1762		0	5/88		1760	
D	199-1	30.000	1761					5/88	3		
D	199-2	30.000	1764		1762		3	5/88		1761	
E	165-1-C		1756					5/88	10,11,20		
E	165-2-C		1758		1760		2	5/88			

* No data were received for samples with S = 29.974 from labs C, J, and K.

Table 8 (cont.)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	$\overline{TCO_2}$ (p) norm	$\overline{TCO_2}$ (e) norm
E	169-1-C	29.974		1758				5/88	10,11,20		
E	169-2-C	29.974		1754				5/88			
E	169-3-C	29.974		1752				5/88			
E	169-4-C	29.974		1753				5/88			
E	169-5-C	29.974		1753				5/88			
E	169-6-C	29.974		1752		1752	6	5/88			1752
E	189-1-C	29.973		1759				5/88	10,11,20		
E	189-2-C	29.973		1756				5/88			
E	189-3-GC	29.973		1758				5/88	19		
E	189-4-GC	29.973		1760		1759	4	5/88			1759
F	159-1	29.990	1824					6/88	9		
F	159-2	29.990	1811					6/88			
F	159-3	29.990	1813		1816		13	6/88		1815	
F	181-1	29.990	1834					6/88	9		
F	181-2	29.990	1823					6/88			
F	181-3	29.990	1826		1828		11	6/88		1827	
G	162-1-C	29.985		1748.7				7/88	10,11		
G	162-2-C	29.991		1750.4		1750	1.7	7/88			1750
G	187-1-C			1748.7				7/88	10,11		
G	187-2-C			1745.2				7/88			
G	187-3-C			1749.3		1747	4.1	7/88			
H	153-1-M			1752.6		1753		7/88	20		
H	153-2-P		1771		1771			7/88	3		
H	197-1-M			1753.6		1754		7/88	20		
H	197-2-P		1765.3		1765.3			7/88	3		
L	168-1-C	29.920		1672.3				6/88	10,11		
L	168-2-C	29.920		1664.9				6/88			
L	168-3-C	29.920		1676.1				6/88			
L	168-4-C	29.920		1664.6				6/88			
L	168-5-C	29.920		1680.8				6/88			
L	168-6-C	29.920		1681.4				6/88			
L	168-7-C	29.920		1675.7				6/88			
L	168-8-C	29.920		1673.9		1675	16.8	6/88			1678
L	185-1-C	29.540		1753.8				6/88	10,11		
L	185-2-C	29.540		1753.4				6/88			
L	185-3-C	29.540		1749.5				6/88			
L	185-4-C	29.540		1753.3				6/88			
L	185-5-C	29.540		1753.8				6/88			
L	185-6-C	29.540		1754.3		1754	4.8	6/88			1780
M	149-1	30.005		1781		1781		10/88	3		1780
M	193-1	30.006		1773		1773		11/88	3		1771

Table 8 (cont.)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	$\overline{TCO_2}$ (p) norm	$\overline{TCO_2}$ (e) norm
Nominal salinity 35.380 (as determined by the Standard Sea Water Service).*											
A	7-1	35.428		2087.0				3/88	13,19		
A	7-2	35.428		2093.0				3/88			
A	7-3	35.428		2107.0		2096	20	3/88			2093
A	79-1	35.427		2093.0				3/88	13,19		
A	79-2	35.427		2093.0				3/88			
A	79-3	35.427		2101.0		2096	8	3/88			2093
B	57-1-CF	35.393	2108					3/88	1		
B	57-2-CF	35.393	2106					3/88			
B	57-3-CF	35.393	2104		2106			3/88		2005	
B	57-1-AF	35.393	2108					3/88			
B	57-2-AF	35.393	2106					3/88			
B	57-3-AF	35.393	2104		2106		4	3/88		2005	
B	63-1-CF	35.391	2105					3/88	1		
B	63-2-CF	35.391	2108					3/88			
B	63-3-CF	35.391	2105		2106			3/88		2005	
B	63-1-AF	35.391	2105					3/88			
B	63-2-AF	35.391	2107					3/88			
B	63-3-AF	35.391	2105		2106		3	3/88		2005	
D	9-1	35.400	2097					5/88	3		
D	9-2	35.400	2098		2098		1	5/88		2097	
D	11-1	35.390	2100					5/88	3		
D	11-2	35.390	2098		2099		2	5/88		2098	
D	13-1		2098					5/88	3		
D	13-2		2096		2097		2	5/88			
D	29-1	35.390	2096					5/88	3		
D	29-2	35.390	2098		2097		2	5/88		2096	
D	33-1	35.400	2096					5/88	3		
D	33-2	35.400	2098		2097		2	5/88		2096	
D	36-1	35.390	2096					5/88	3		
D	36-2	35.390	2099		2098		3	5/88		2097	
D	55-1	35.400	2095					5/88	3		
D	55-2	35.400	2096		2096		1	5/88		2095	
D	65-1	35.400	2099					5/88	3		
D	65-2	35.400	2095		2097		4	5/88		2096	
D	70-1	35.400	2104					5/88	3		
D	70-2	35.400	2102		2103		2	5/88		2102	
D	76-1	35.410	2100					5/88	3		
D	76-2	35.410	2100		2100		0	5/88		2098	
D	80-1		2105					5/88	3		
D	80-2		2102		2104		3	5/88			

* No data were received for samples with S = 35.380 from labs C, J, and K.

Table 8 (cont.)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	$\overline{TCO_2}$ (p) norm	$\overline{TCO_2}$ (e) norm
D	88-1	35.390	2098					5/88	3		
D	88-2	35.390	2101		2100		3	5/88		2099	
E	14-1-C	35.388		2082.0				5/88	10,11,20		
E	14-2-C	35.388		2084.0				5/88			
E	14-3-C	35.388		2082.0				5/88			
E	14-4-C	35.388		2082.0				5/88			
E	14-5-C	35.388		2082.0				5/88			
E	14-6-C	35.388		2081.0		2082	3	5/88			2081
E	37-7-C			2080.0				5/88	10,11,20		
E	37-2-C			2082.0				5/88			
E	37-3-C			2082.0		2081	2	5/88			
E	42-1-C			2085.0				5/88	10,11,20		
E	42-2-GC			2071.0				5/88	19		
E	42-3-GC			2077.0		2078	14	5/88			
E	44-1-C			2086.0				5/88	10,11,20		
E	44-2-C			2084.0				5/88			
E	44-3-C			2082.0		2084	4	5/88			
F	15-1	35.390	2143					6/88	9		
F	15-2	35.390	2160					6/88			
F	15-3	35.390	2153					6/88			
F	15-4	35.390	2151		2152		17	6/88		2151	
F	60-1	35.390	2152					6/88	9		
F	60-2	35.390	2147					6/88			
F	60-3	35.390	2156		2152		9	6/88		2151	
G	38-1-C	35.390		2073.7				7/88	10,11		
G	38-2-C	35.390		2072.2				7/88			
G	38-3-C	35.390		2071.8		2073	1.9	7/88			2072
G	75-1-C	35.386		2073.4				7/88	10,11		
G	75-2-C	35.384		2073.8				7/88			
G	75-3-C	35.384		2074.2		2074	0.8	7/88			2074
H	8-1-M	35.380		2080.3		2080.3		3/88	20		2080
H	8-2-P	35.380	2098.1					3/88	3		
H	8-3-P	35.380	2090.6		2094		7.43	3/88		2094	
H	10-1-M	35.382		2082.2		2082.2		3/88	20		2082
H	10-2-P	35.382	2096.2					3/88	3		
H	10-3-P	35.382	2090.6		2093		5.58	3/88		2093	
H	21-1-M	35.384		2080.7		2080.7		3/88	20		2081
H	21-2-P	35.384	2099.8					3/88	3		
H	21-3-P	35.384	2095		2097		4.82	3/88		2097	
H	31-1-M			2081.3		2081.3		5/88	20		
H	31-2-P		2093.6		2093.6			5/88	3		
H	46-1-M	35.397		2079.4		2079.4		4/88	20		2078
H	46-2-P	35.397	2103.6		2103.6			4/88	3	2103	

Table 8 (cont.)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	$\overline{TCO_2}$ (p) norm	$\overline{TCO_2}$ (e) norm
L	22-1-C	35.310		2082.9				6/88	10,11		
L	22-2-C	35.310		2088.6				6/88			
L	22-3-C	35.310		2085.5				6/88			
L	22-4-C	35.310		2086.0				6/88			
L	22-5-C	35.310		2084.9				6/88			
L	22-6-C	35.310		2083.0		2085	5.7	6/88			2089
L	68-1-C	35.370		2002.1				6/88	10,11		
L	68-2-C	35.370		1995.1				6/88			
L	68-3-C	35.370		1995.4				6/88			
L	68-4-C	35.370		1989.6				6/88			
L	68-5-C	35.370		1999.1				6/88			
L	68-6-C	35.370		1988.4				6/88			
L	68-7-C	35.370		1993.3		1995	13.7	6/88			1996
M	2-1	35.391	2119		2119			10/88	3	2118	
M	90-1	35.398	2106		2106			11/88	3	2105	
Nominal salinity 38.254 (as determined by the Standard Sea Water Service).*											
A	99-1	38.261		2234.0				3/88	13,19		
A	99-2	38.261		2230.0				3/88			
A	99-3	38.261		2243.0		2236	13	3/88			2236
A	128-1	38.261		2238.0				3/88	13,19		
A	128-2	38.261		2244.0				3/88			
A	128-3	38.261		2230.0		2237	14	3/88			2237
B	103-1-CF	38.269	2235					3/88	1		
B	103-2-CF	38.269	2236					3/88			
B	103-3-CF	38.269	2233		2235			3/88		2234	
B	103-1-AF	38.269	2235					3/88			
B	103-2-AF	38.269	2237					3/88			
B	103-3-AF	38.269	2234		2235		4	3/88		2234	
B	140-1-CF	38.270	2235					3/88	1		
B	140-2-CF	38.270	2236					3/88			
B	140-3-CF	38.270	2232		2234			3/88		2233	
B	140-1-AF	38.270	2235					3/88			
B	140-2-AF	38.270	2236					3/88			
B	140-3-AF	38.270	2234		2235		4	3/88		2234	
D	101-1	38.260	2225					5/88	3		
D	101-2	38.260	2225		2225		0	5/88		2225	
D	139-1	38.260	2227					5/88	3		
D	139-2	38.260	2228		2228		1	5/88		2228	

* No data were received for samples with S = 38.254 from labs C, J, and K.

Table 8 (cont.)

Lab	Bottle/run	Salinity	TCO_2 (p)	TCO_2 (e)	$\overline{TCO_2}$ (p)	$\overline{TCO_2}$ (e)	range	Date	Ref.	$\overline{TCO_2}$ (p) norm	$\overline{TCO_2}$ (e) norm
E	116-1-C			2215.0				5/88	10,11,20		
E	116-2-C			2213.0				5/88			
E	116-3-GC			2215.0		2214	2	5/88	19		
E	129-1-C	38.261		2213.0				5/88	10,11,20		
E	129-2-C	38.261		2212.0				5/88			
E	129-3-C	38.261		2214.0				5/88			
E	129-4-C	38.261		2212.0				5/88			
E	129-5-C	38.261		2211.0				5/88			
E	129-6-C	38.261		2209.0				5/88			
E	129-7-C	38.261		2211.0		2212	5	5/88			2212
F	106-1	38.250	2276					6/88	9		
F	106-2	38.250	2272					6/88			
F	106-3	38.250	2283		2277		11	6/88		2277	
F	136-1	38.250	2282					6/88	9		
F	136-2	38.250	2279					6/88			
F	136-3	38.250	2271		2277		11	6/88		2277	
G	109-1-C			2199.2				7/88	10,11		
G	109-2-C			2201.1				7/88			
G	109-3-C			2198.6		2200	2.5	7/88			
G	125-1-C			2201.1				7/88	10,11		
G	125-2-C			2200.2				7/88			
G	125-3-C			2200.5		2201	0.9	7/88			
H	104-1-M			2208.9		2208.9		5/88	20		
H	104-2-P		2226.2		2226.2			5/88	3		
H	138-1-M			2209.4		2209.4		7/88	20		
H	138-2-P		2229.6		2229.6			7/88	3		
L	114-1-C			2202.7				6/88	10,11		
L	114-2-C			2201.3				6/88			
L	114-3-C			2201.5				6/88			
L	114-4-C			2197.4				6/88			
L	114-5-C			2203.9				6/88			
L	114-6-C			2202.8				6/88			
L	114-7-C			2198.7				6/88			
L	114-8-C			2198.6		2201	6.5	6/88			
L	131-1-C	38.160		2211.4				6/88	10,11		
L	131-2-C	38.160		2210.7				6/88			
L	131-3-C	38.160		2208.5				6/88			
L	131-4-C	38.160		2212.4				6/88			
L	131-5-C	38.160		2212.2				6/88			
L	131-6-C	38.160		2210.8				6/88			
L	131-7-C	38.160		2212.2		2211	3.9	6/88			2216
M	96-1	38.257	2244		2244			10/88	3	2244	
M	144-1	38.273	2245		2245			11/88	3	2244	

Table 9. Measured pH

		Direct Measurements				Initial Potential				pH (25°C)			
Lab	Bottle/run	Scale	t (°C)	pH (t)	pH (25°C)	Scale	t(°C)	pH (t)	pH (25°C)	Direct	Initial potential	Date	Ref.
Nominal salinity 7.950 (as determined by the Standard Sea Water Service).*													
A	206-1	NBS	25.0	7.964	7.964					7.964		3/88	12
A	242-1	NBS	25.0	7.937	7.937					7.937		3/88	12
B	208-1	NBS		7.856								3/88	
B	239-1	NBS		7.837								3/88	
C	210-1	NBS	22.8	7.890	7.865					7.865		3/88	
C	248-1	NBS	22.8	7.900	7.875					7.875		4/88	
D	207-1					SWS	21.90	7.829	7.794			5/88	3
D	207-2					SWS	21.97	7.793	7.758		7.776	5/88	
D	241-1					SWS	21.84	7.812	7.776			5/88	3
D	241-2					SWS	21.92	7.800	7.765		7.770	5/88	
J	212-1	NBS	15.0	7.640	7.526					7.526		6/88	15
J	234-1	NBS	15.0	7.694	7.580					7.580		6/88	15
Nominal salinity 29.974 (as determined by the Standard Sea Water Service).†													
A	154-1	NBS	25.00	8.063	8.063					8.063		3/88	12
A	198-1	NBS	25.00	8.064	8.064					8.064		3/88	12
B	156-1	NBS		8.082								3/88	
B	179-1	NBS		8.081								3/88	
C	148-1	NBS	22.80	8.240	8.215					8.215		3/88	
C	192-1	NBS	22.80	8.260	8.235					8.235		4/88	
D	155-1					SWS	22.05	7.909	7.875			5/88	3
D	155-2					SWS	22.11	7.906	7.873		7.874	5/88	
D	199-1					SWS	22.07	7.908	7.875			5/88	3
D	199-2					SWS	22.18	7.893	7.861		7.868	5/88	
J	120-1	NBS	15.00	8.083	7.969					7.969		6/88	15
J	158-1	NBS	15.00	8.087	7.973					7.973		6/88	15
K	163-1	SWS	22.47	7.881	7.846							5/88	8
K	163-2	SWS	22.53	7.881	7.846							5/88	
K	163-3	SWS	22.47	7.884	7.849							5/88	
K	163-4	SWS	22.54	7.884	7.849							5/88	
K	163-5	SWS	22.51	7.884	7.849							5/88	
K	163-6	SWS	22.88	7.879	7.849							5/88	
K	163-7	SWS	22.89	7.879	7.849							5/88	
K	163-8	SWS	22.85	7.882	7.852							5/88	
K	163-9	SWS	22.92	7.882	7.853							5/88	
K	163-10	SWS	22.92	7.882	7.853					7.849		5/88	

* No data were received for samples with S = 7.950 from labs E, F, G, H, K, L, and M.

† No data were received for samples with S = 29.974 from labs E, F, G, H, and L.

Table 9 (cont.)

		Direct Measurements				Initial Potential				pH (25°C)			
Lab	Bottle/run	Scale	t (°C)	pH (t)	pH (25°C)	Scale	t(°C)	pH (t)	pH (25°C)	Direct	Initial potential	Date	Ref.
K	178-1	SWS	22.70	7.885	7.853							5/88	8
K	178-2	SWS	22.73	7.888	7.856							5/88	
K	178-3	SWS	22.75	7.889	7.857							5/88	
K	178-4	SWS	22.69	7.889	7.856							5/88	
K	178-5	SWS	22.76	7.888	7.856							5/88	
K	178-6	SWS	22.77	7.886	7.855							5/88	
K	178-7	SWS	22.80	7.885	7.854							5/88	
K	178-8	SWS	22.77	7.884	7.853							5/88	
K	178-9	SWS	22.80	7.883	7.852							5/88	
K	178-10	SWS	22.80	7.882	7.851							5/88	
K	178-11	SWS	22.91	7.880	7.851							5/88	
K	178-12	SWS	22.97	7.880	7.851							5/88	
K	178-13	SWS	22.97	7.880	7.851					7.854		5/88	
M	149-1	NBS	25.00	7.963	7.963					7.963		10/88	
M	193-1	NBS	25.00	7.963	7.963					7.963		11/88	
Nominal salinity 35.380 (as determined by the Standard Sea Water Service).*													
A	7-1	NBS	25.00	8.021	8.021					8.021		3/88	12
A	79-1	NBS	25.00	8.027	8.027					8.027		3/88	12
B	57-1	NBS		8.069								3/88	
B	63-1	NBS		8.096								3/88	
C	1-1	NBS	22.80	8.220	8.195					8.195		3/88	
C	92-1	NBS	22.80	8.210	8.185					8.185		4/88	
D	9-1					SWS	21.87	7.880	7.844			5/88	3
D	9-2					SWS	22.18	7.873	7.841		7.843	5/88	
D	11-1					SWS	21.98	7.881	7.847			5/88	3
D	11-2					SWS	22.08	7.873	7.840		7.843	5/88	
D	13-1					SWS	21.98	7.882	7.848			5/88	3
D	13-2					SWS	22.10	7.878	7.845		7.846	5/88	
D	29-1					SWS	21.97	7.885	7.850			5/88	3
D	29-2					SWS	22.04	7.881	7.847		7.849	5/88	
D	33-1					SWS	22.03	7.880	7.846			5/88	3
D	33-2					SWS	22.17	7.871	7.839		7.842	5/88	
D	36-1					SWS	22.18	7.869	7.837			5/88	3
D	36-2					SWS	22.23	7.868	7.836		7.837	5/88	
D	55-1					SWS	22.13	7.872	7.839			5/88	3
D	55-2					SWS	22.16	7.869	7.837		7.838	5/88	
D	65-1					SWS	22.01	7.871	7.837			5/88	3
D	65-2					SWS	22.20	7.866	7.834		7.835	5/88	
D	70-1					SWS	22.00	7.880	7.846			5/88	3
D	70-2					SWS	22.11	7.879	7.846		7.846	5/88	
D	76-1					SWS	22.05	7.874	7.840			5/88	3
D	76-2					SWS	22.14	7.869	7.836		7.838	5/88	

* No data were received for samples with S = 35.380 from labs E, F, G, H, and L.

Table 9 (cont.)

		Direct Measurements				Initial Potential				pH (25°C)			
Lab	Bottle/run	Scale	t (°C)	pH (t)	pH (25°C)	Scale	t(°C)	pH (t)	pH (25°C)	Direct	Initial potential	Date	Ref.
D	80-1					SWS	22.13	7.859	7.826			5/88	3
D	80-2					SWS	22.16	7.876	7.844		7.835	5/88	
D	88-1					SWS	22.14	7.869	7.836			5/88	3
D	88-2					SWS	22.17	7.866	7.834		7.835	5/88	
J	25-1	NBS	15.00	8.037	7.923					7.923		6/88	15
J	47-1	NBS	15.00	8.041	7.927					7.927		6/88	15
K	16-1	SWS	22.36	7.853	7.815							5/88	8
K	16-2	SWS	22.38	7.852	7.814							5/88	
K	16-3	SWS	22.36	7.849	7.811							5/88	
K	16-4	SWS	22.37	7.849	7.811							5/88	
K	16-5	SWS	22.38	7.851	7.813							5/88	
K	16-6	SWS	22.40	7.853	7.815							5/88	
K	16-7	SWS	22.75	7.848	7.816							5/88	
K	16-8	SWS	22.86	7.847	7.816							5/88	
K	16-9	SWS	22.70	7.849	7.816							5/88	
K	16-10	SWS	22.78	7.847	7.815							5/88	
K	16-11	SWS	23.15	7.843	7.816							5/88	
K	16-12	SWS	23.17	7.842	7.816					7.814		5/88	
K	54-1	SWS	22.18	7 853	7.812							5/88	8
K	54-2	SWS	22.23	7.852	7.812							5/88	
K	54-3	SWS	22.82	7.842	7.811							5/88	
K	54-4	SWS	22.91	7.842	7.812							5/88	
K	54-5	SWS	22.83	7.842	7.811							5/88	
K	54-6	SWS	22.99	7.841	7.812					7.812		5/88	
M	2-1	NBS	25.00	7.949	7.949					7.949		10/88	
M	90-1	NBS	25.00	7.952	7.952					7.952		11/88	
Nominal salinity 38.254 (as determined by the Standard Sea Water Service).*													
A	99-1	NBS	25.00	8.080	8.080					8.080		3/88	12
A	128-1	NBS	25.00	8.077	8.077					8.077		3/88	12
B	103-1	NBS		8.108								3/88	
B	140-1	NBS		8.106								3/88	
C	95-1	NBS	22.80	8.290	8.265					8.265		3/88	
C	143-1	NBS	22.80	8.280	8.255					8.255		4/88	
D	101-1					SWS	21.92	7.925	7.890			5/88	3
D	101-2					SWS	22.08	7.924	7.891		7.890	5/88	
D	139-1					SWS	21.98	7.932	7.898			5/88	3
D	139-2					SWS	22.08	7.933	7.900		7.899	5/88	
J	108-1	NBS	15.00	8.095	7.981					7.981		6/88	15
J	135-1	NBS	15.00	8.101	7.987					7.987		6/88	15

* No data were received for samples with S = 38.254 from labs E, F, G, H, and L.

Table 9 (cont.)

Lab	Bottle/run	Direct Measurements Scale	t (°C)	pH (t)	pH (25°C)	Initial Potential Scale	t(°C)	pH (t)	pH (25°C)	pH (25°C) Direct	pH (25°C) Initial potential	Date	Ref.
K	110-1	SWS	22.46	7.899	7.862							5/88	8
K	110-2	SWS	22.52	7.899	7.862							5/88	
K	110-3	SWS	22.47	7.902	7.865							5/88	
K	110-4	SWS	22.51	7.901	7.864							5/88	
K	110-5	SWS	22.55	7.901	7.865							5/88	
K	110-6	SWS	22.75	7.899	7.866							5/88	
K	110-7	SWS	22.82	7.898	7.866							5/88	
K	110-8	SWS	22.78	7.899	7.866					7.864		5/88	
K	133-1	SWS	22.34	7.901	7.862							5/88	8
K	133-2	SWS	22.38	7.903	7.864							5/88	
K	133-3	SWS	22.39	7.903	7.864							5/88	
K	133-4	SWS	22.39	7.904	7.865							5/88	
K	133-5	SWS	22.78	7.899	7.866					7.864		5/88	
M	96-1	NBS	25.00	7.998	7.998					7.998		10/88	
M	144-1	NBS	25.00	8.002	8.002					8.002		11/88	

Table 10. Measured pH for samples with varied salinities (as determined by the Standard Sea Water Service).

Salinity	pH (25 °C) Direct Measurements NBS	pH (25 °C) Direct Measurements SWS	pH (25 °C) Initial potential SWS
7.954	7.791 s = 0.189		7.773
29.974	8.056 s = 0.113	7.852	7.871
35.380	8.022 s = 0.111	7.813	7.841 s=0.005
38.254	8.081 s = 0.117	7.864	7.890

Table 11. Measured p(CO_2) for samples (μatm).

Lab	Bottle/run	Measurement p(CO_2)	Measurement t(°C)	p(CO_2) (25 °C)	$\overline{\text{p}(CO_2)}$ (25 °C)	Date	Ref.
Nominal salinity 7.950 (as determined by the Standard Sea Water Service).							
A	206-1	317.4	26	309		3/88	13
A	206-2	316.2	26	308	308.5	3/88	
A	242-1	313.7	26	306		3/88	13
A	242-2	311.2	26	303	304.5	3/88	
E	238-1	266.91	20	304	304	7/88	16
G	215-1	207.3	18	258		7/88	17
G	215-2	204.9	18	256		7/88	
G	215-3	206.5	18	258		7/88	
G	215-4	208.8	18	260	258	7/88	
Nominal salinity 29.974 (as determined by the Standard Sea Water Service).							
A	154-1	583.5	26	565		3/88	13
A	154-2	581.6	26	563	564	3/88	
A	198-1	584.4	26	565		3/88	13
A	198-2	584.9	26	566	565.5	3/88	
E	161-1	450.12	20	540	540	7/88	16
G	162-1	424.8	18	547		7/88	17
G	162-2	421.2	18	544		7/88	
G	162-3	423.8	18	547		7/88	
G	162-4	422.2	18	545	545.8	7/88	
G	187-1	420.6	18	544		7/88	17
G	187-2	419.0	18	542		7/88	
G	187-3	418.2	18	541		7/88	
G	187-4	417.6	18	541	542	7/88	
Nominal salinity 35.380 (as determined by the Standard Sea Water Service).							
A	7-1	719.5	26	694		3/88	13
A	7-2	716.6	26	690	692	3/88	
A	79-1	717.2	26	691	691	3/88	13
E	32-1	560.06	20	682	682	7/88	16
G	38-1	519.2	18	685		7/88	17
G	38-2	520.5	18	687		7/88	
G	38-3	519.3	18	685		7/88	
G	38-4	522.1	18	688	686.2	7/88	
G	75-1	524.6	18	691		7/88	17
G	75-2	524.2	18	690		7/88	
G	75-3	526.0	18	692		7/88	
G	75-4	522.7	18	689	690.5	7/88	
Nominal salinity 38.254 (as determined by the Standard Sea Water Service).							
A	99-1	659.7	26	637		3/88	13
A	99-2	660.9	26	638	637.5	3/88	
A	128-1	659.6	26	637		3/88	13
A	128-2	659.9	26	637	637	3/88	
E	112-1	517.76	20	625	625	7/88	16
G	109-1	477.2	18	624		7/88	17
G	109-2	473.3	18	620		7/88	
G	109-3	475.3	18	622		7/88	
G	109-4	477.2	18	624	622.5	7/88	

Fig. 1,a :

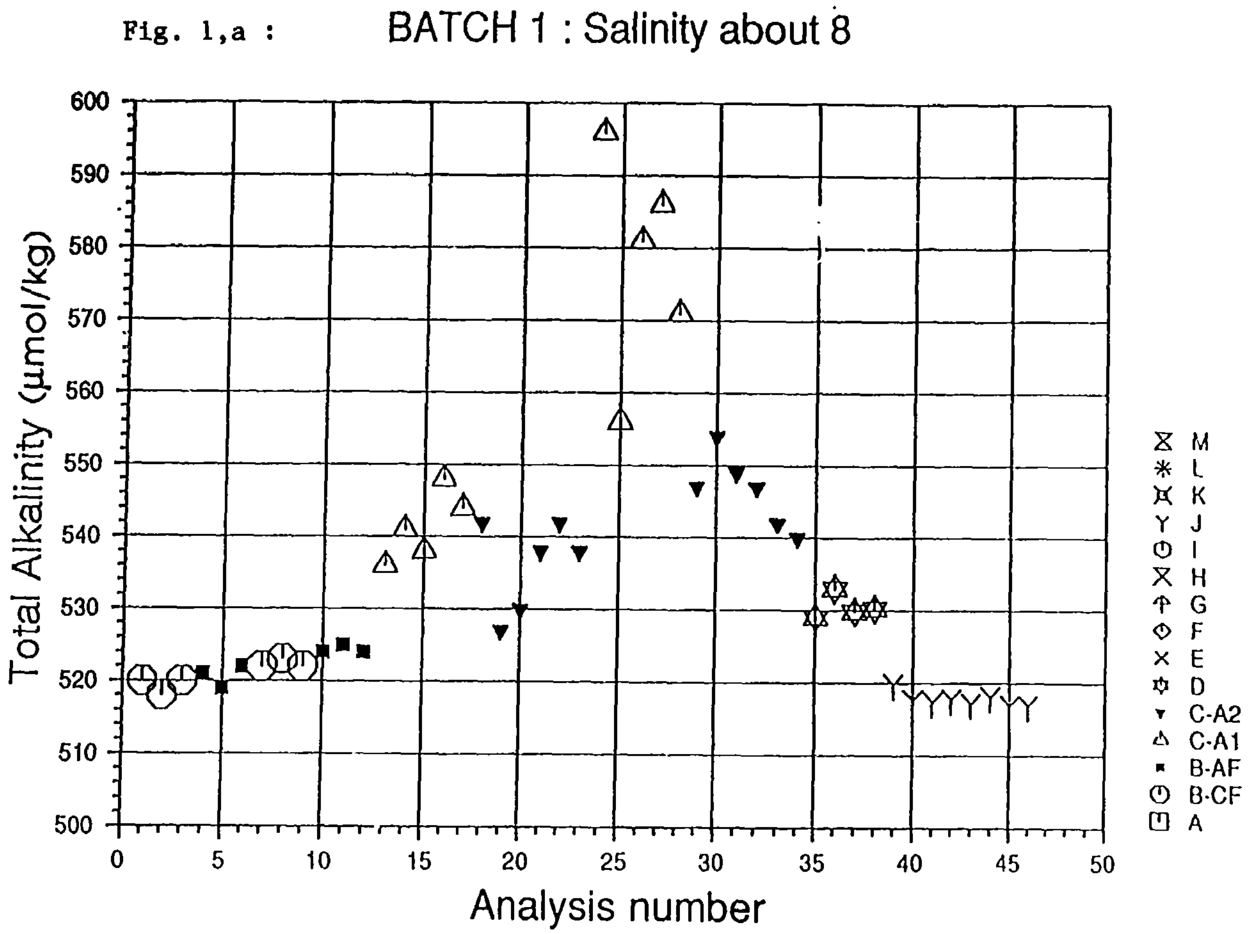

BATCH 1 : Salinity about 8
Total Alkalinity (µmol/kg)
600
590
580
570
560
550
540
530
520
510
500
0
5
10
15
20
25
30
35
40
45
50
Analysis number
M
L
K
J
I
H
G
F
E
D
C-A2
C-A1
B-AF
B-CF
A

Fig. 1,b :

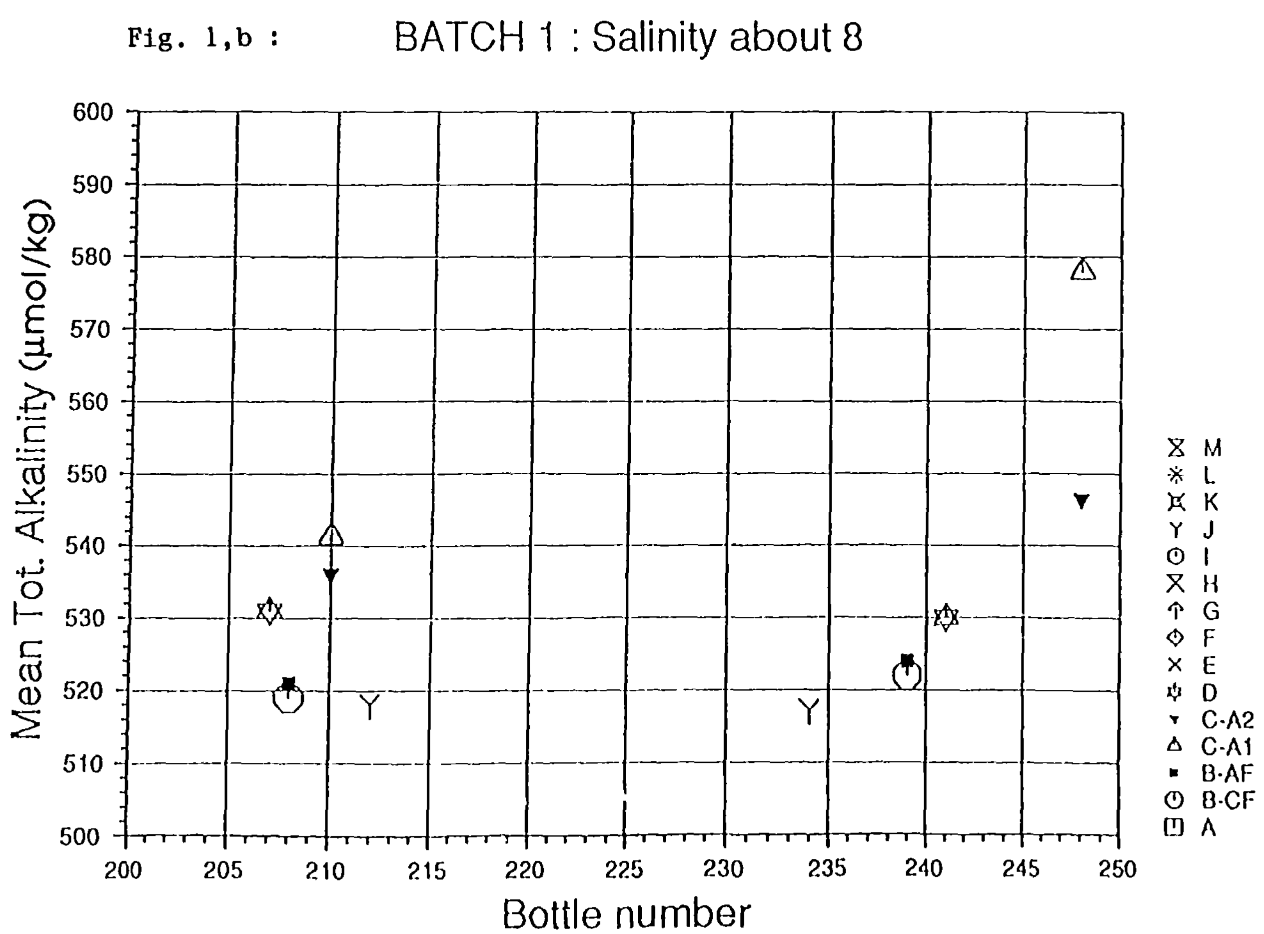

BATCH 1 : Salinity about 8
Mean Tot. Alkalinity (µmol/kg)
600
590
580
570
560
550
540
530
520
510
500
200
205
210
215
220
225
230
235
240
245
250
Bottle number
M
L
K
J
I
H
G
F
E
D
C-A2
C-A1
B-AF
B-CF
A

Fig. 1,c : BATCH 1 : Salinity about 8

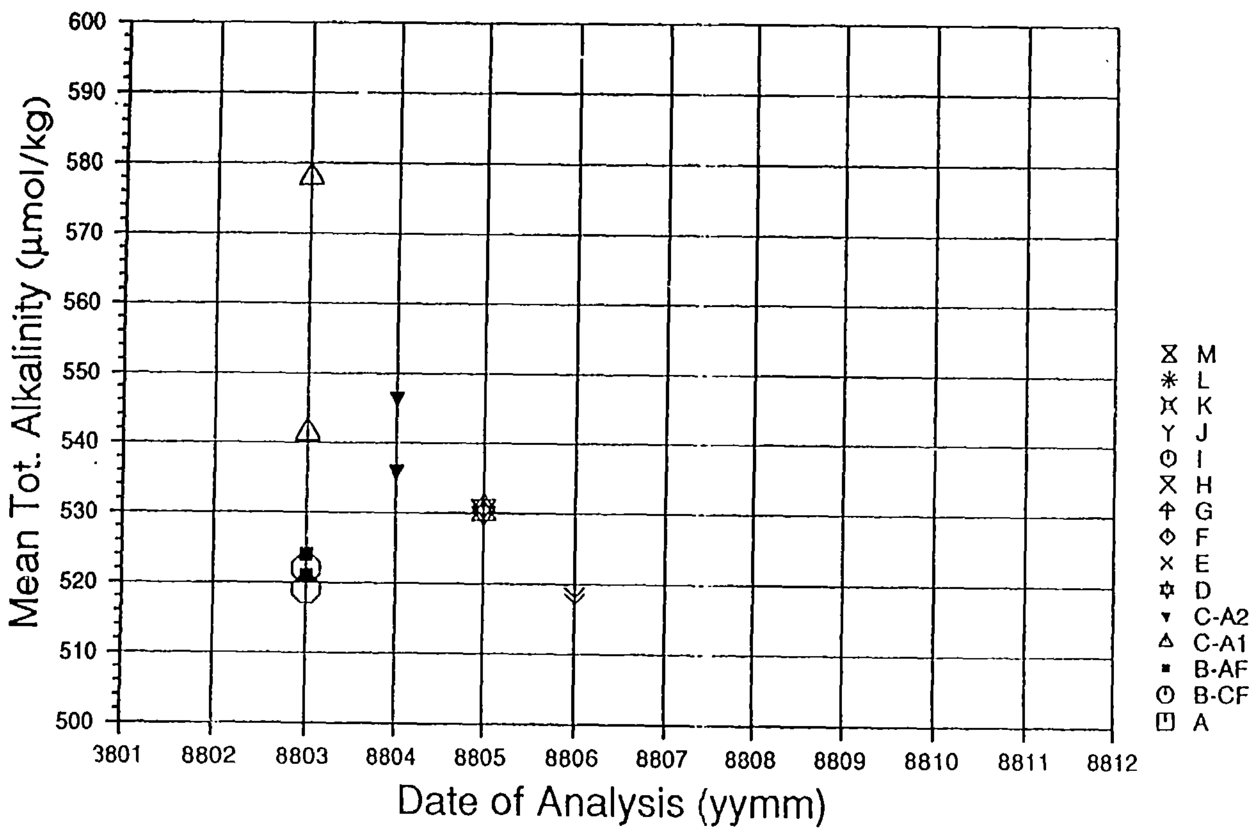


Fig. 1,d : BATCH 1 : Salinity about 8

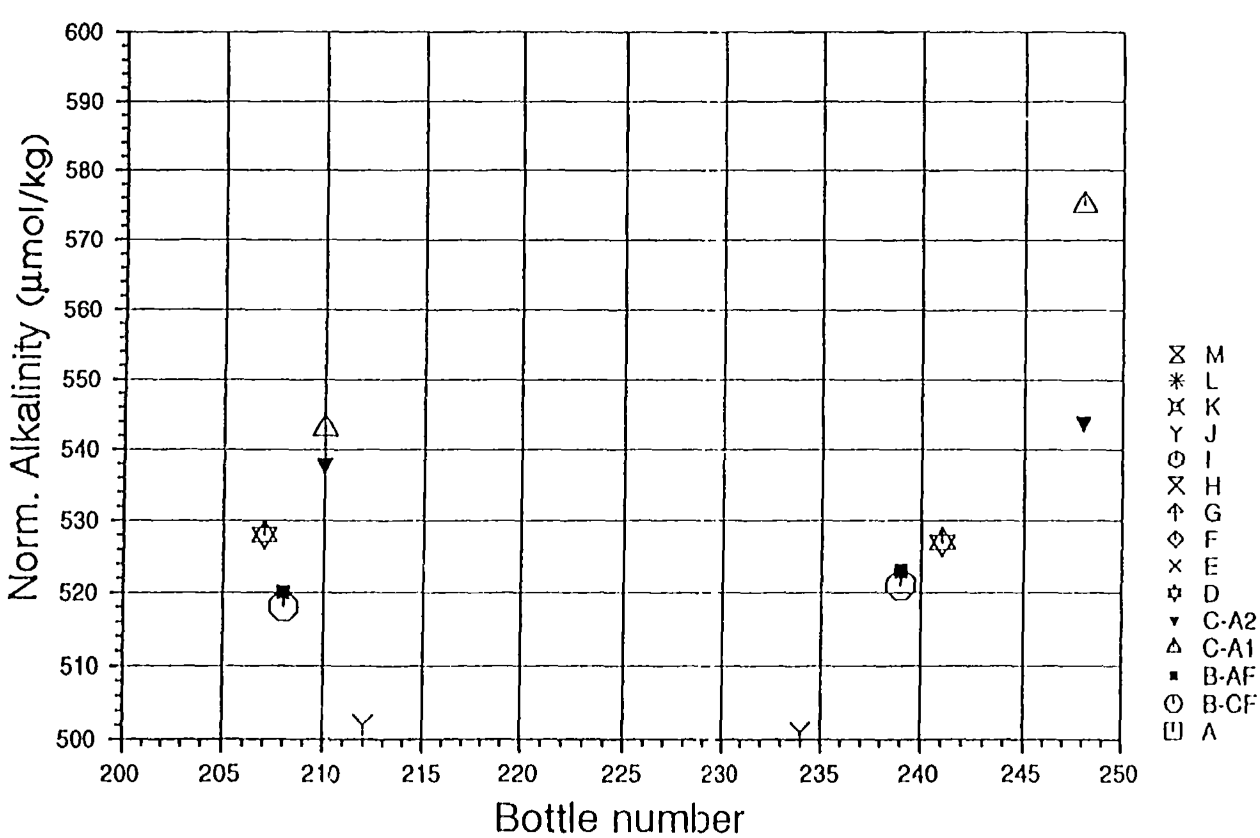


Fig. 2,a : BATCH 2 : Salinity about 30

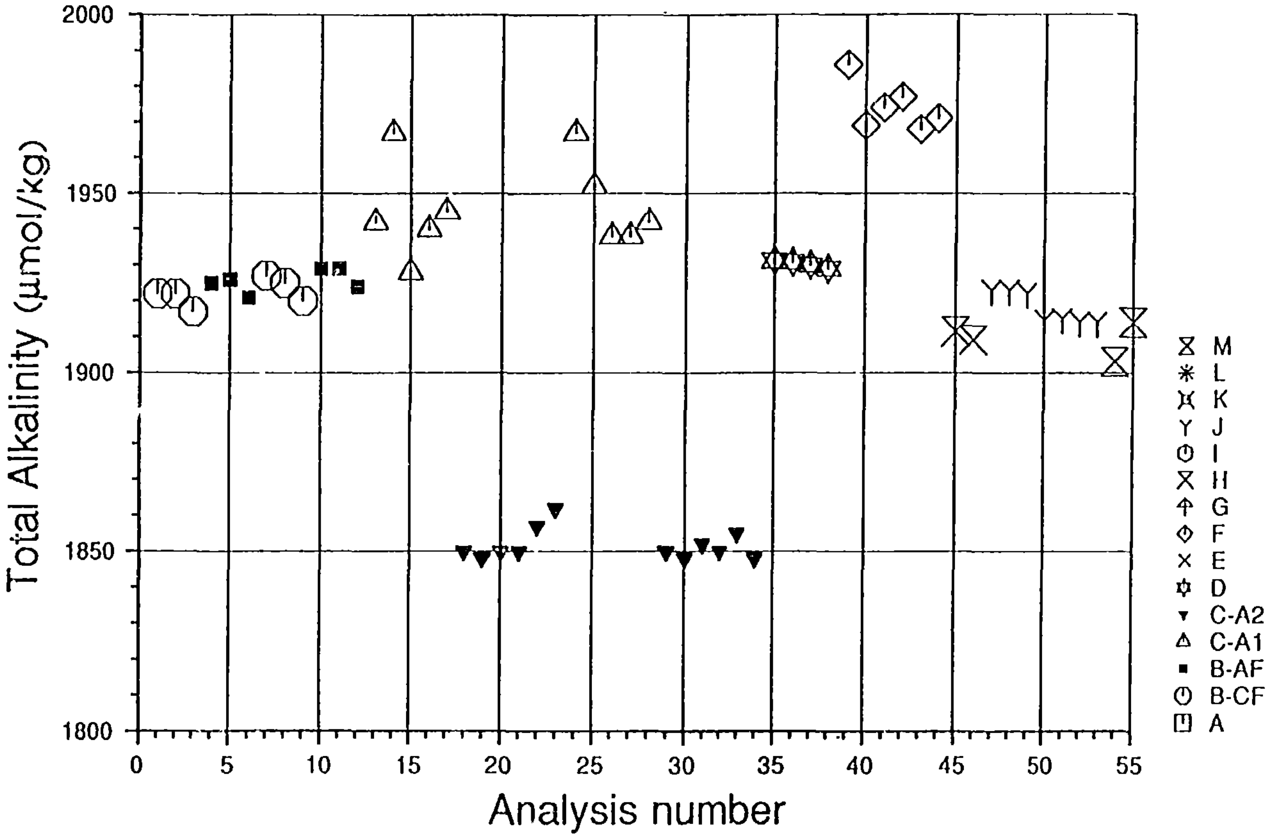


Fig. 2,b : BATCH 2 : Salinity about 30

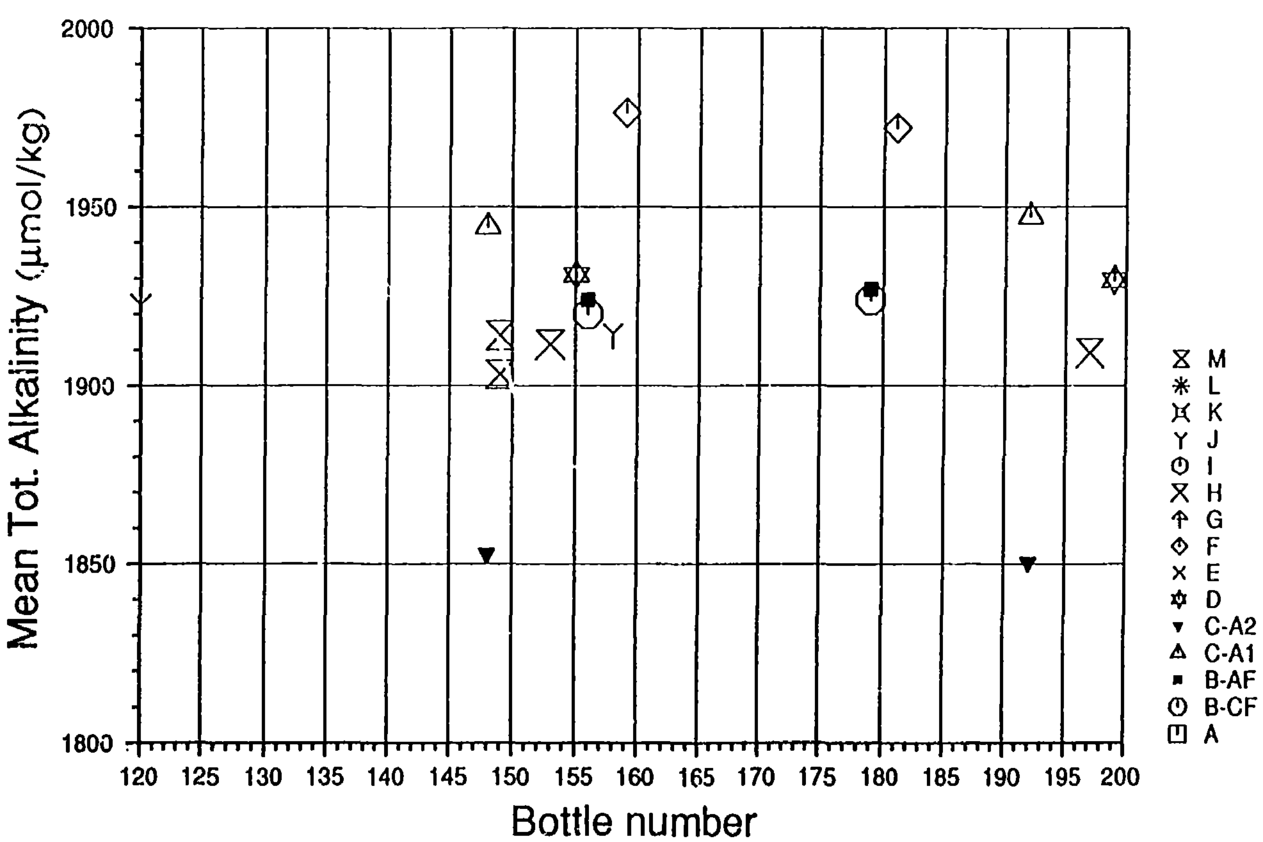


Fig. 2,c : BATCH 2 : Salinity about 30

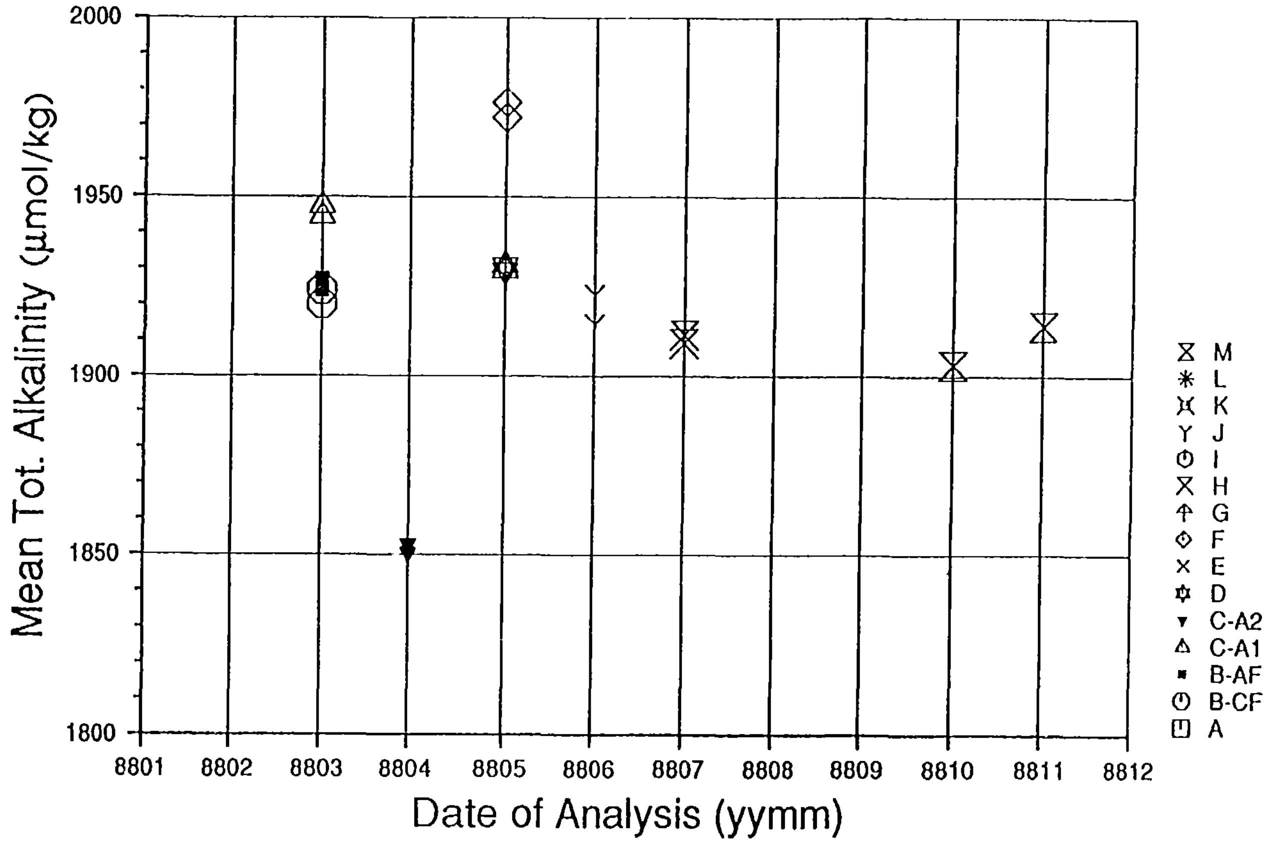


Fig. 2,d : BATCH 2 : Salinity about 30

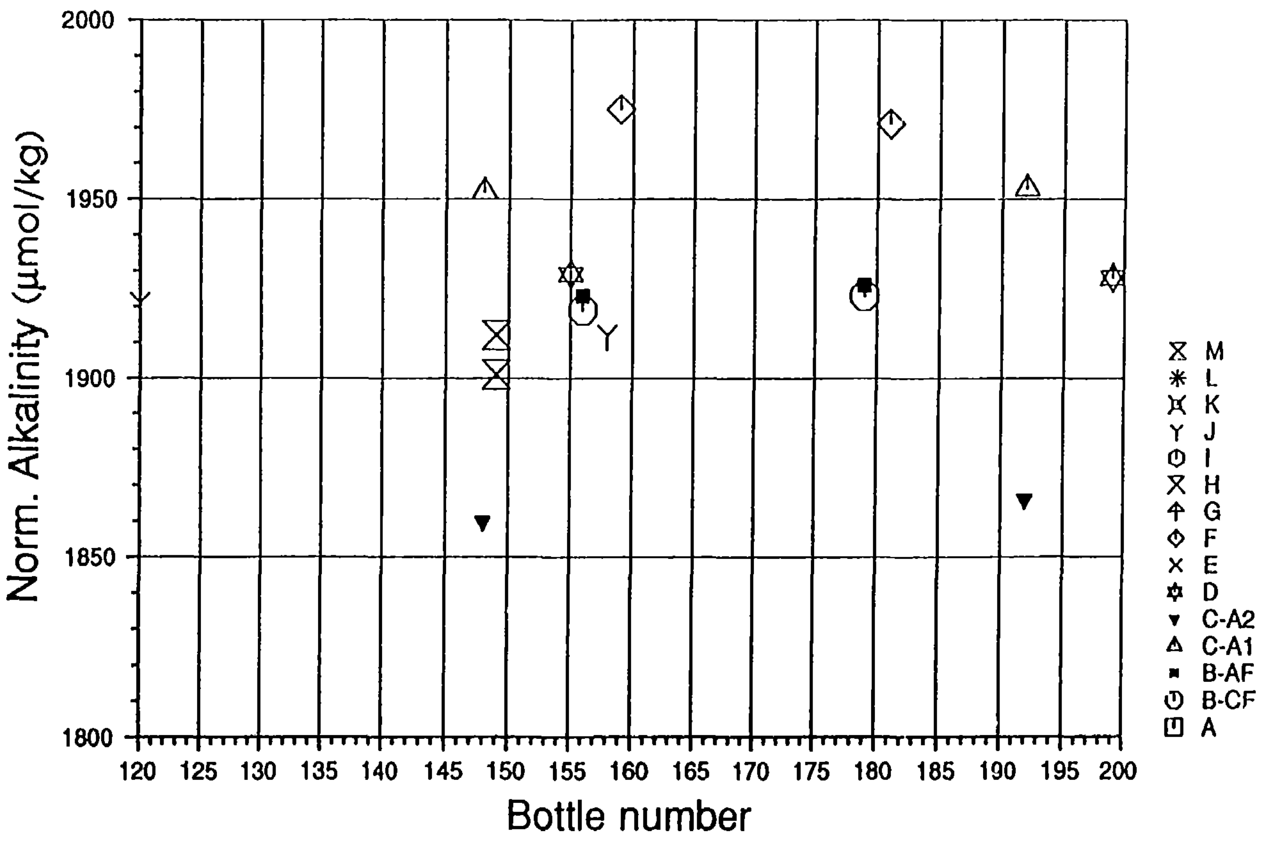


Fig. 3,a : BATCH 3 : Salinity about 35

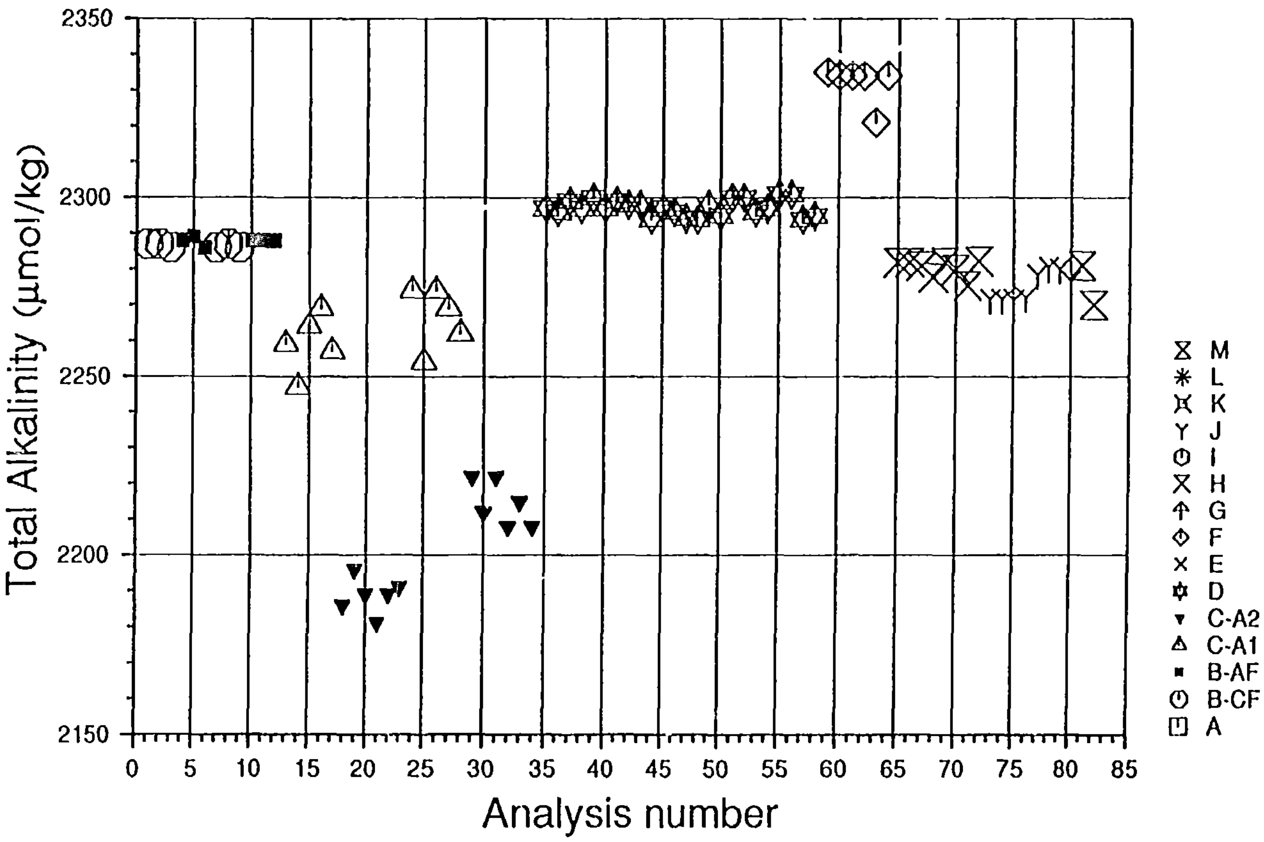


Fig. 3,b : BATCH 3 : Salinity about 35

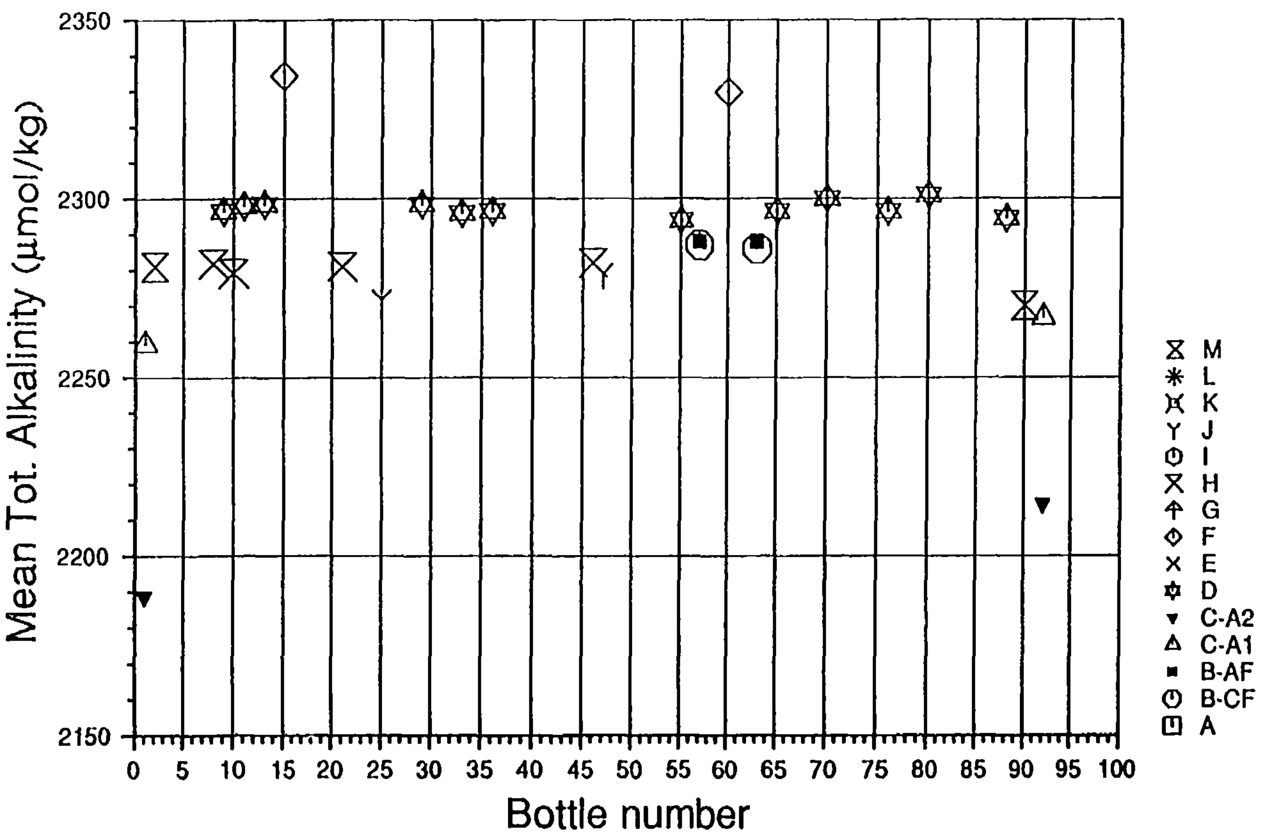


Fig. 3,c : BATCH 3 : Salinity about 35

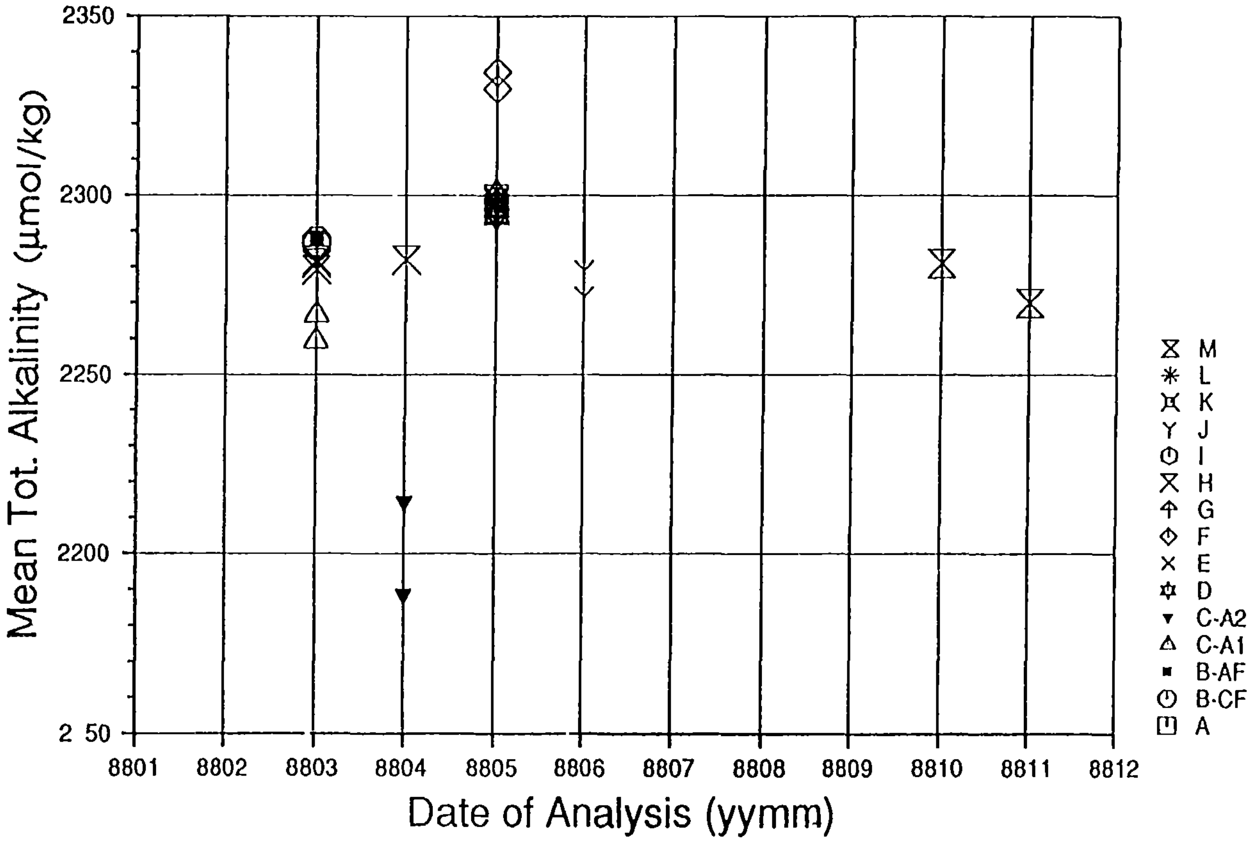


Fig. 3,d : BATCH 3 : Salinity about 35

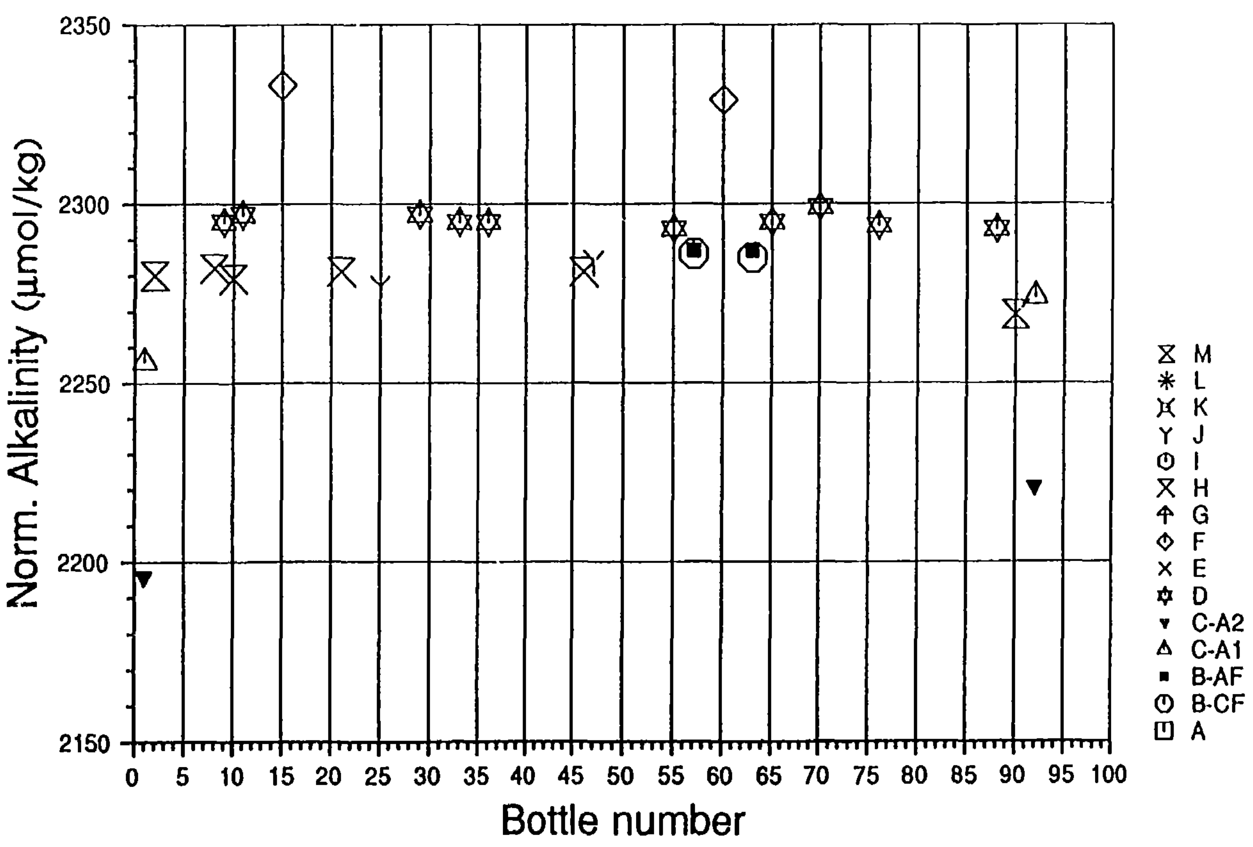


Fig. 4,a : BATCH 4 : Salinity about 38

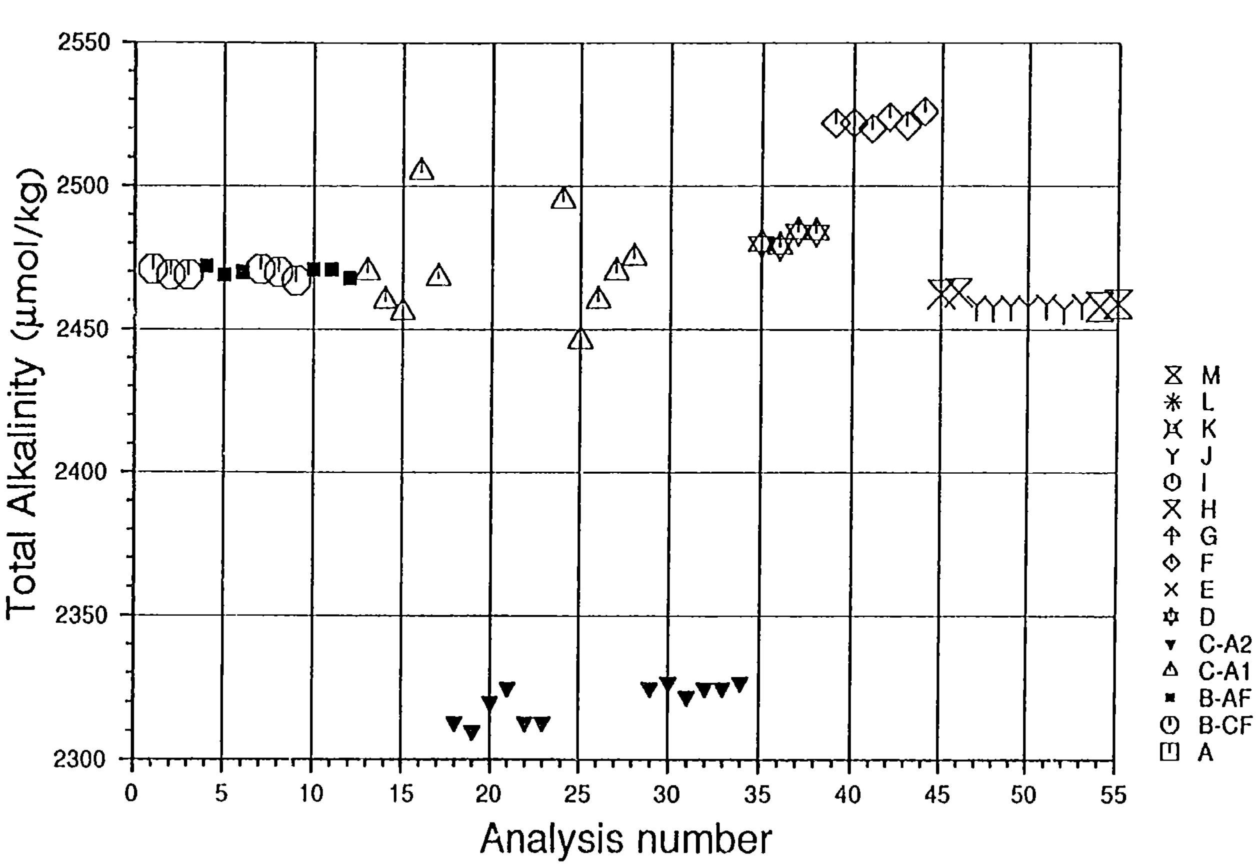


Fig. 4,b : BATCH 4 : Salinity about 38

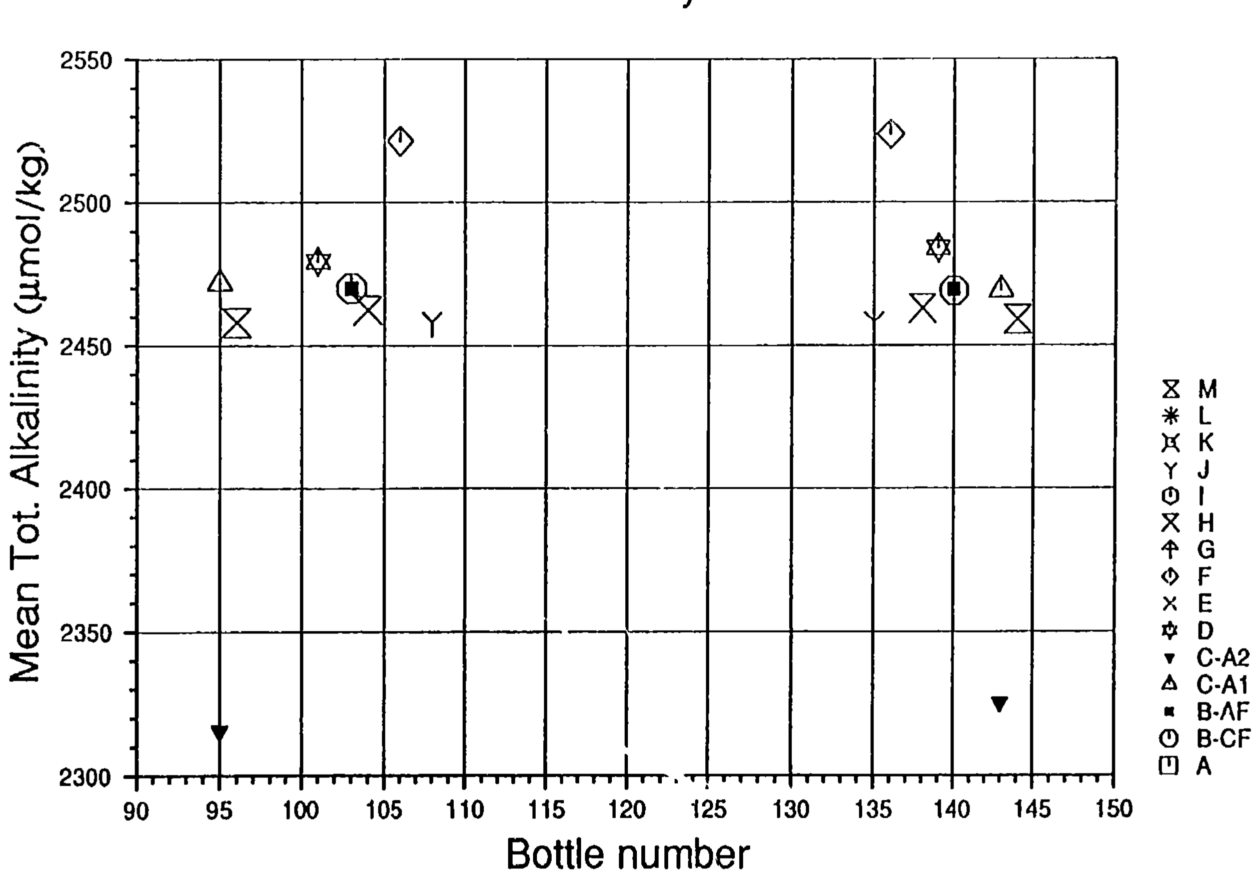


Fig. 4,c : BATCH 4 : Salinity about 38

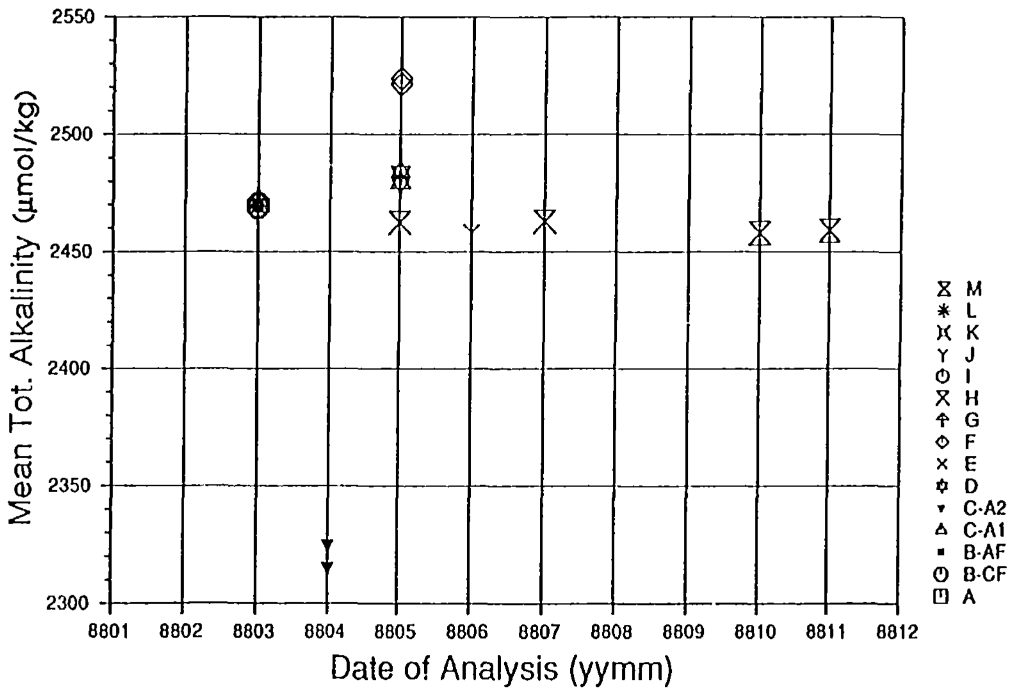


Fig. 4,d : BATCH 4 : Salinity about 38

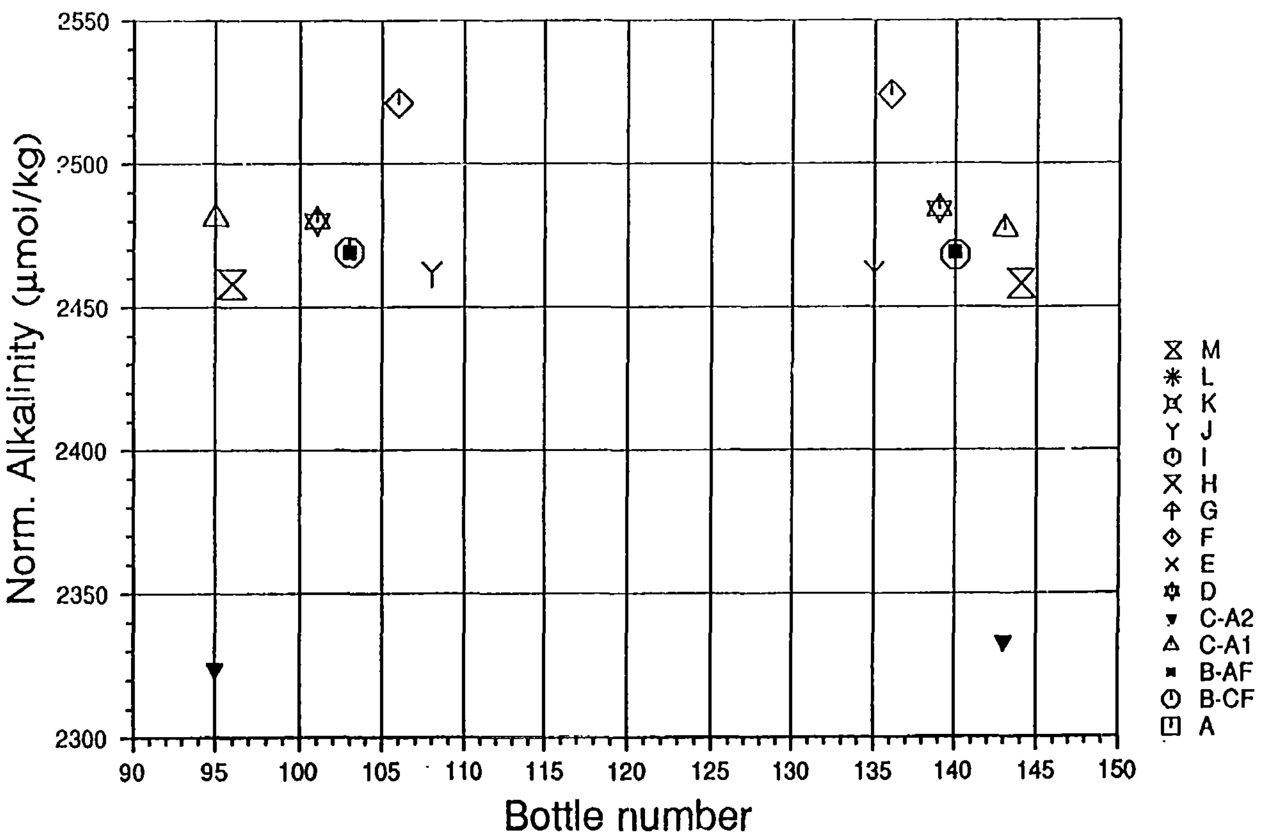


Fig. 5,a : BATCH 1 : Salinity about 8

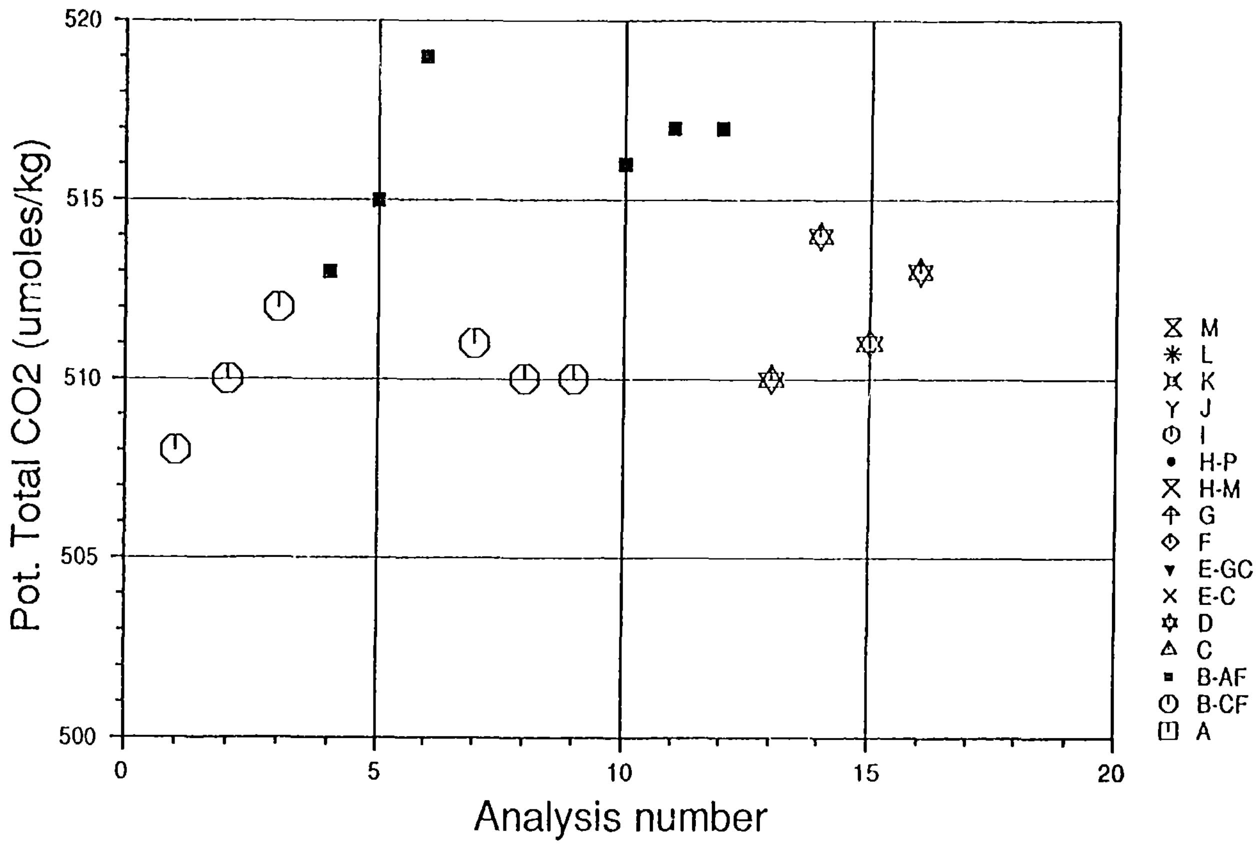


Fig. 5,b : BATCH 1 : Salinity about 8

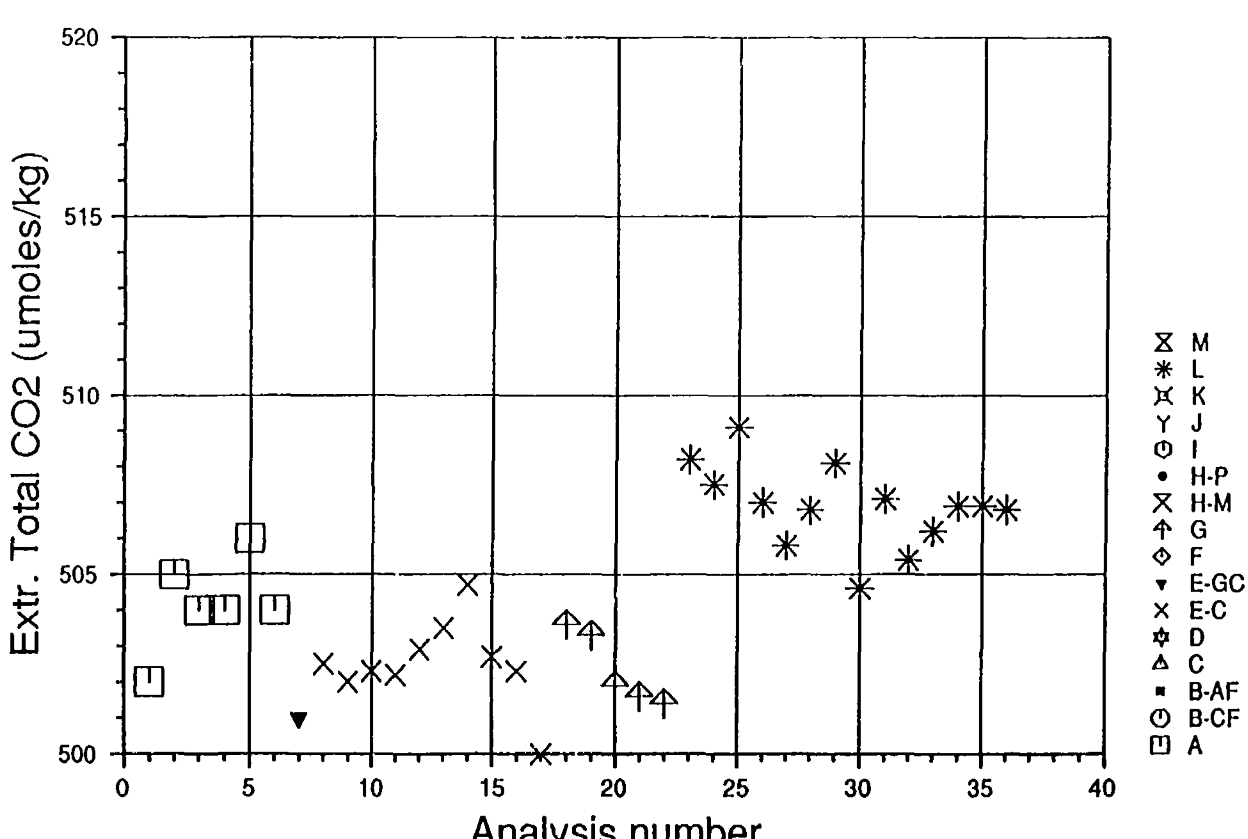


Fig. 5,c : BATCH 1 : Salinity about 8

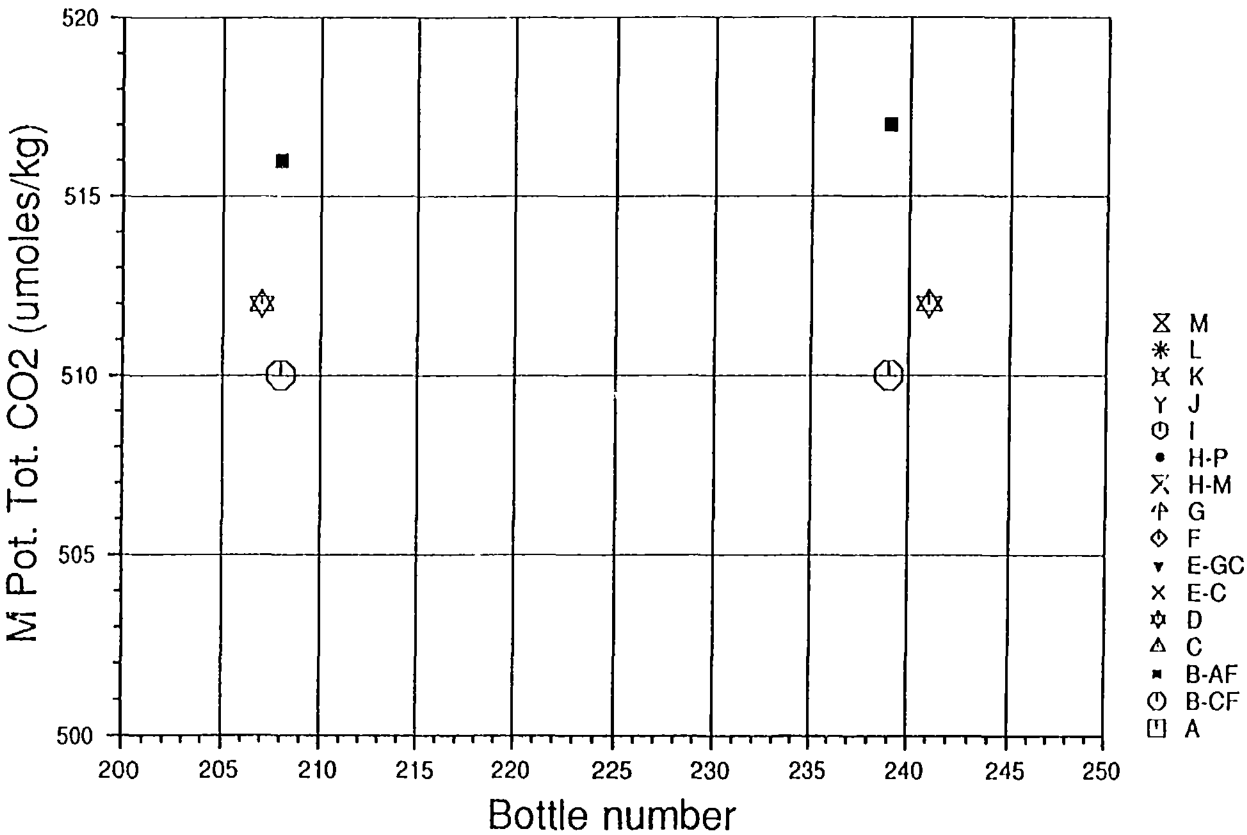


Fig. 5,d : BATCH 1 : Salinity about 8

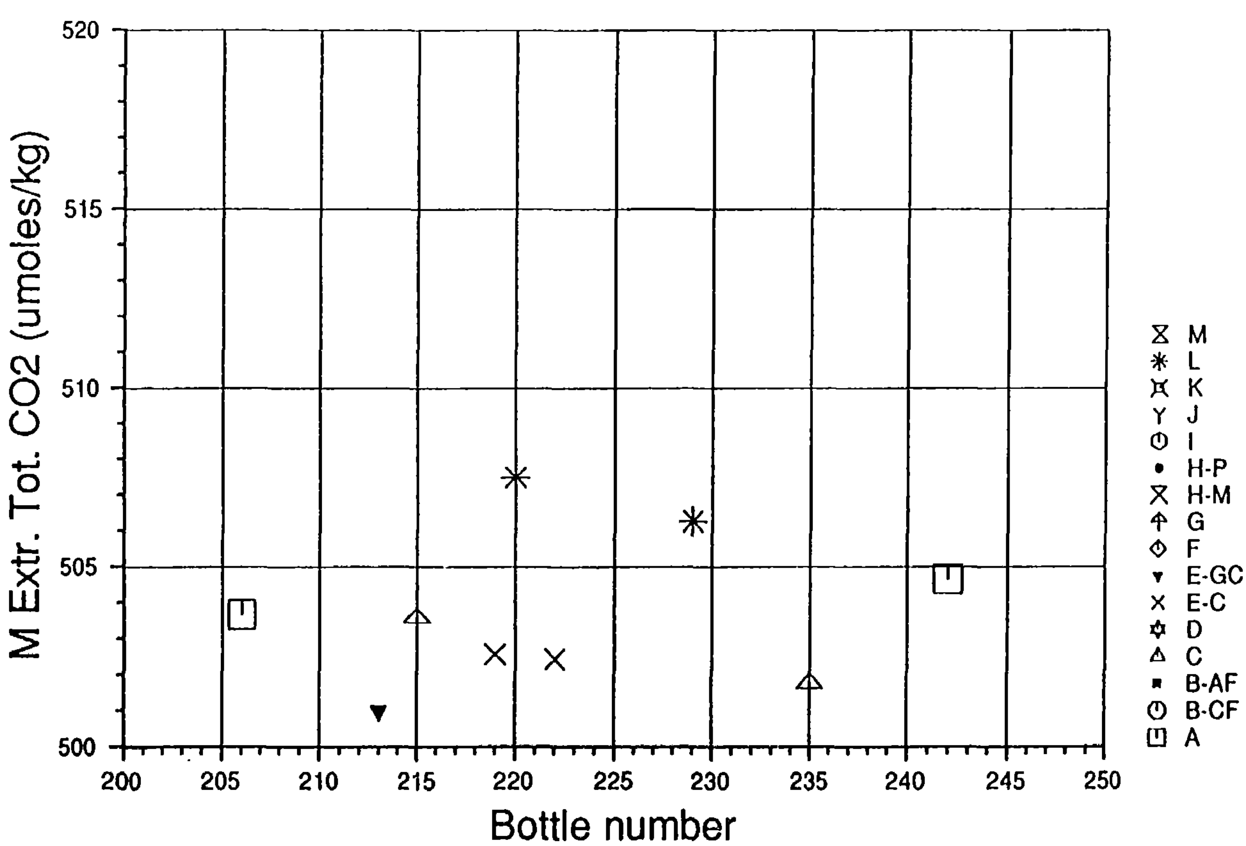


Fig. 5,e : BATCH 1 : Salinity about 8

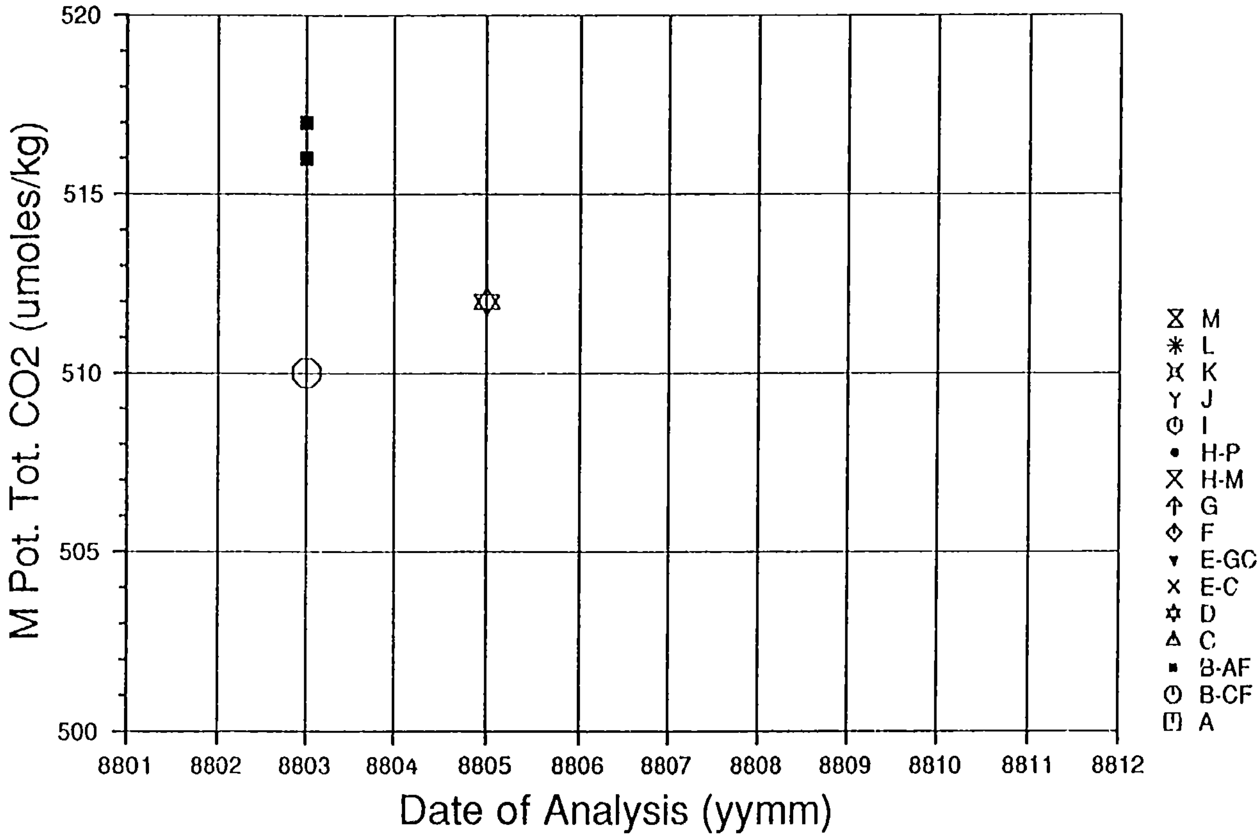


Fig. 5,f : BATCH 1 : Salinity about 8

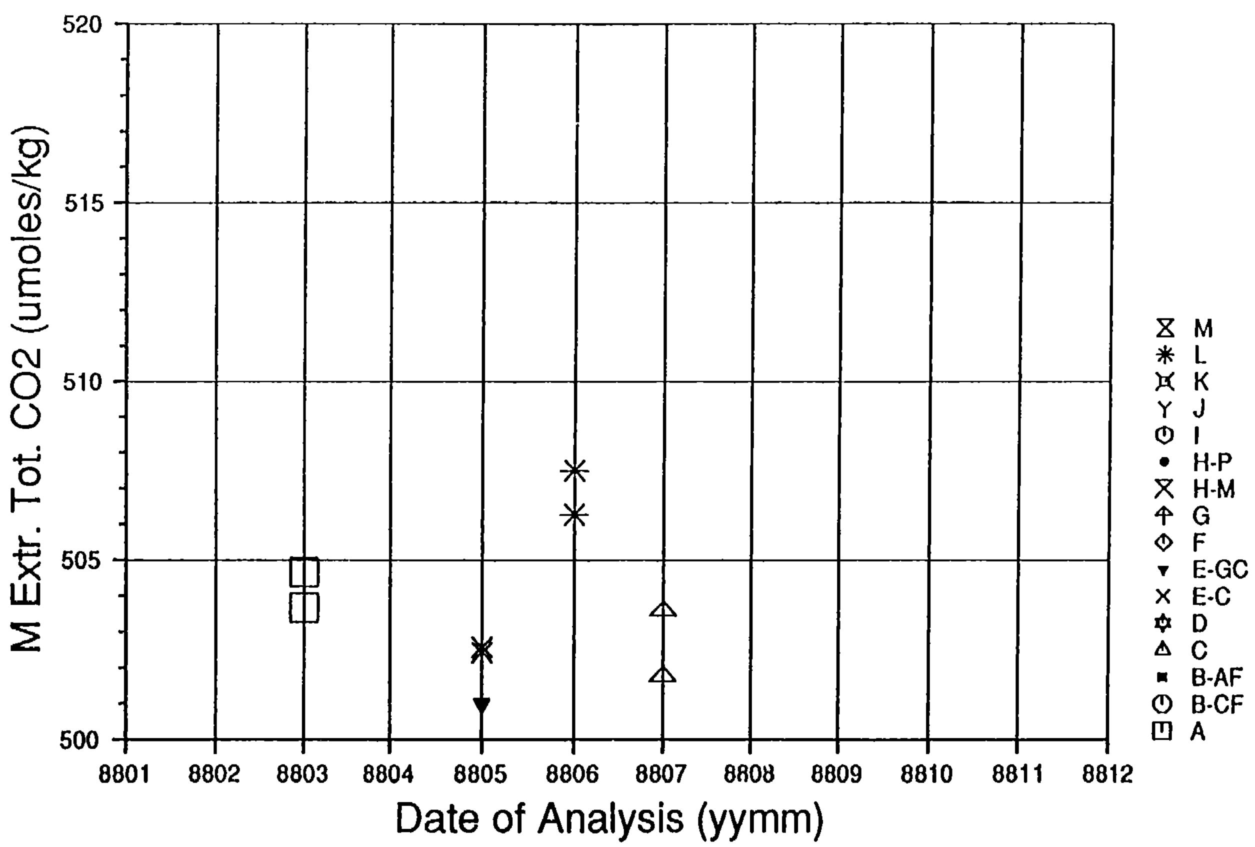


Fig. 5,g : BATCH 1 : Salinity about 8

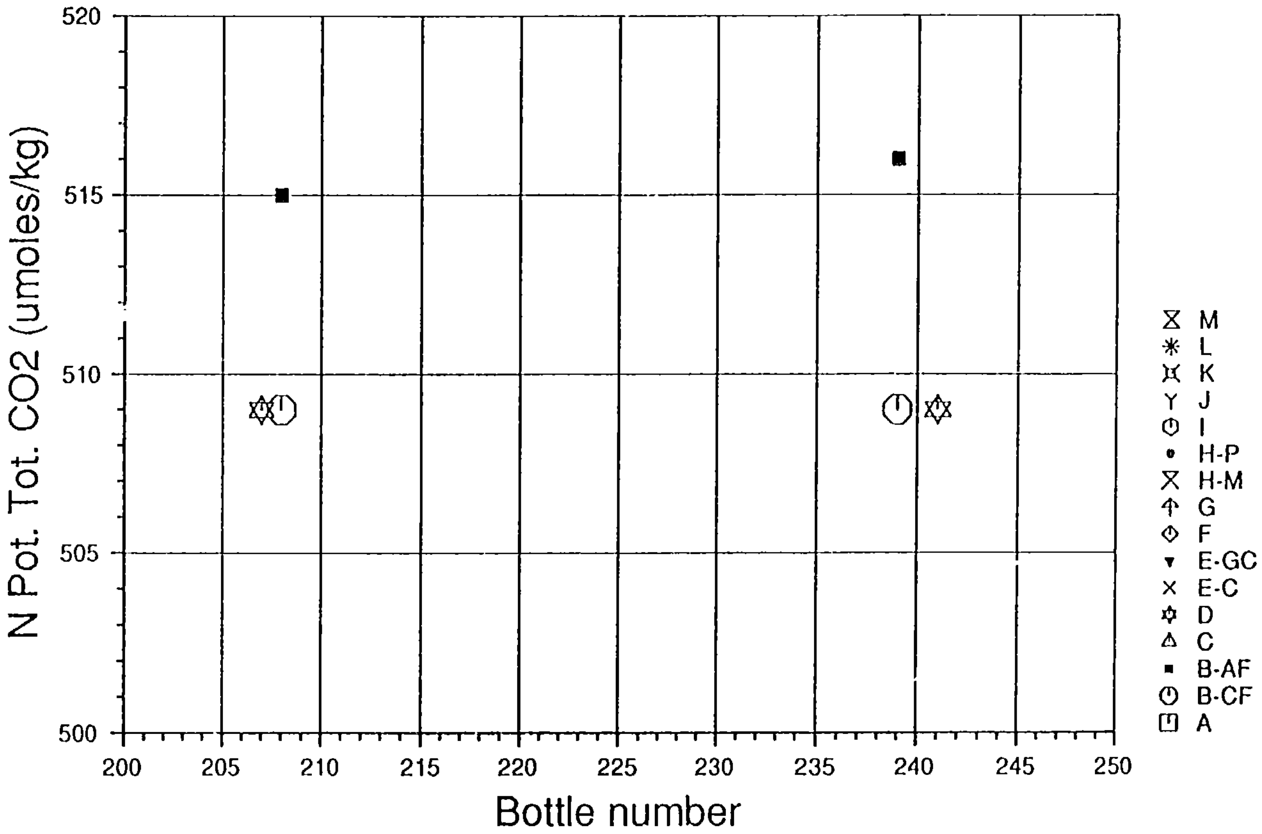


Fig. 5,h : BATCH 1 : Salinity about 8

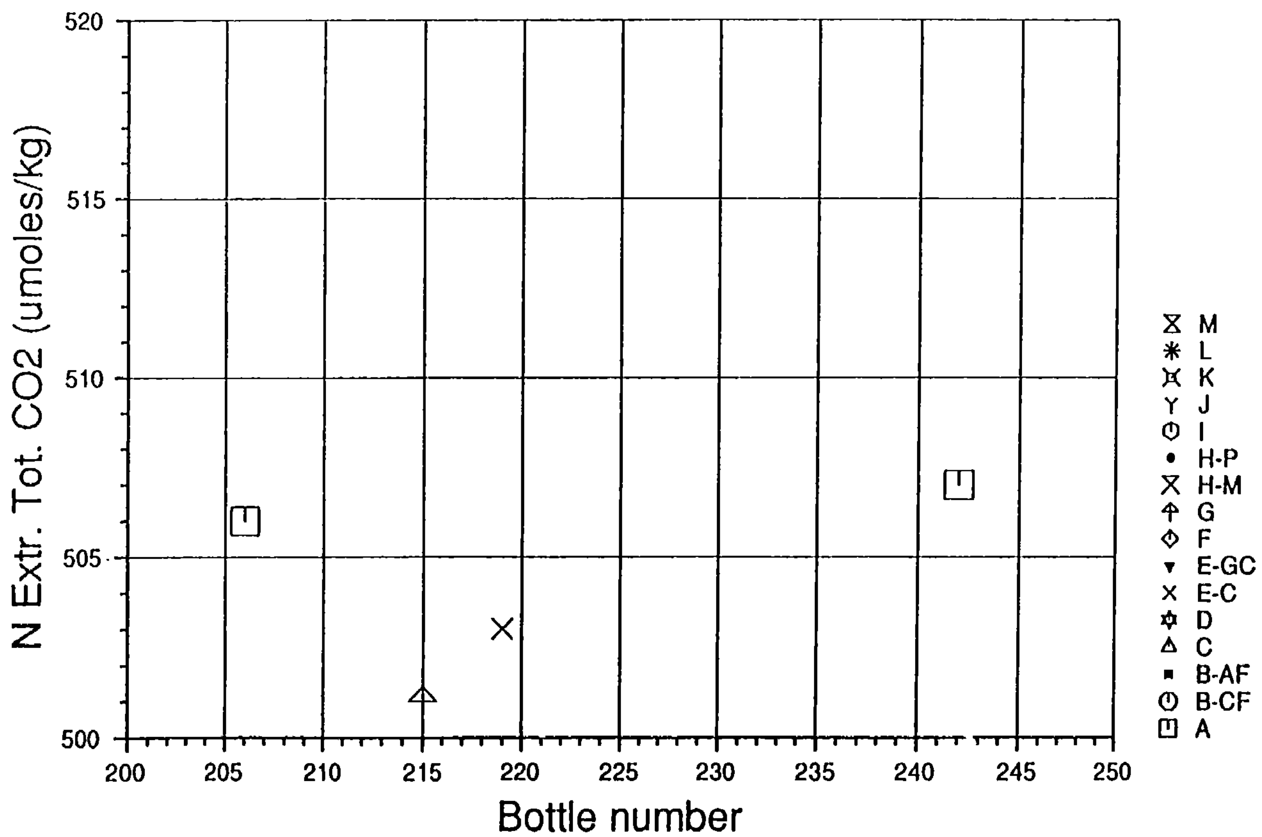


Fig. 6,a : BATCH 2 : Salinity about 30

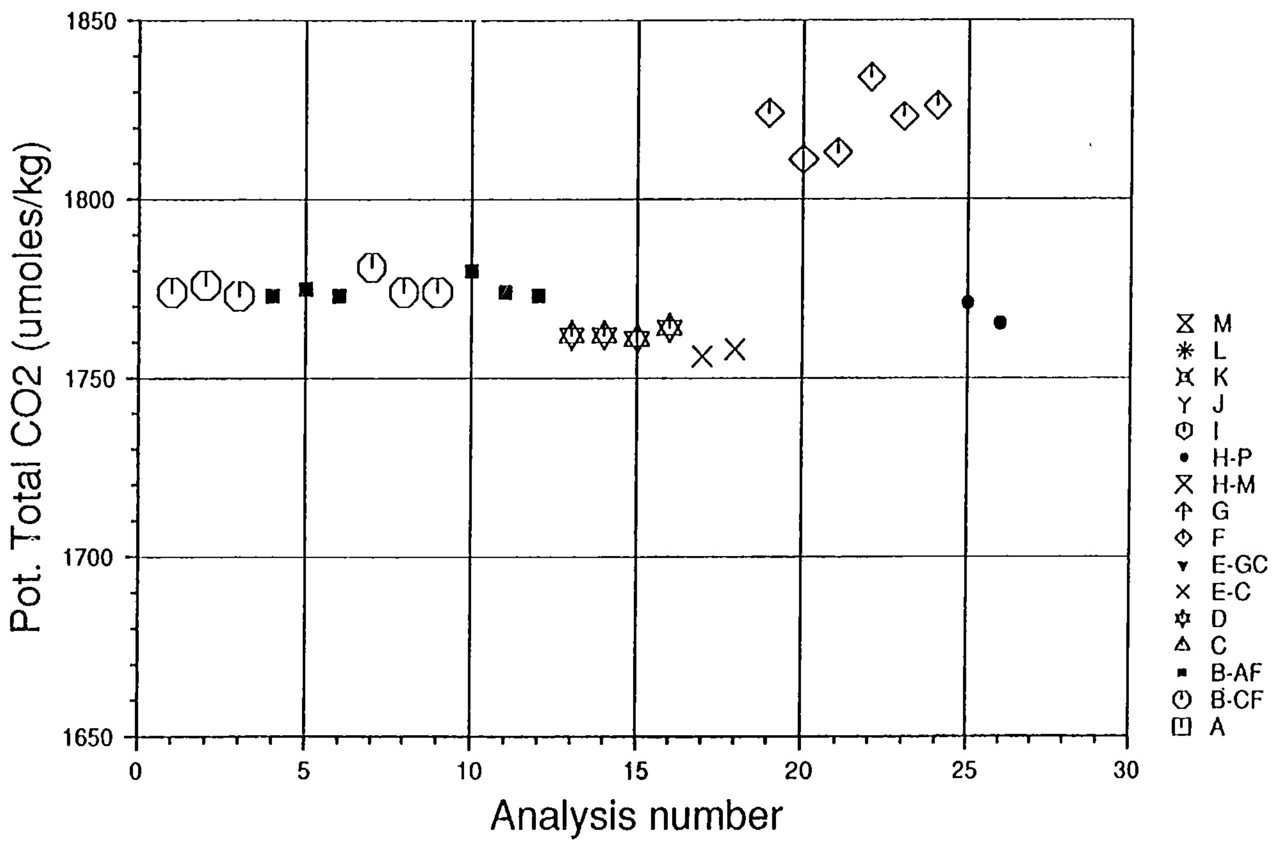


Fig. 6,b : BATCH 2 : Salinity about 30

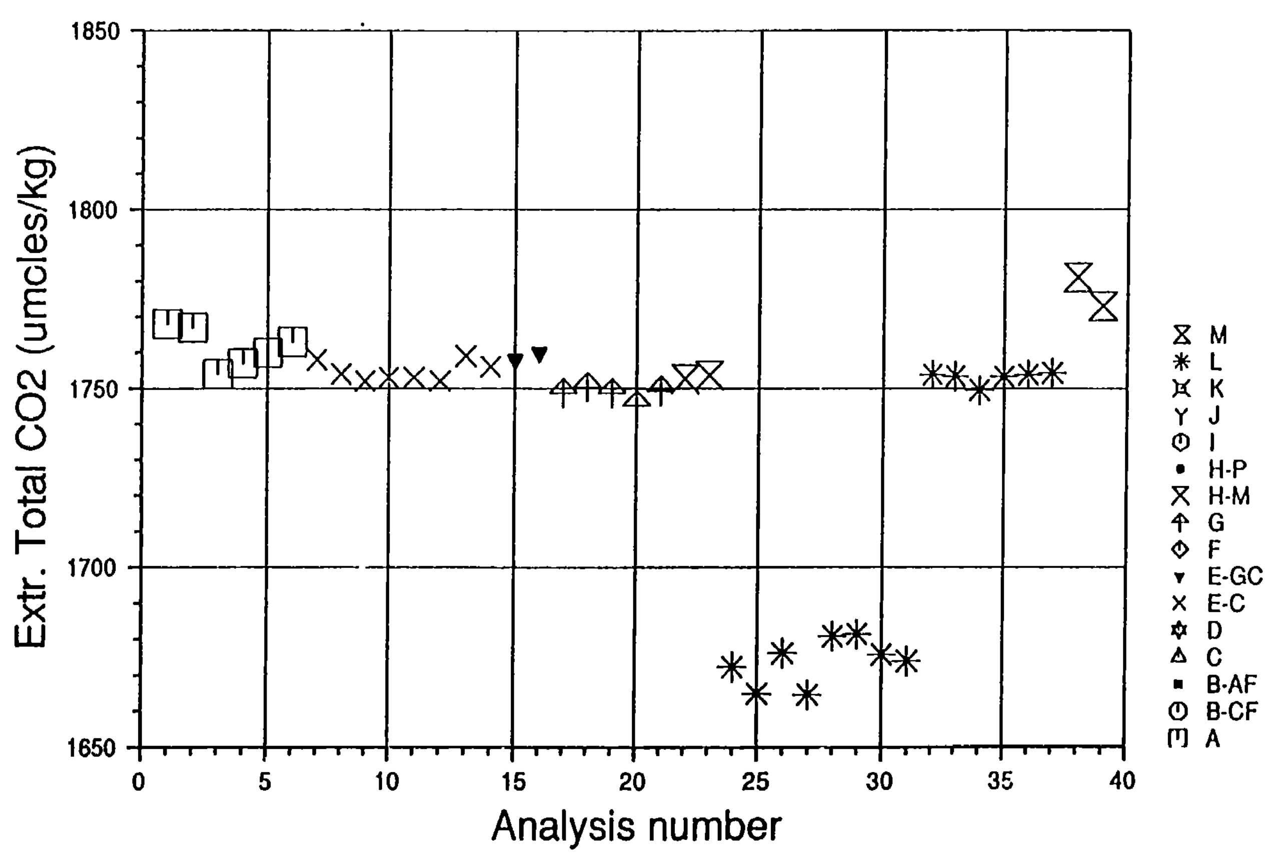


Fig. 6,c :

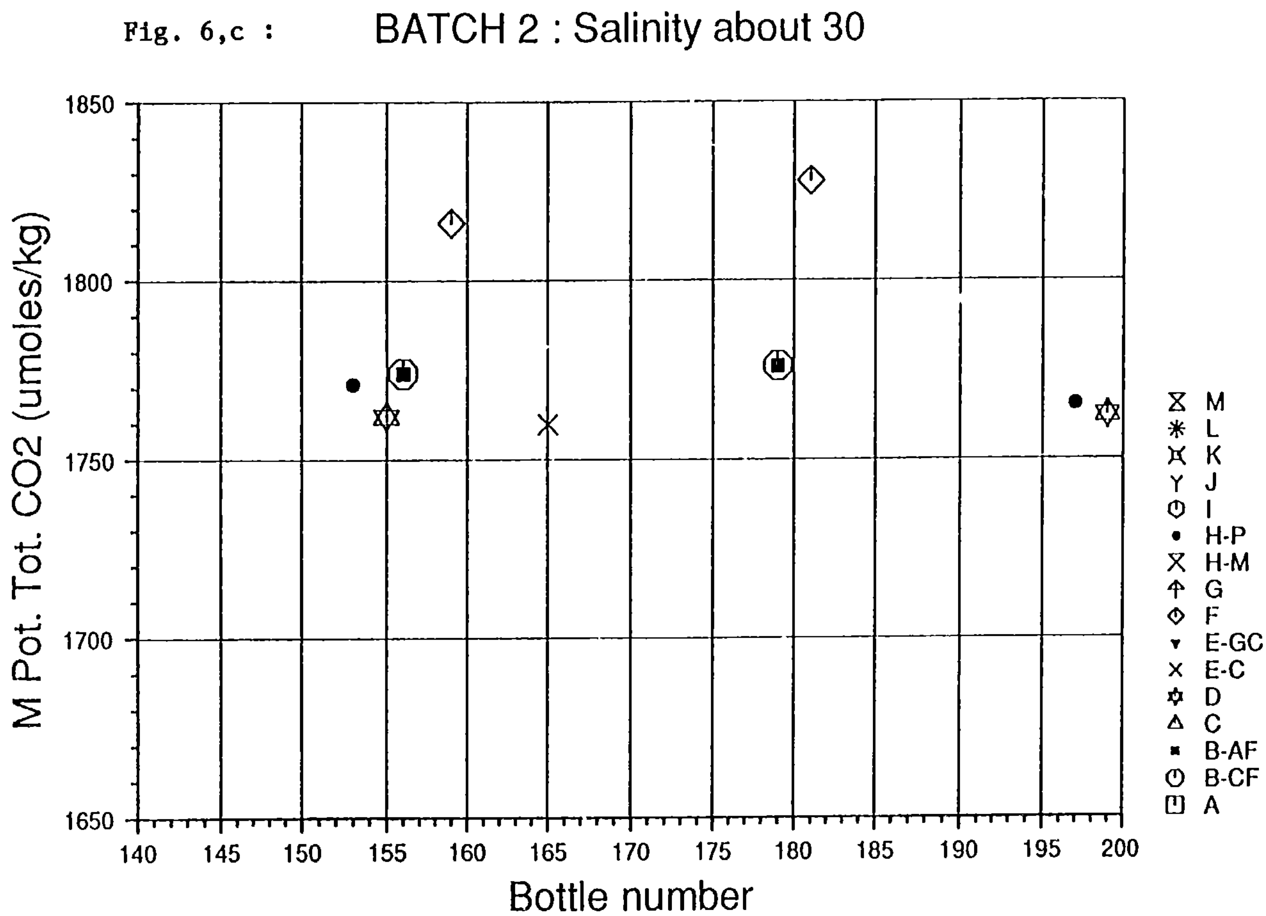

BATCH 2 : Salinity about 30
M Pot. Tot. CO2 (umoles/kg)
1850
1800
1750
1700
1650
140
145
150
155
160
165
170
175
180
185
190
195
200
Bottle number
M
L
K
J
I
H-P
H-M
G
F
E-GC
E-C
D
C
B-AF
B-CF
A

Fig. 6,d :

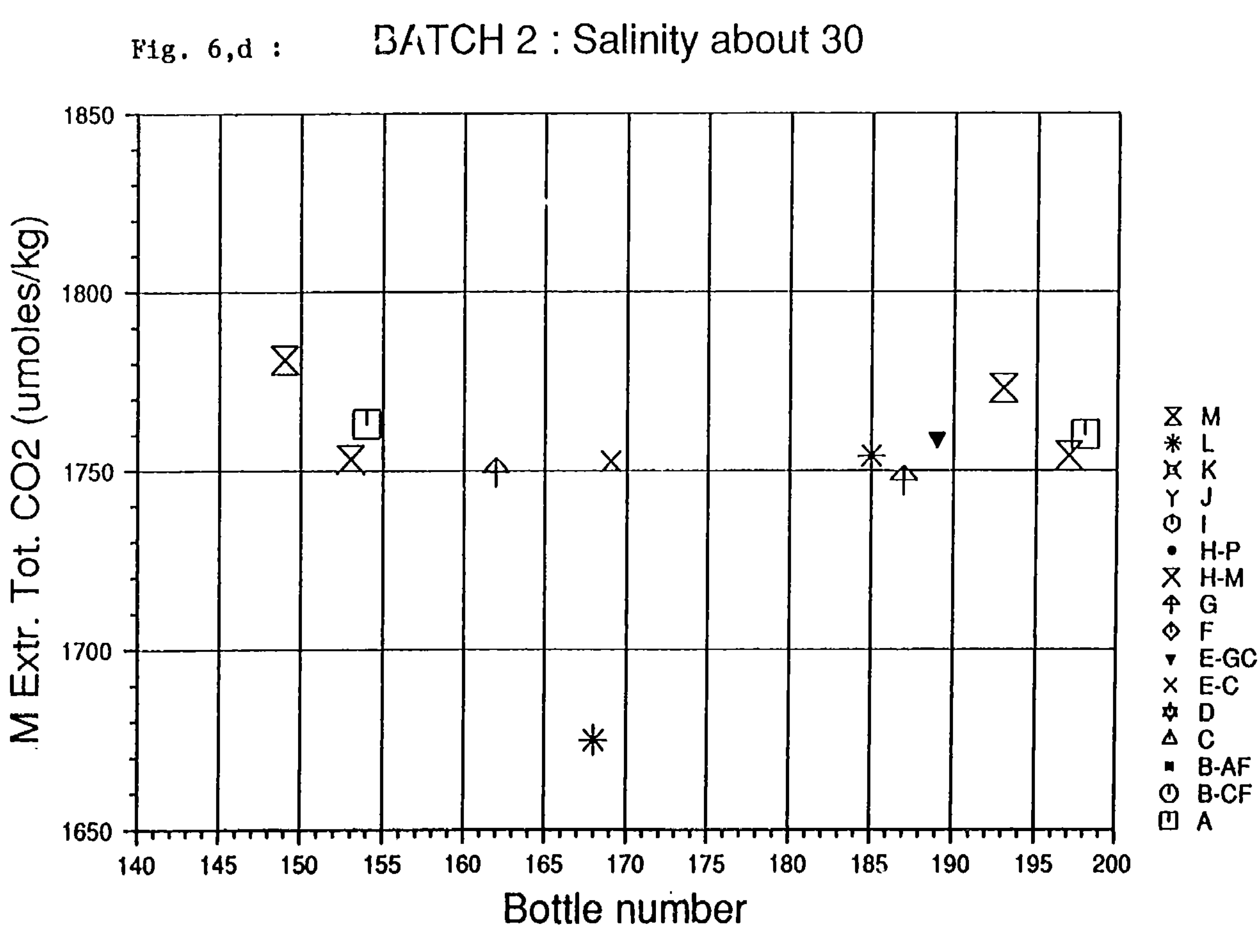

BATCH 2 : Salinity about 30
M Extr. Tot. CO2 (umoles/kg)
1850
1800
1750
1700
1650
140
145
150
155
160
165
170
175
180
185
190
195
200
Bottle number
M
L
K
J
I
H-P
H-M
G
F
E-GC
E-C
D
C
B-AF
B-CF
A

Fig. 6,e :

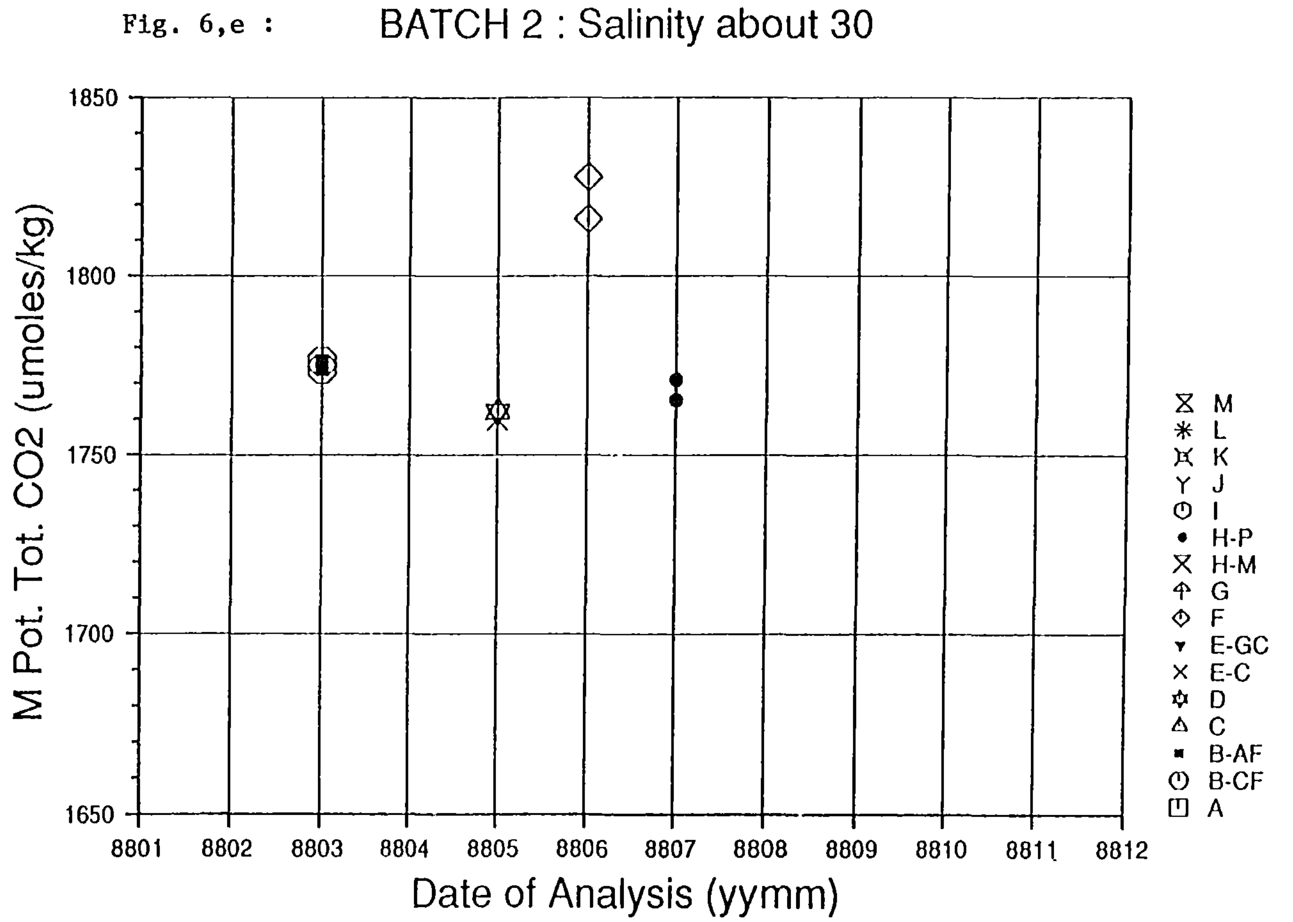

BATCH 2 : Salinity about 30
M Pot. Tot. CO2 (umoles/kg)
1850
1800
1750
1700
1650
8801
8802
8803
8804
8805
8806
8807
8808
8809
8810
8811
8812
Date of Analysis (yymm)
M
L
K
J
I
H-P
H-M
G
F
E-GC
E-C
D
C
B-AF
B-CF
A

Fig. 6,f :

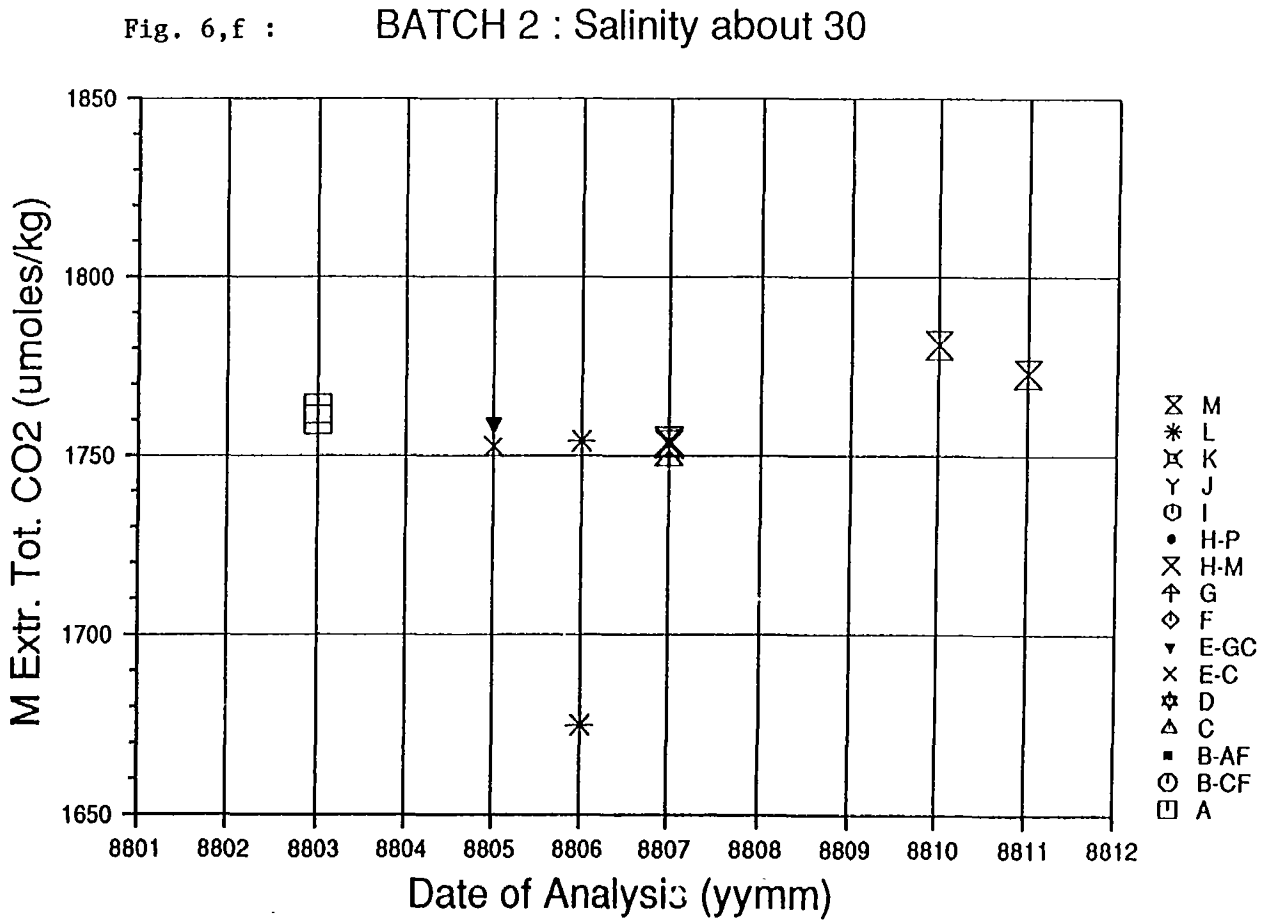

BATCH 2 : Salinity about 30
M Extr. Tot. CO2 (umoles/kg)
1850
1800
1750
1700
1650
8801
8802
8803
8804
8805
8806
8807
8808
8809
8810
8811
8812
Date of Analysis (yymm)
M
L
K
J
I
H-P
H-M
G
F
E-GC
E-C
D
C
B-AF
B-CF
A

Fig. 6,g :

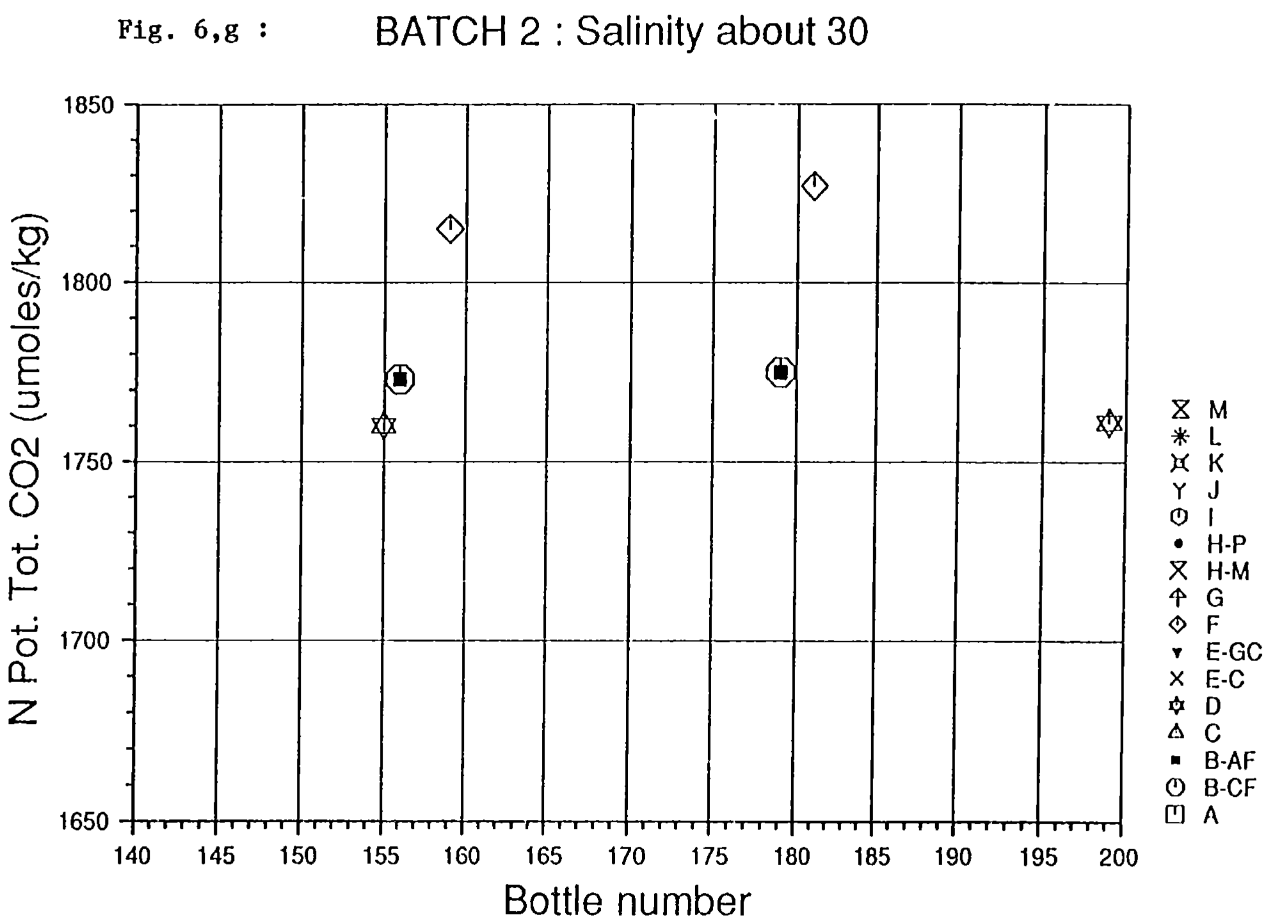
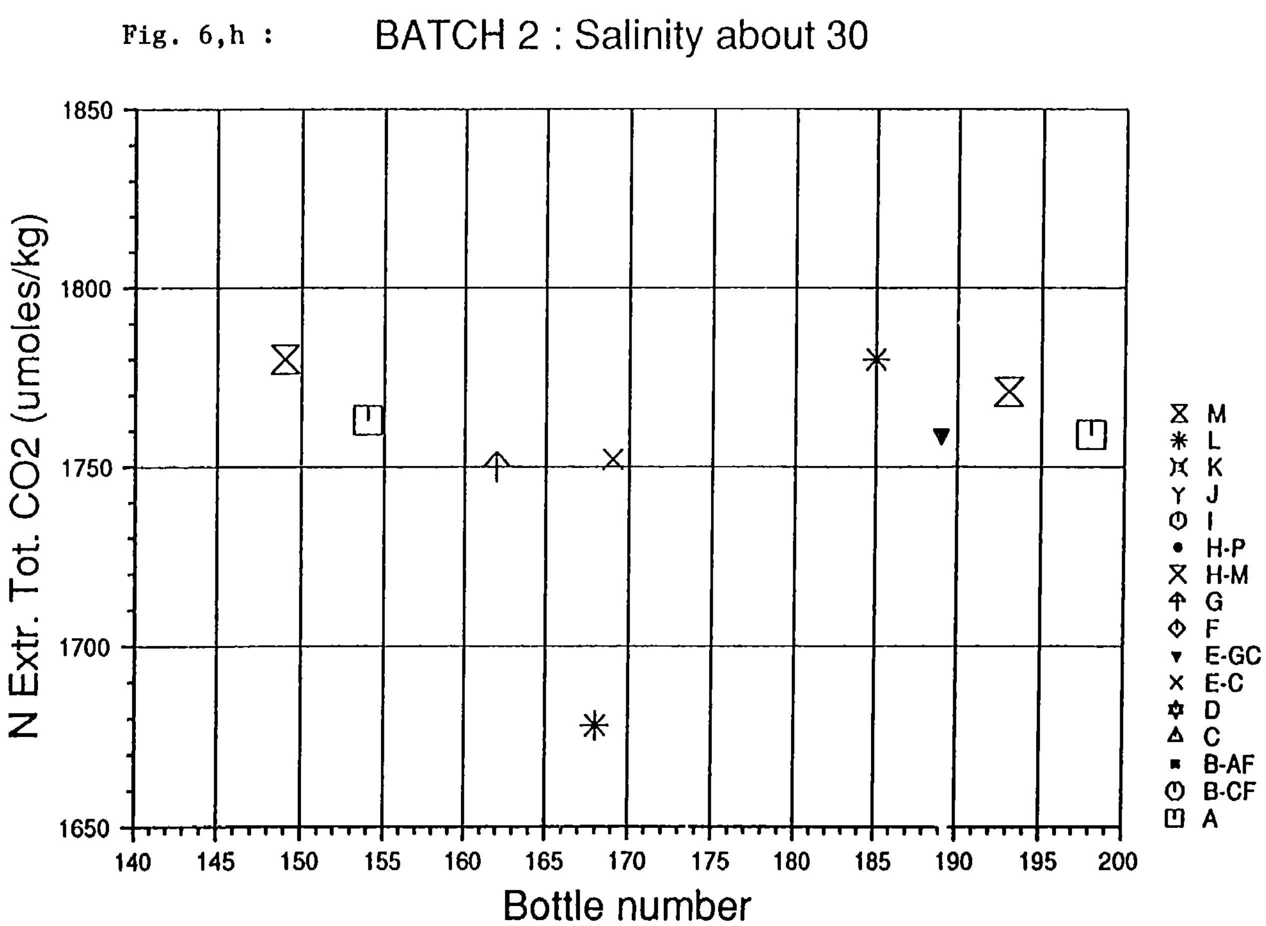

BATCH 2 : Salinity about 30
N Pot. Tot. CO2 (umoles/kg)
1850
1800
1750
1700
1650
140
145
150
155
160
165
170
175
180
185
190
195
200
Bottle number
M
L
K
J
I
H-P
H-M
G
F
E-GC
E-C
D
C
B-AF
B-CF
A

Fig. 6,h :


BATCH 2 : Salinity about 30
N Extr. Tot. CO2 (umoles/kg)
1850
1800
1750
1700
1650
140
145
150
155
160
165
170
175
180
185
190
195
200
Bottle number
M
L
K
J
I
H-P
H-M
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F
E-GC
E-C
D
C
B-AF
B-CF
A

Fig. 7,a : BATCH 3 : Salinity about 35

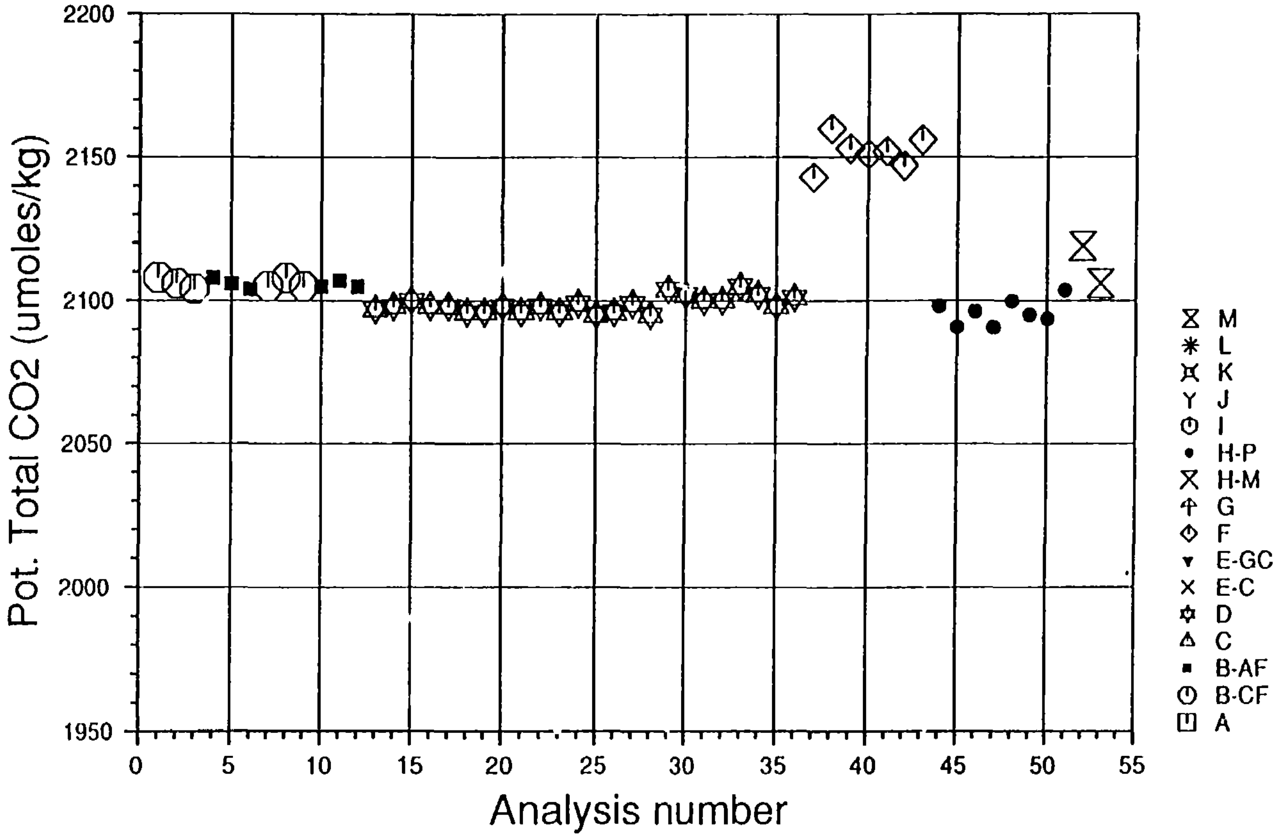


Fig. 7,b : BATCH 3 : Salinity about 35

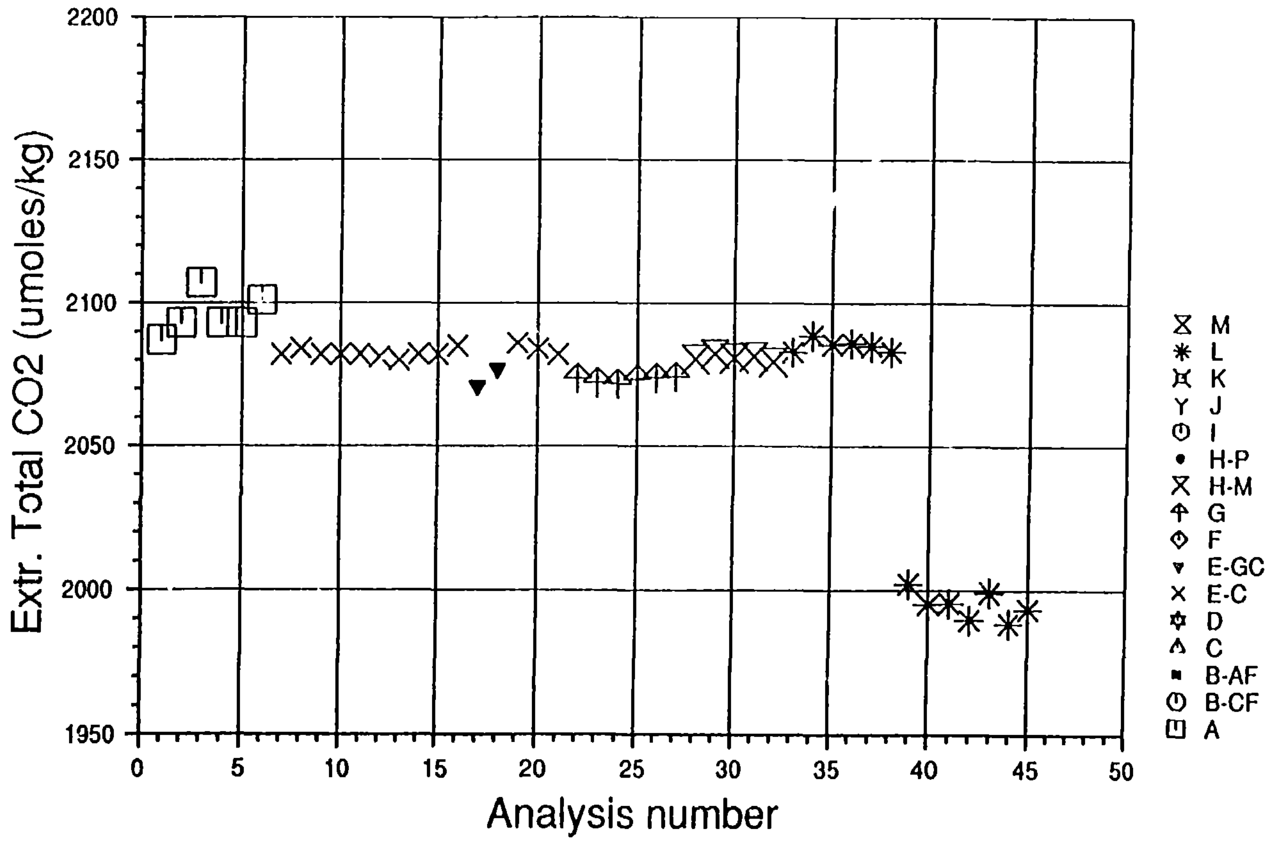


Fig. 7,c : BATCH 3 : Salinity about 35

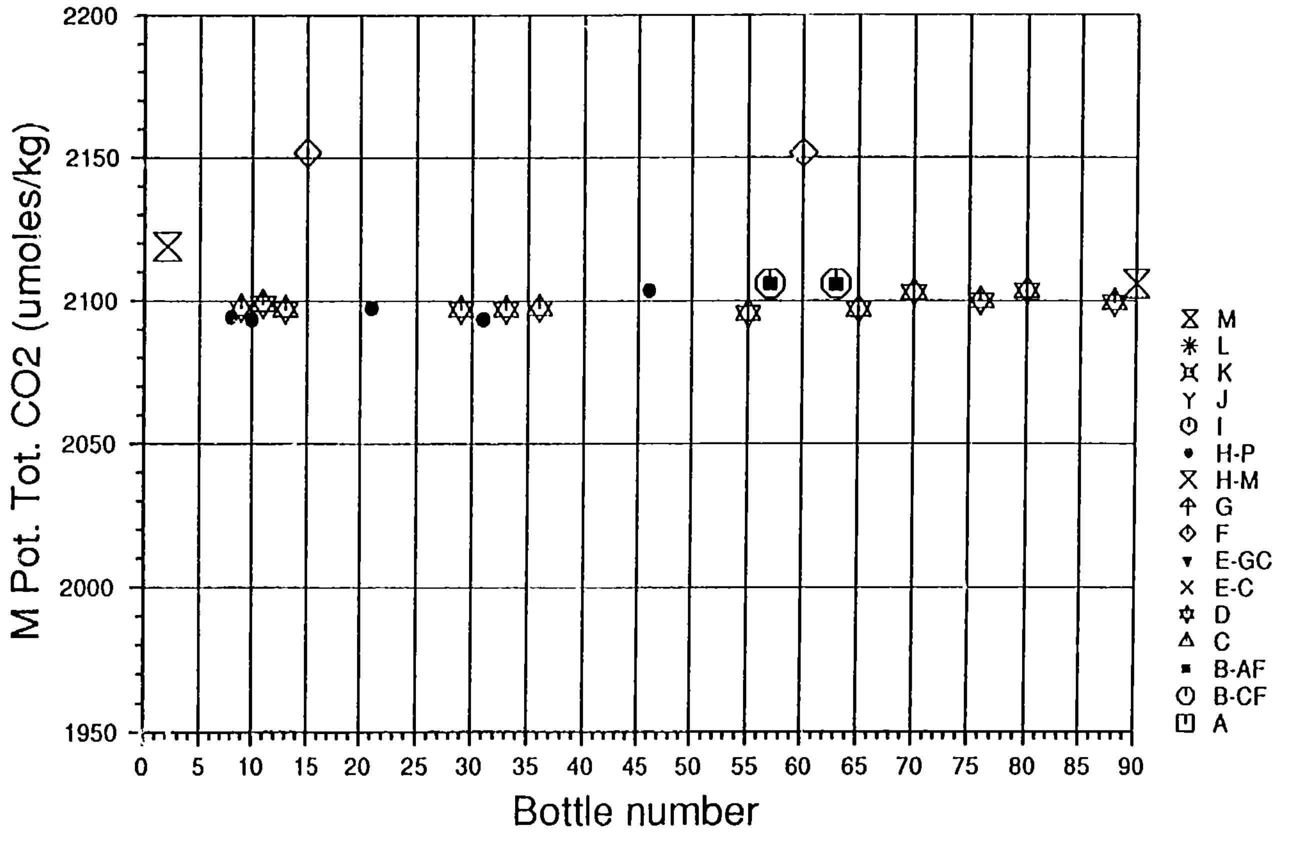


Fig. 7,d : BATCH 3 : Salinity about 35

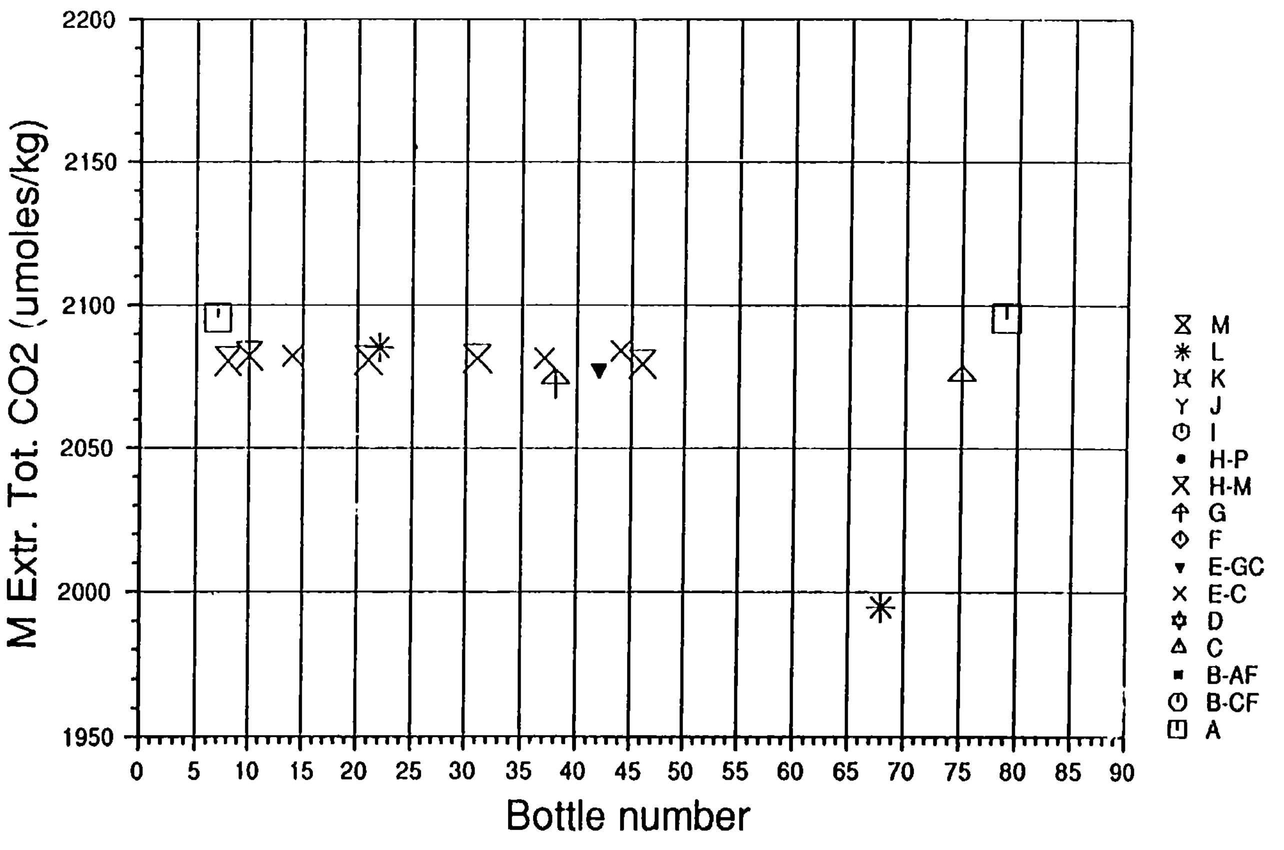


Fig. 7,e : BATCH 3 : Salinity about 35

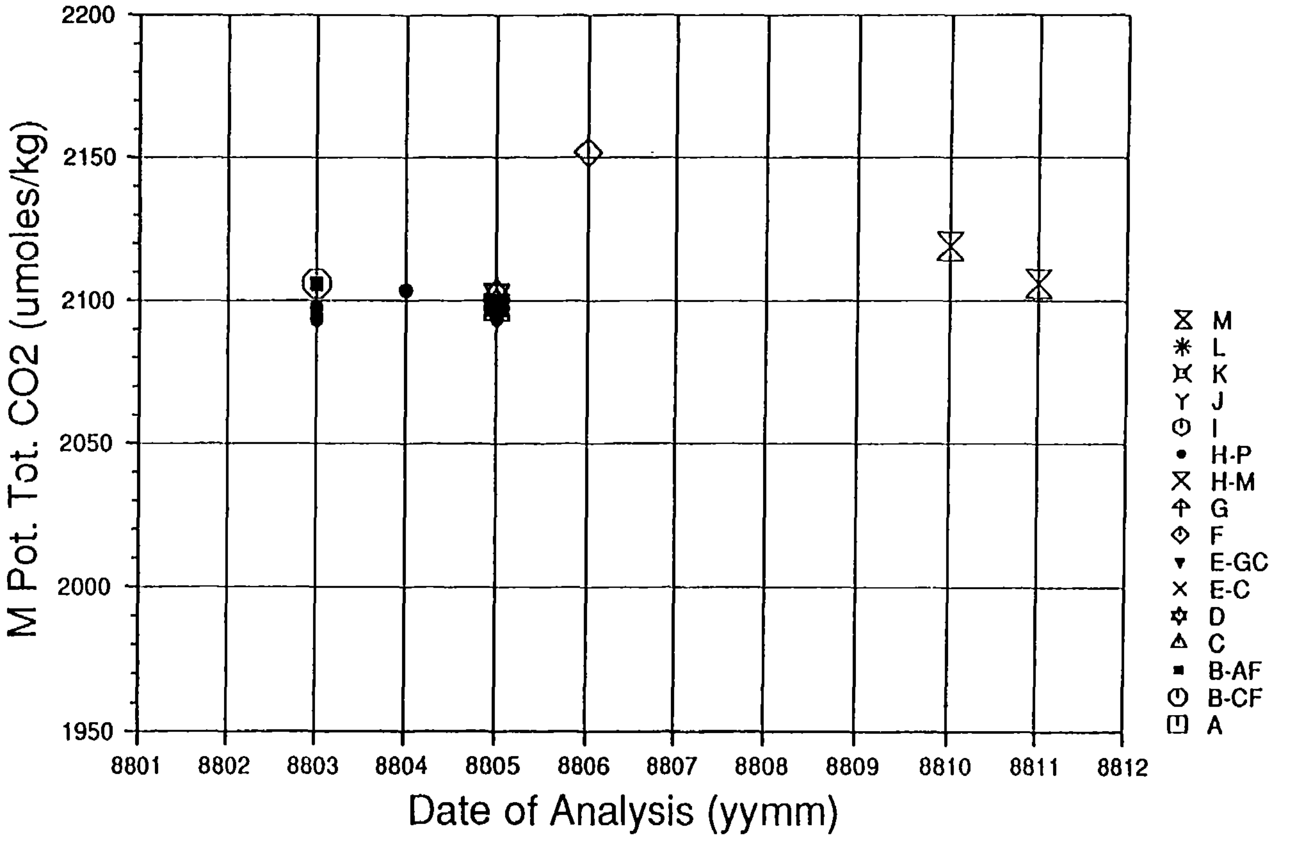


Fig. 7,f : BATCH 3 : Salinity about 35

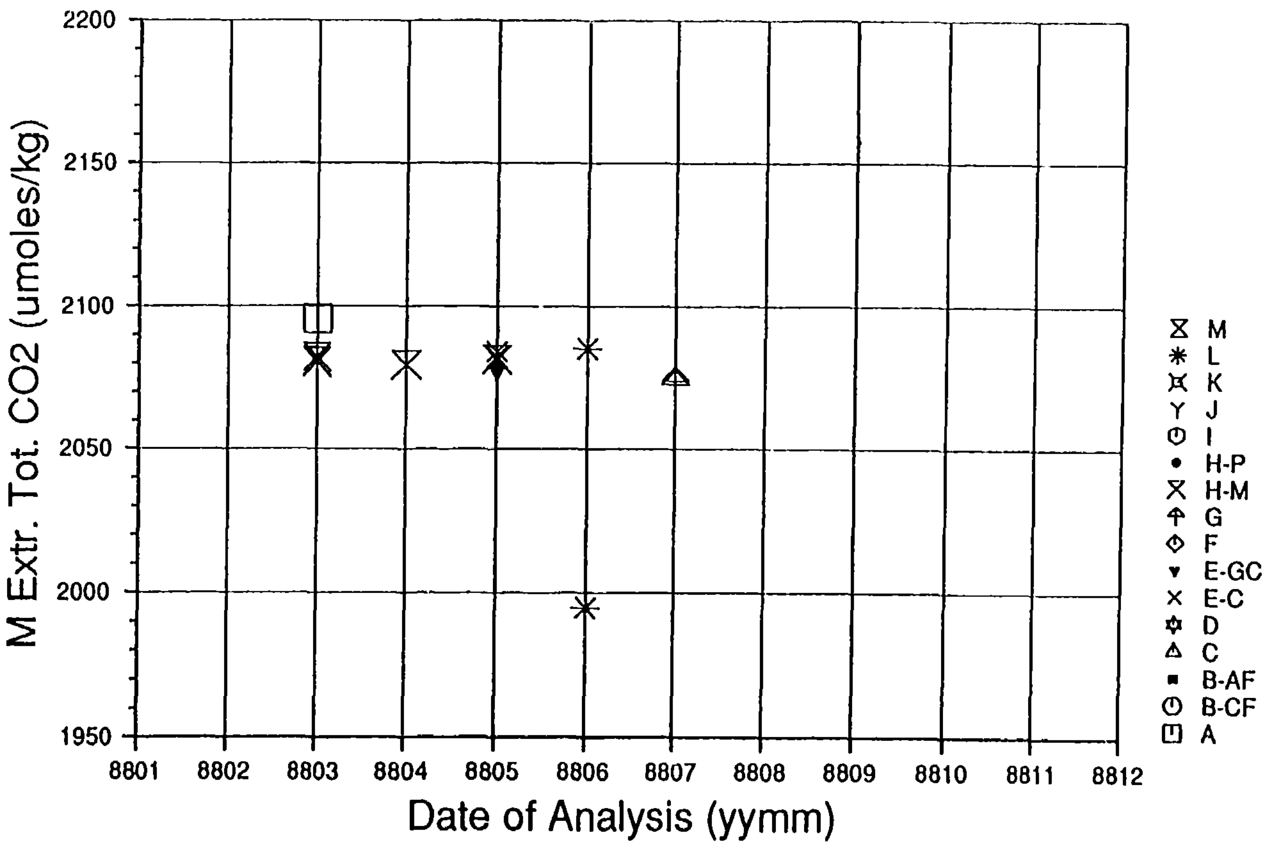


Fig. 7,g : BATCH 3 : Salinity about 35

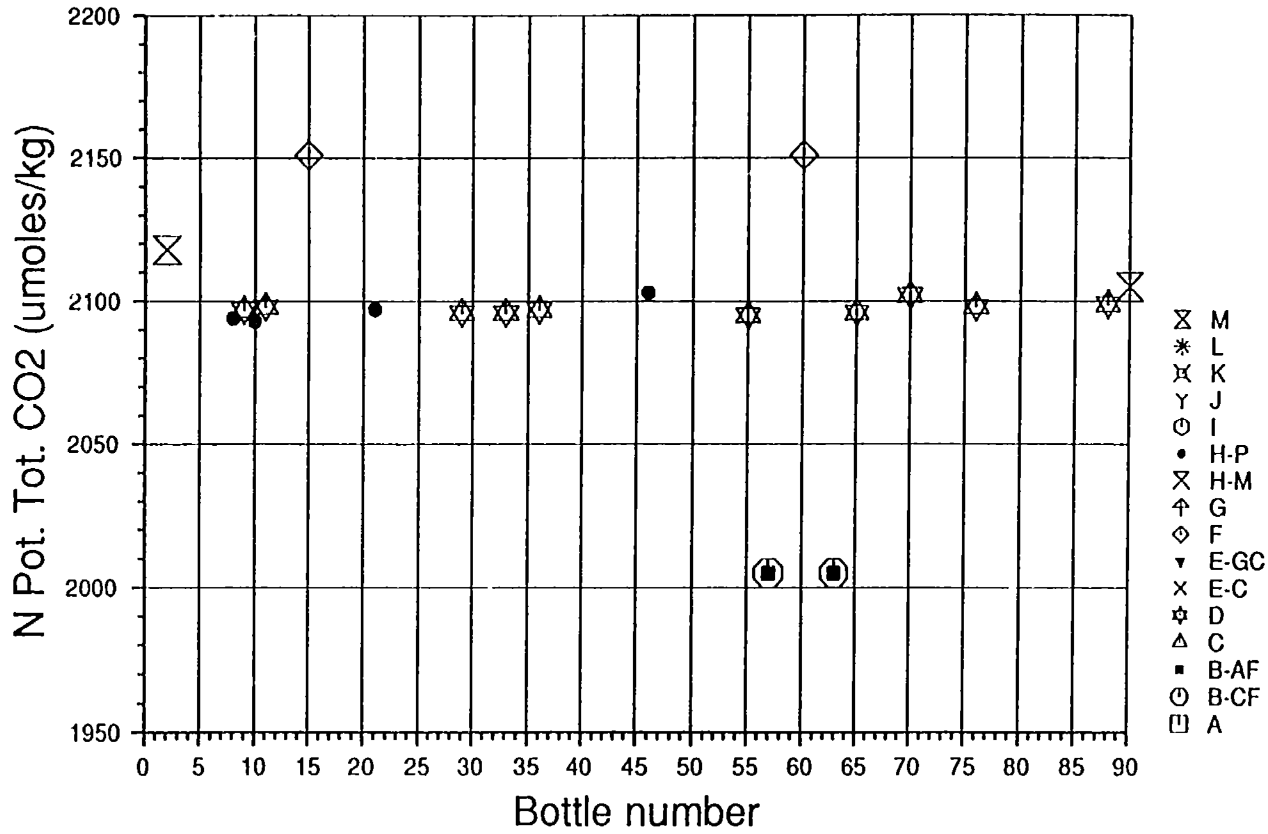


Fig. 7,h : BATCH 3 : Salinity about 35

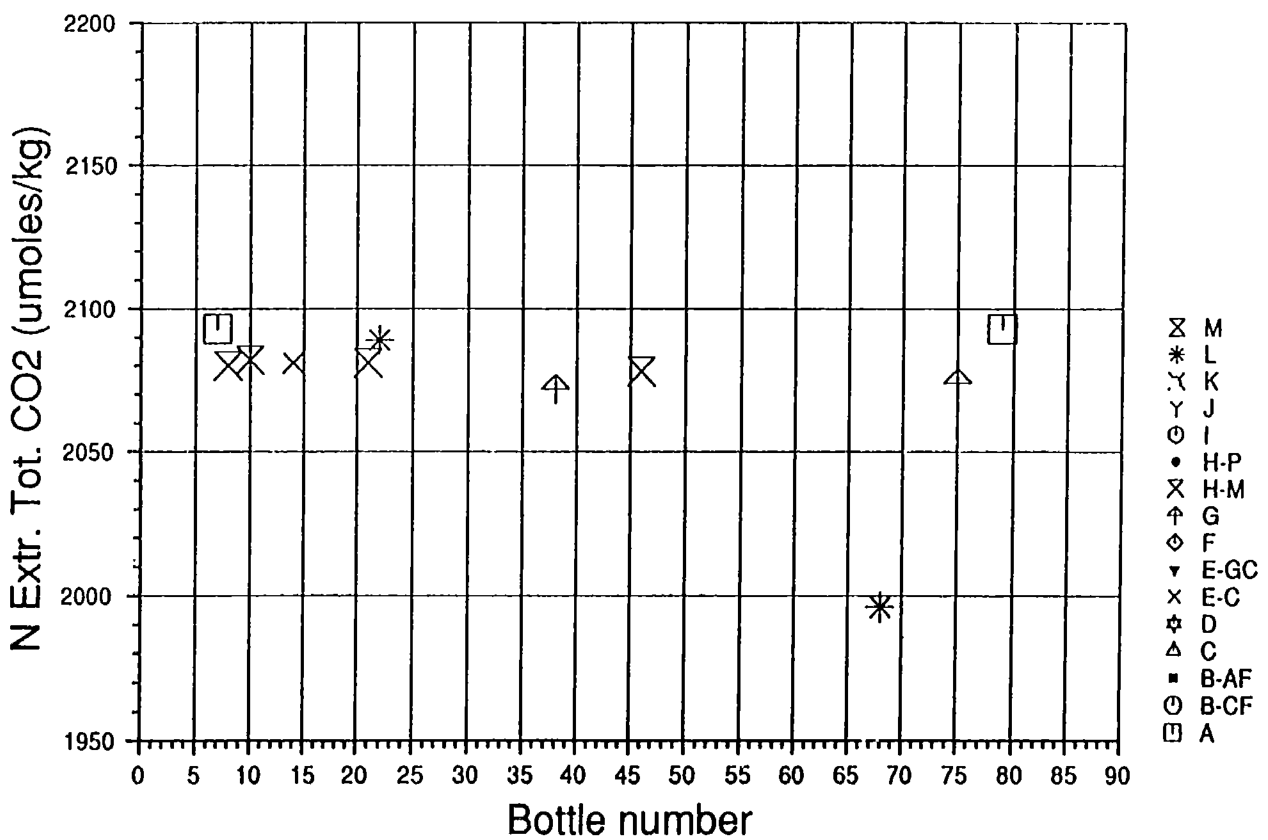


Fig. 8,a : BATCH 4 : Salinity about 38

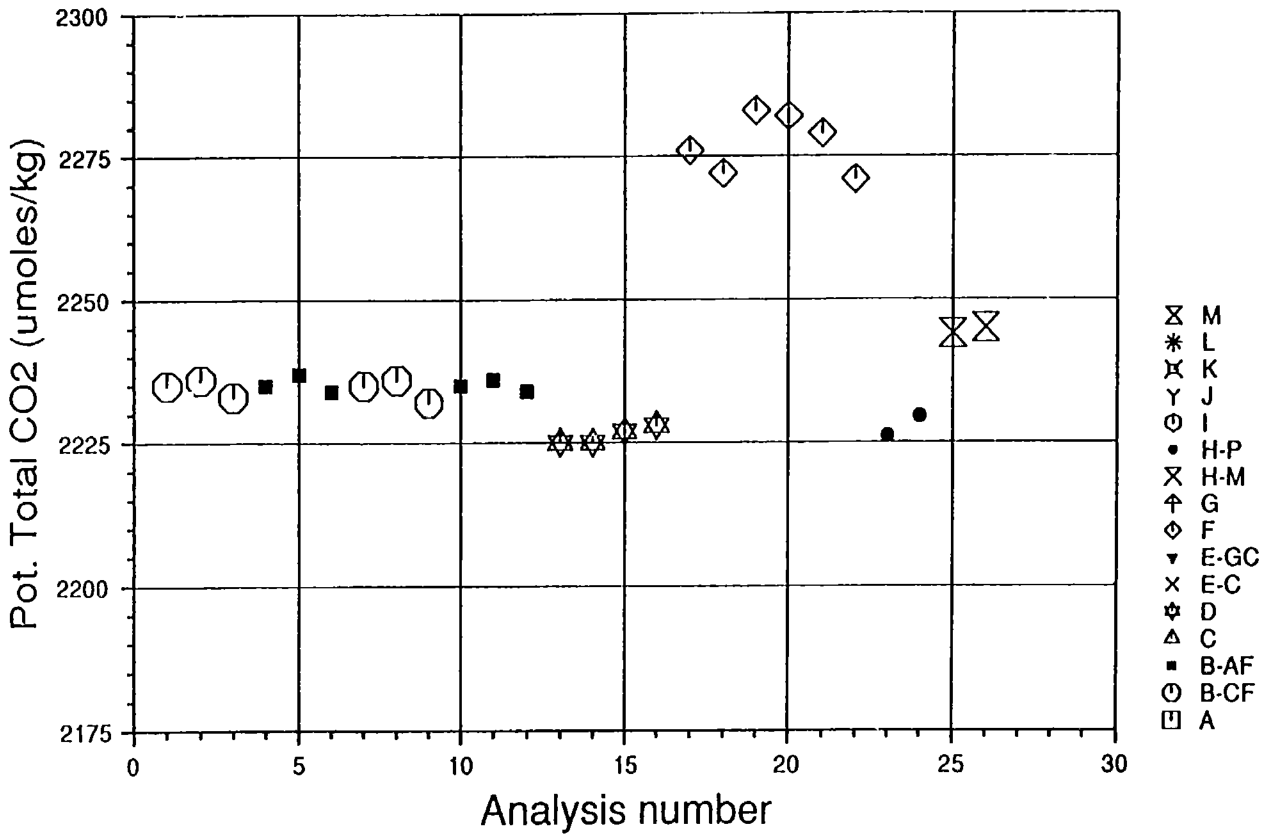


Fig. 8,b : BATCH 4 : Salinity about 38

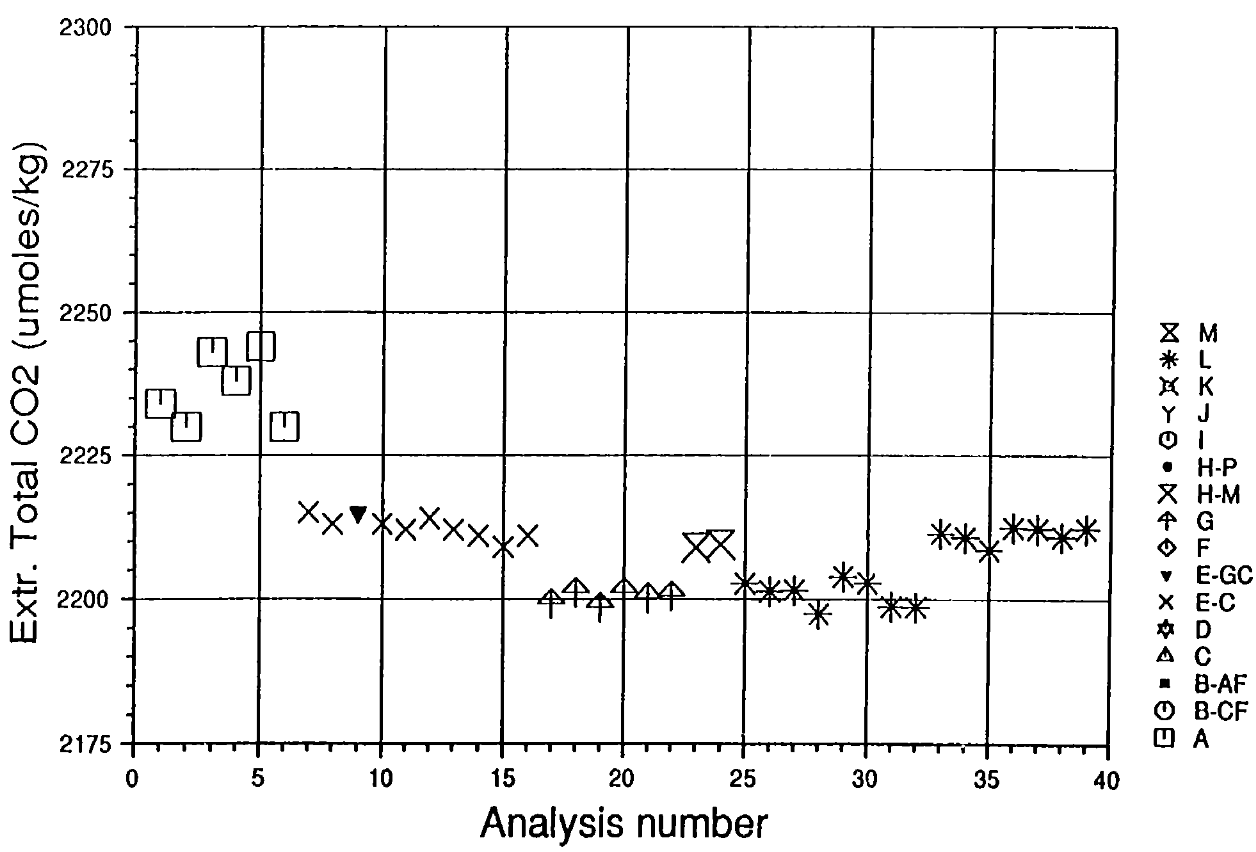


Fig. 8,c : BATCH 4 : Salinity about 38

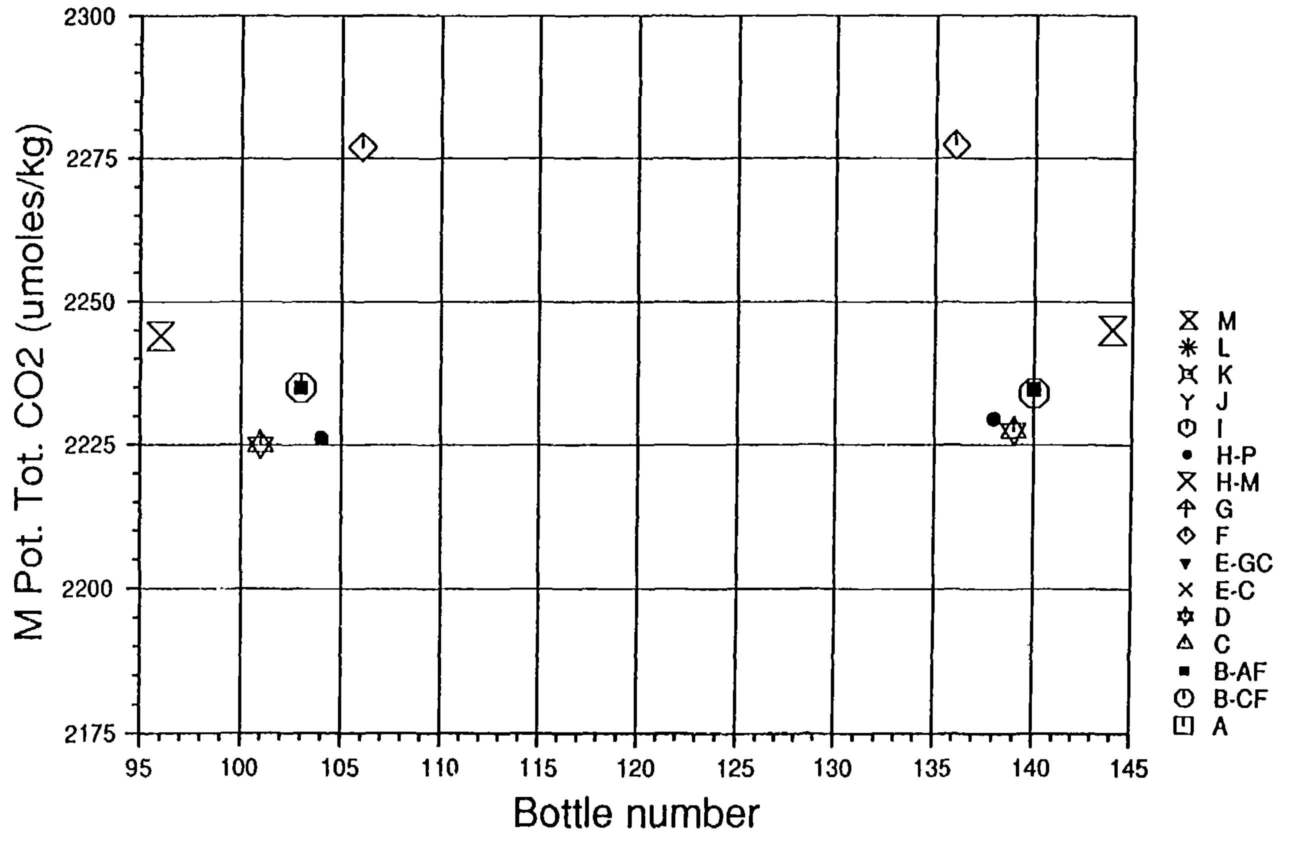


Fig. 8,d : BATCH 4 : Salinity about 38

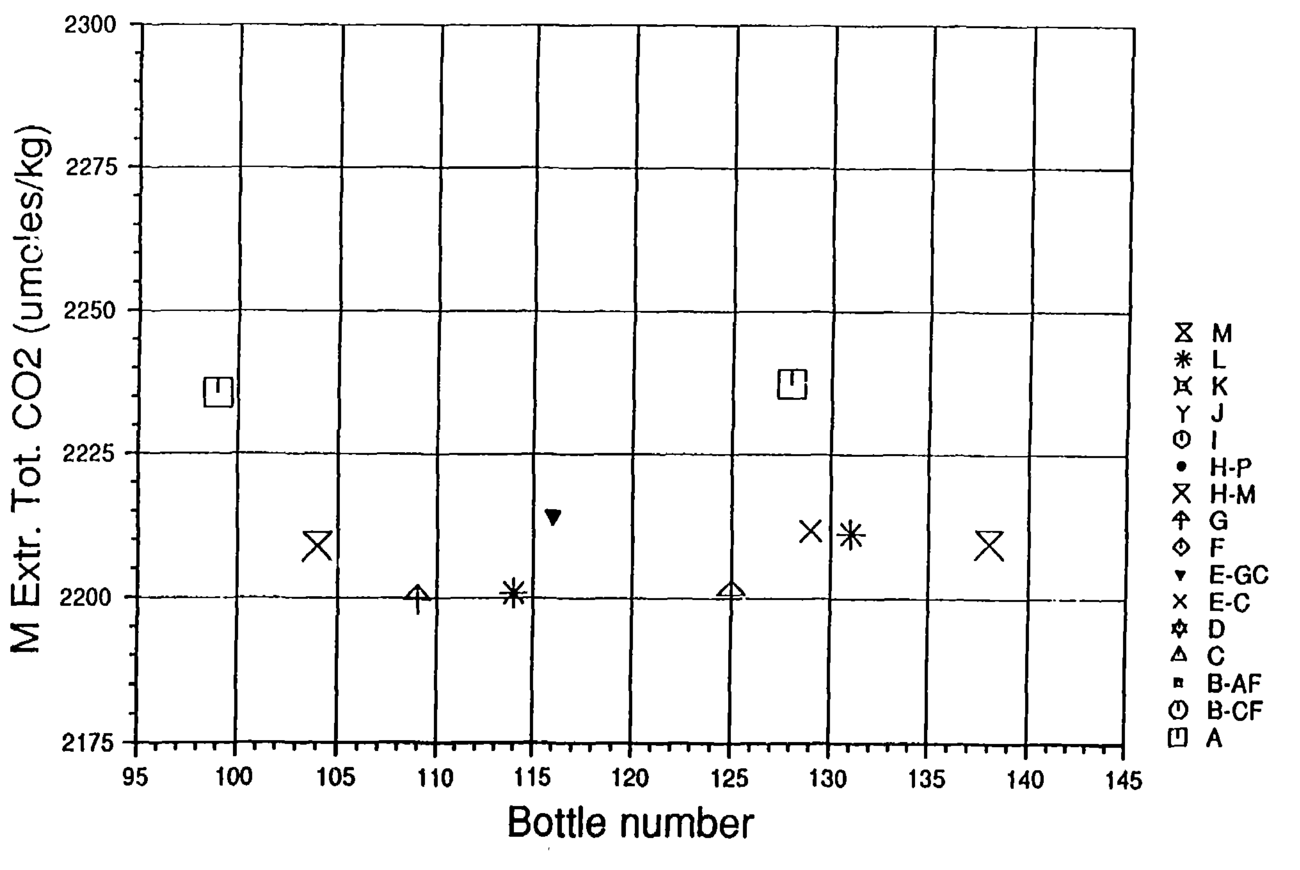


Fig. 8,e : BATCH 4 : Salinity about 38

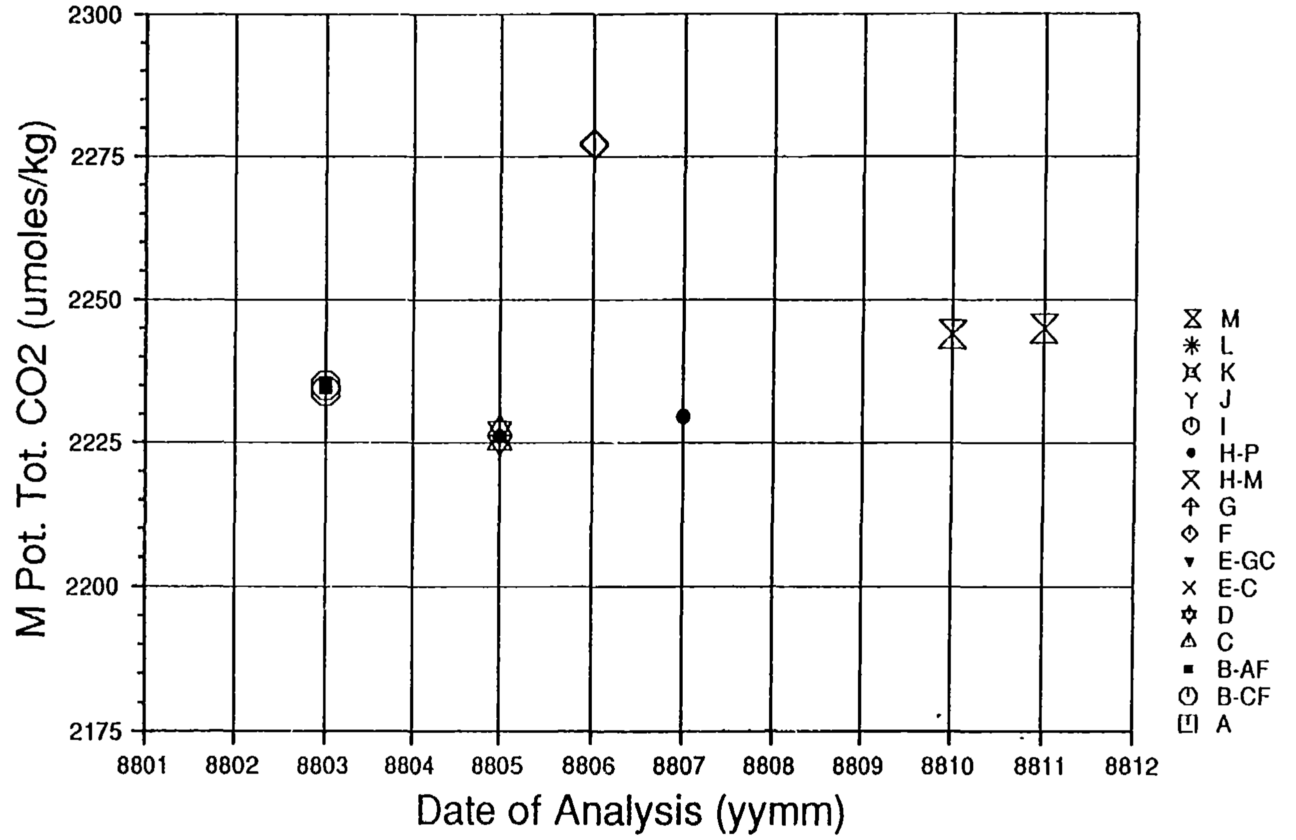


Fig. 8,f : BATCH 4 : Salinity about 38

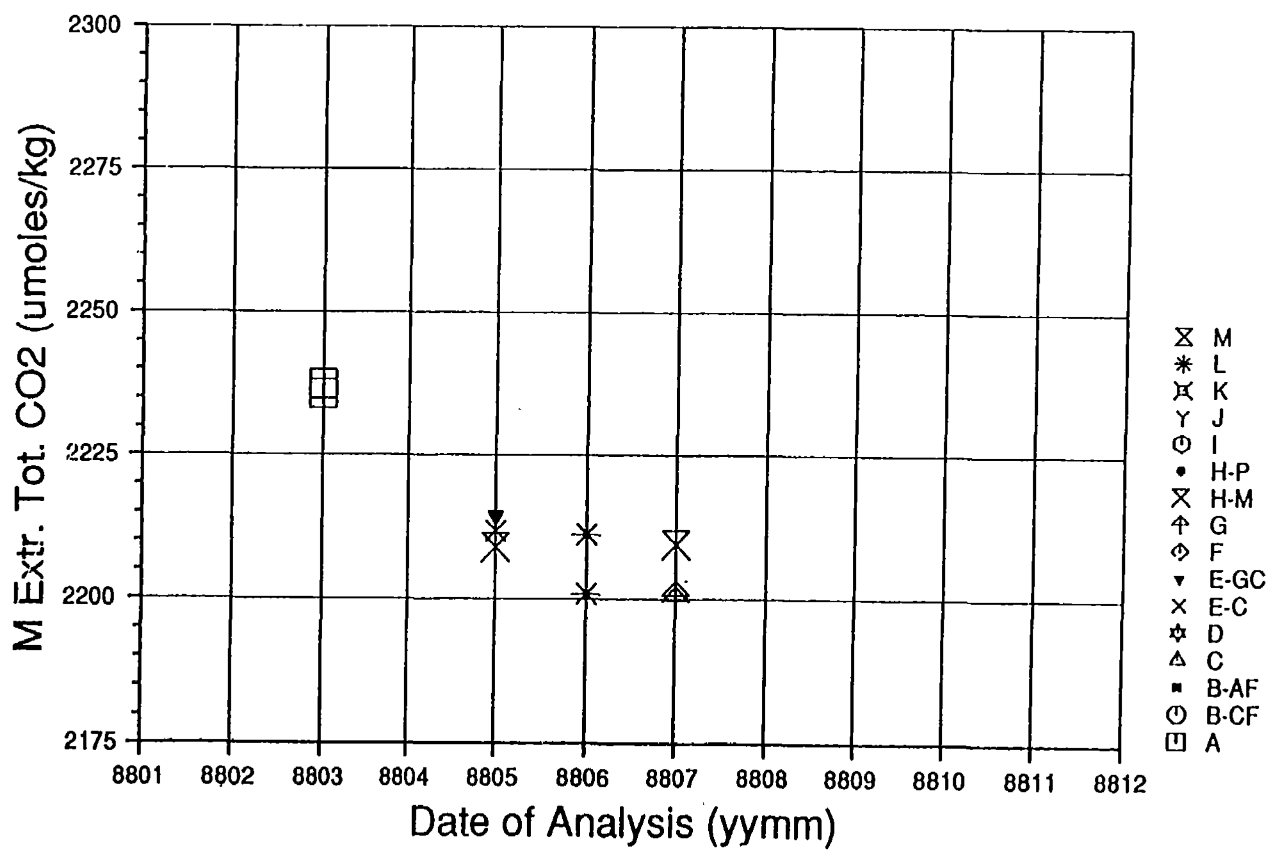


Fig. 8,g : BATCH 4 : Salinity about 38

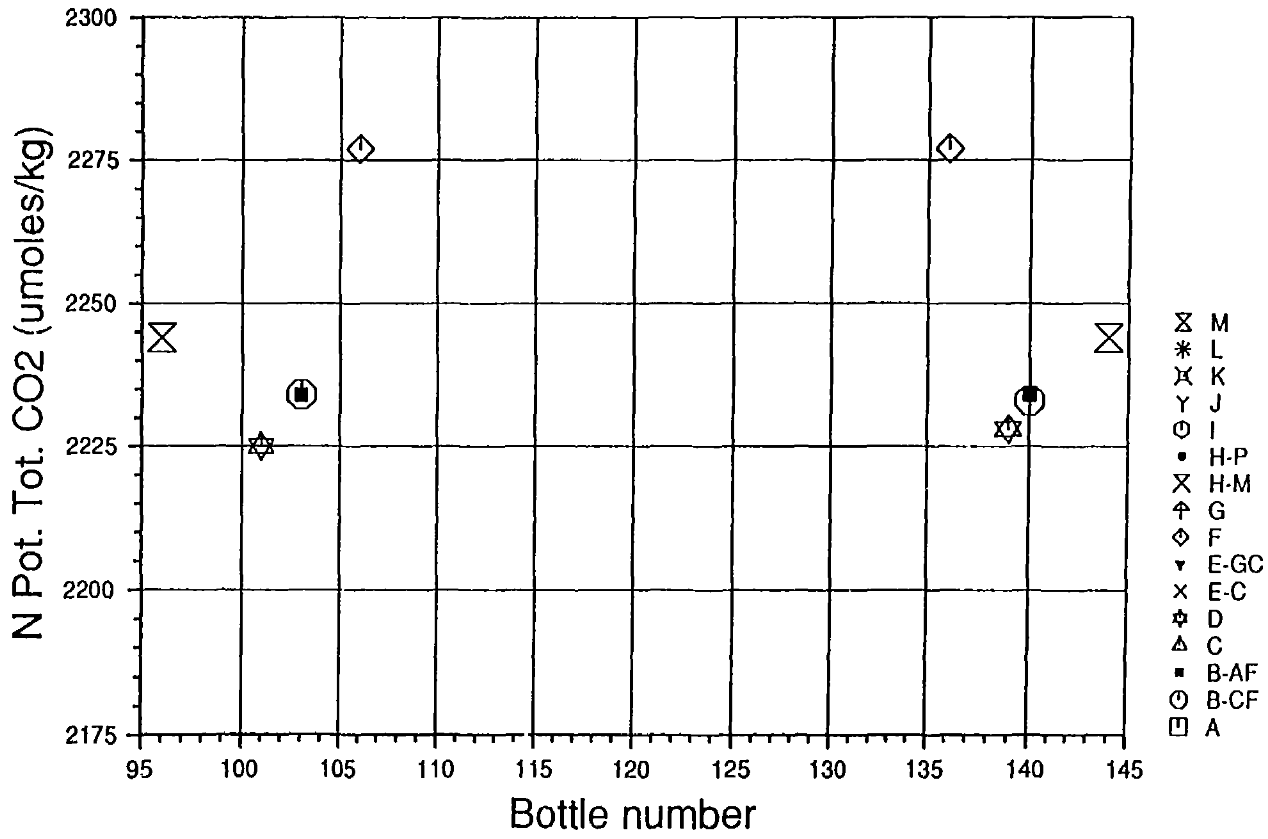


Fig. 8,h : BATCH 4 : Salinity about 38

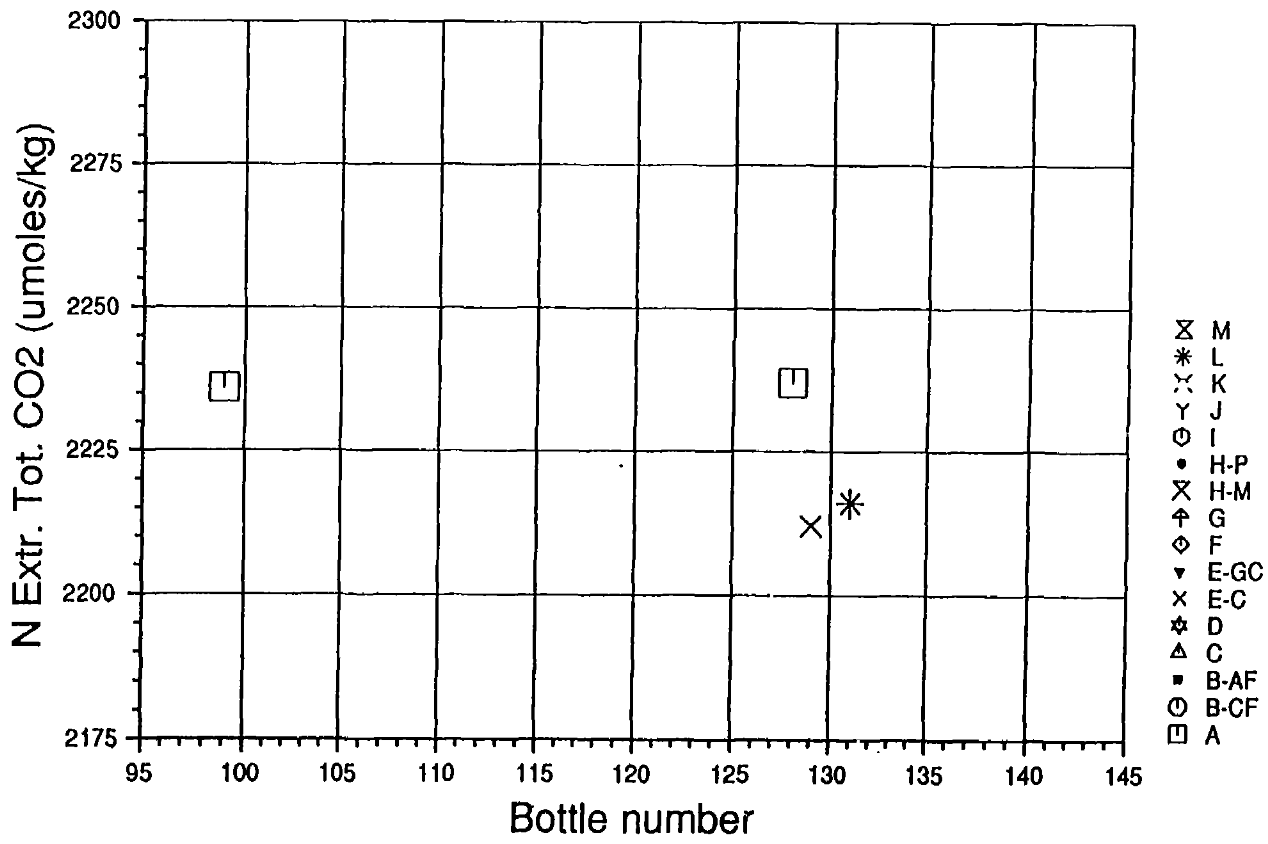


Fig. 9,a : BATCH 1 : Salinity about 8

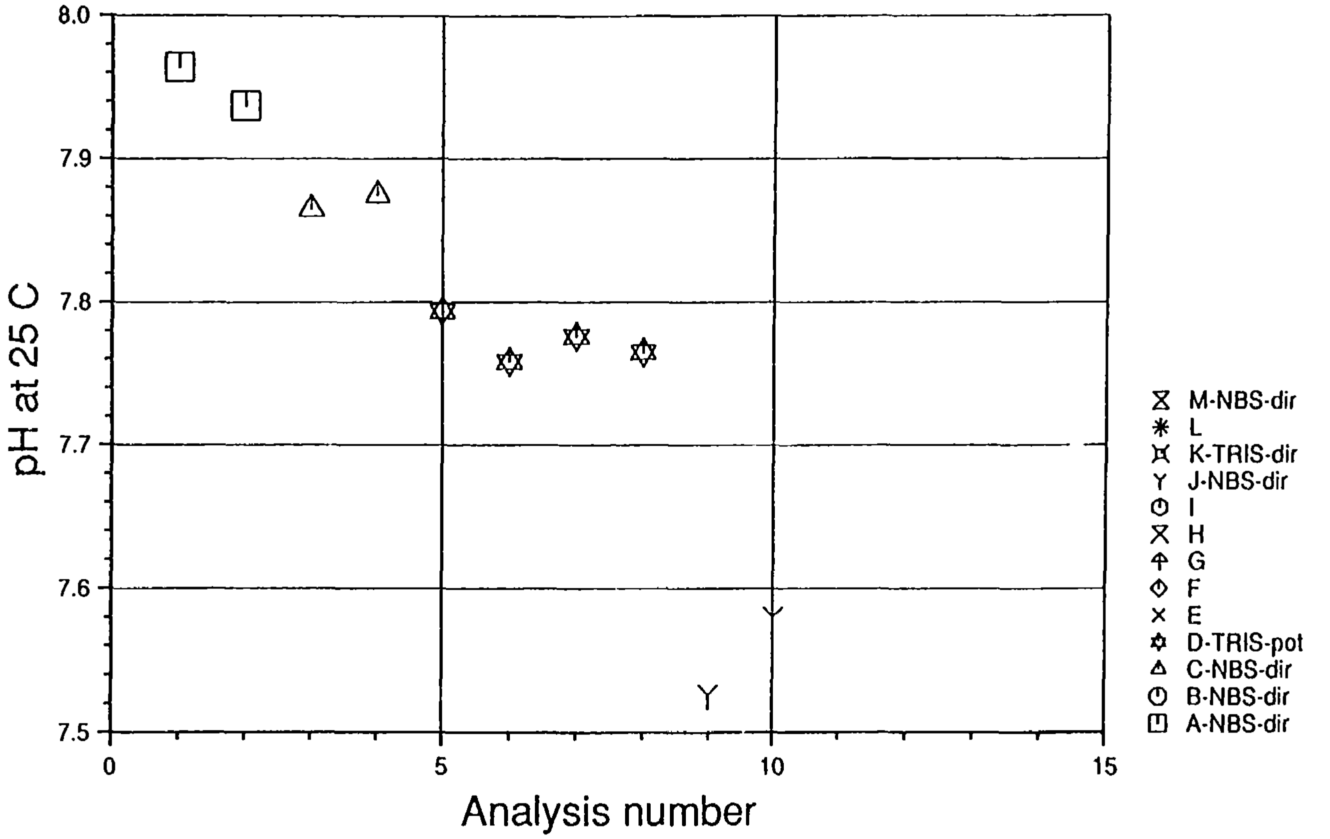


Fig. 9,b : BATCH 1 : Salinity about 8

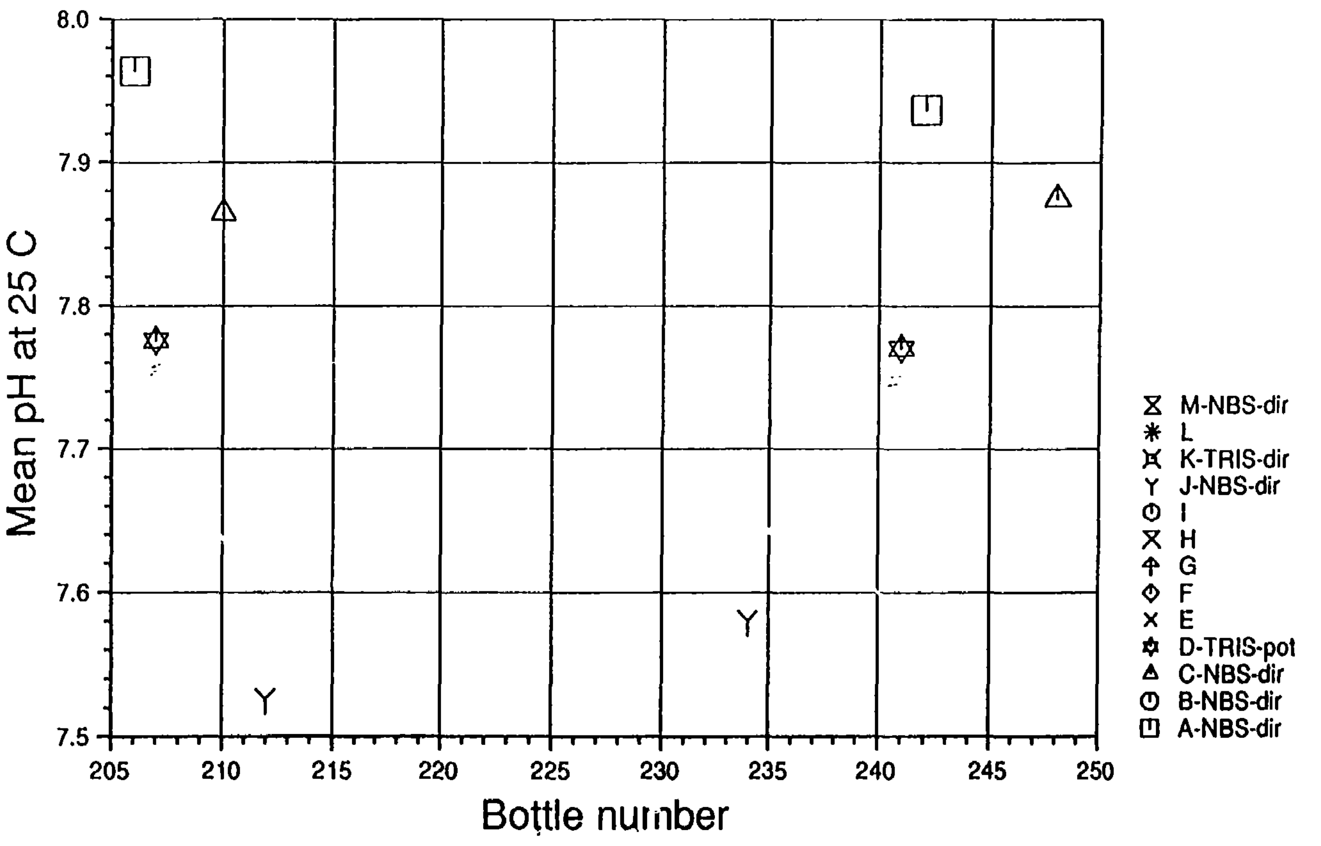


Fig. 9,c : BATCH 1 : Salinity about 8

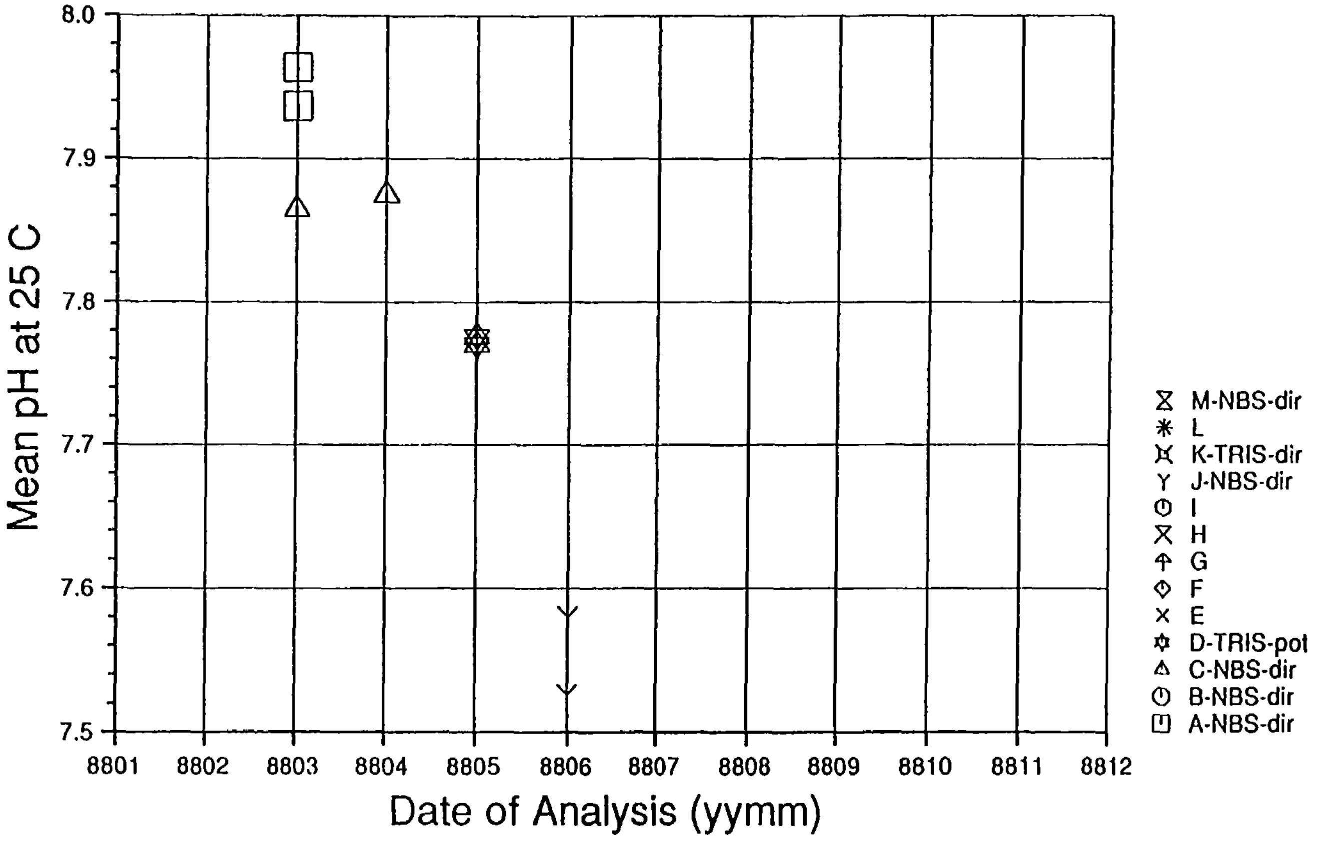


Fig. 10,a : BATCH 2 : Salinity about 30

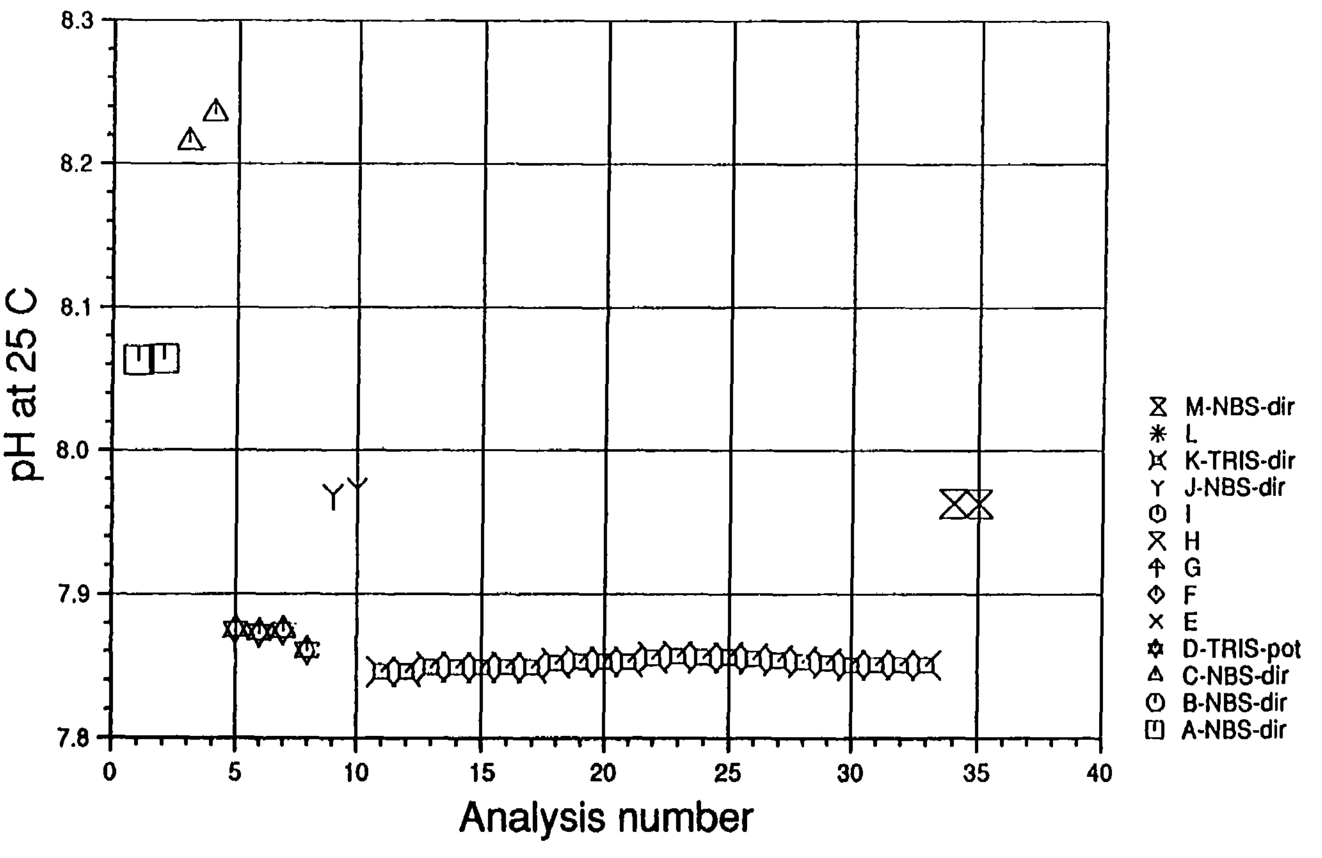


Fig. 10,b : BATCH 2 : Salinity about 30

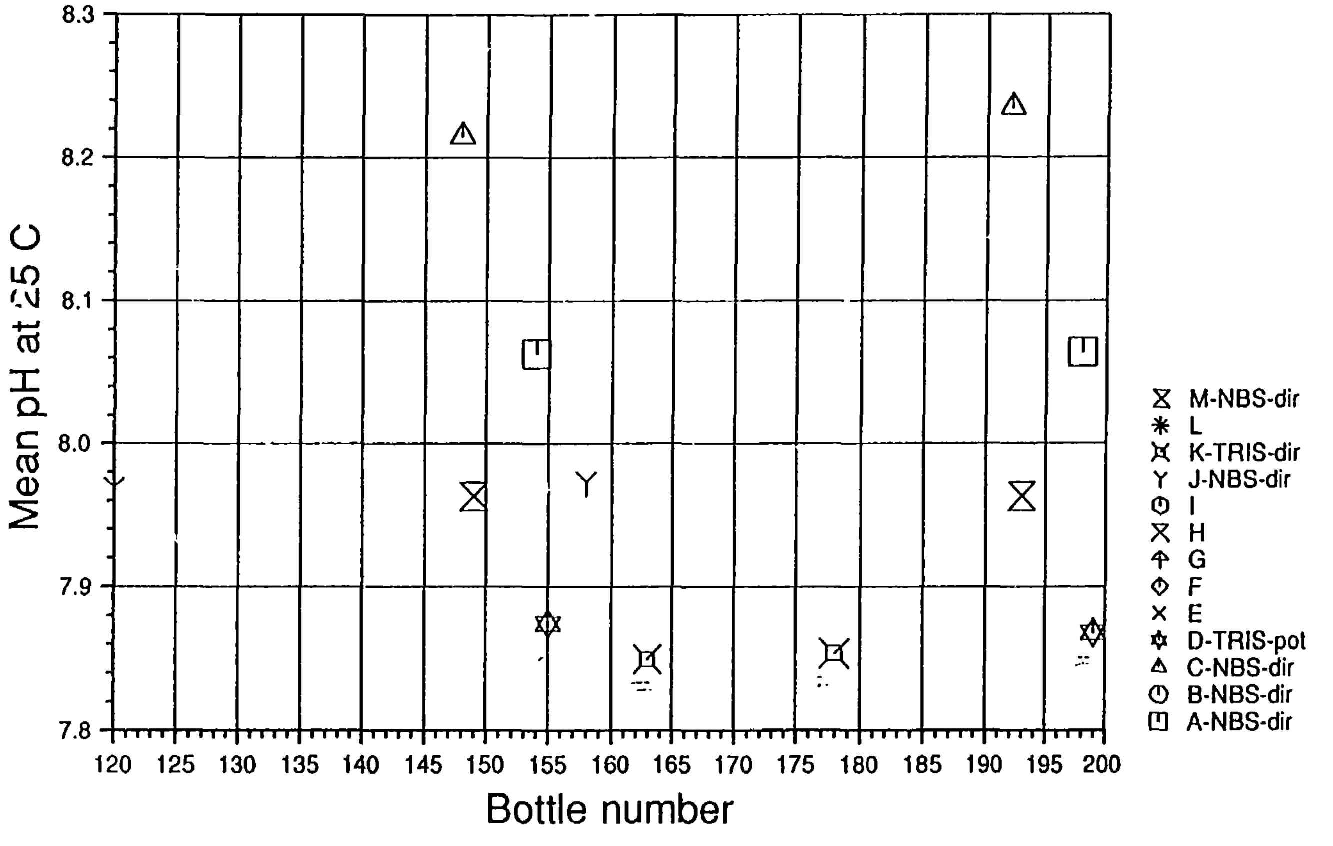


Fig. 10,c : BATCH 2 : Salinity about 30

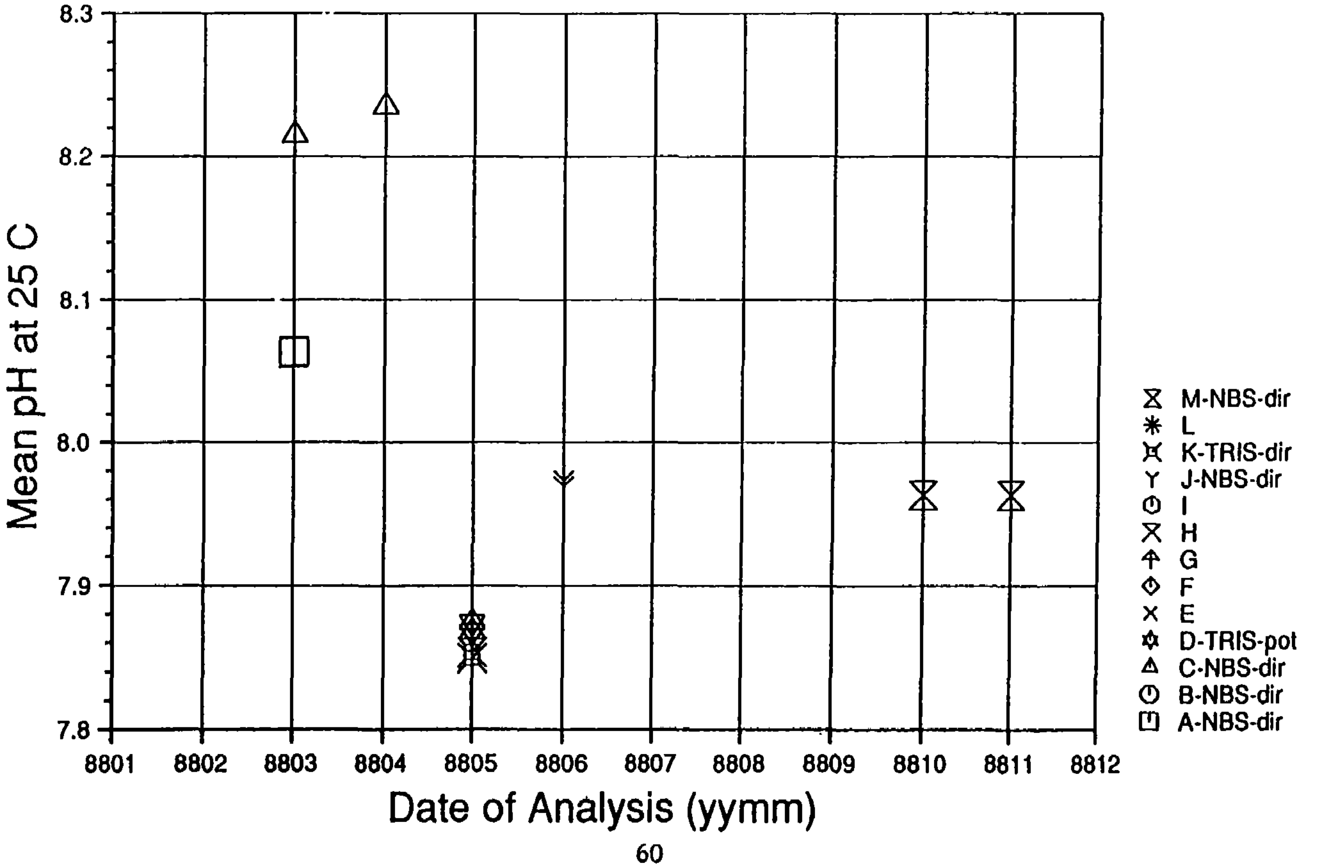


Fig. 11,a :

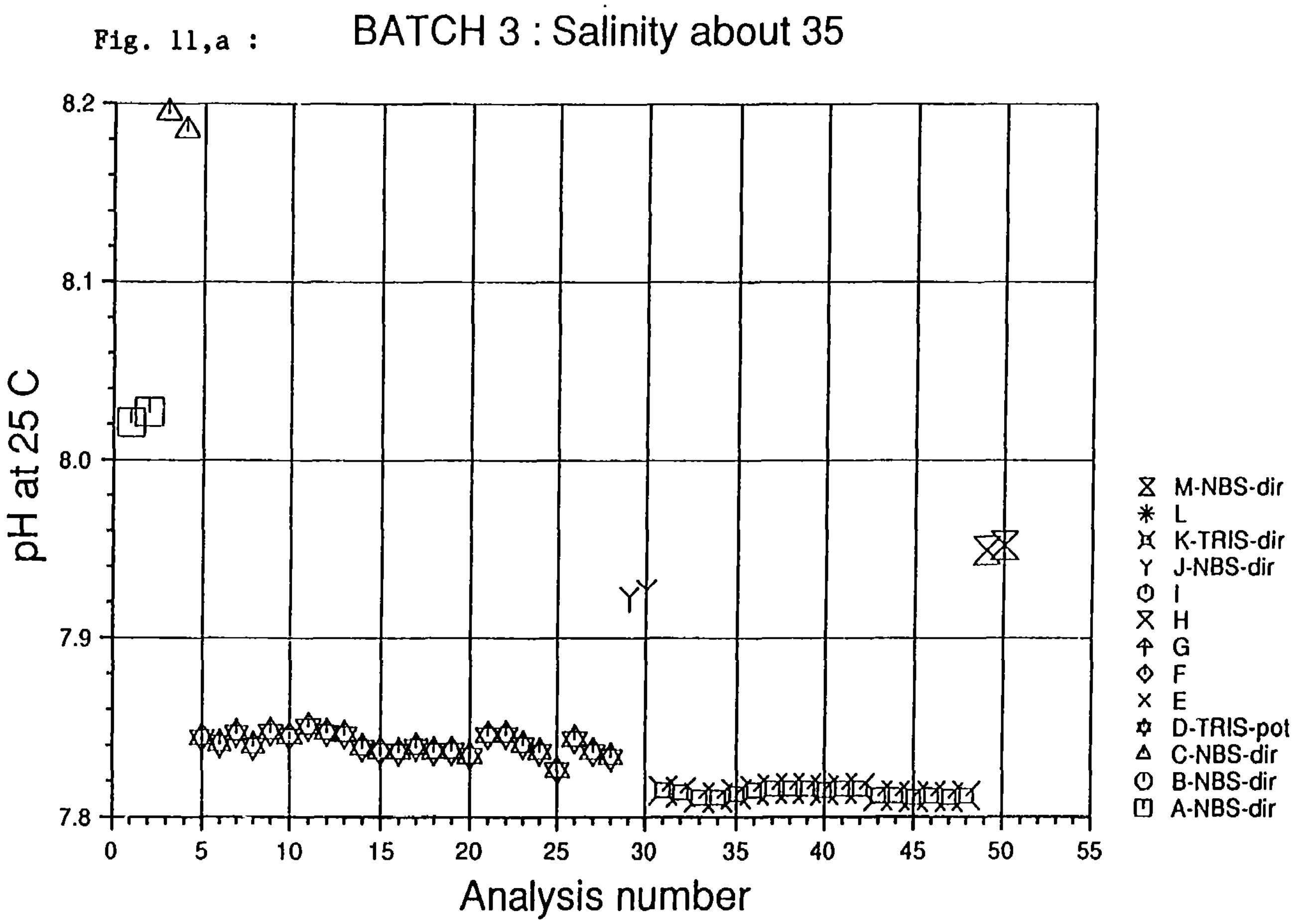


Fig. 11,b :

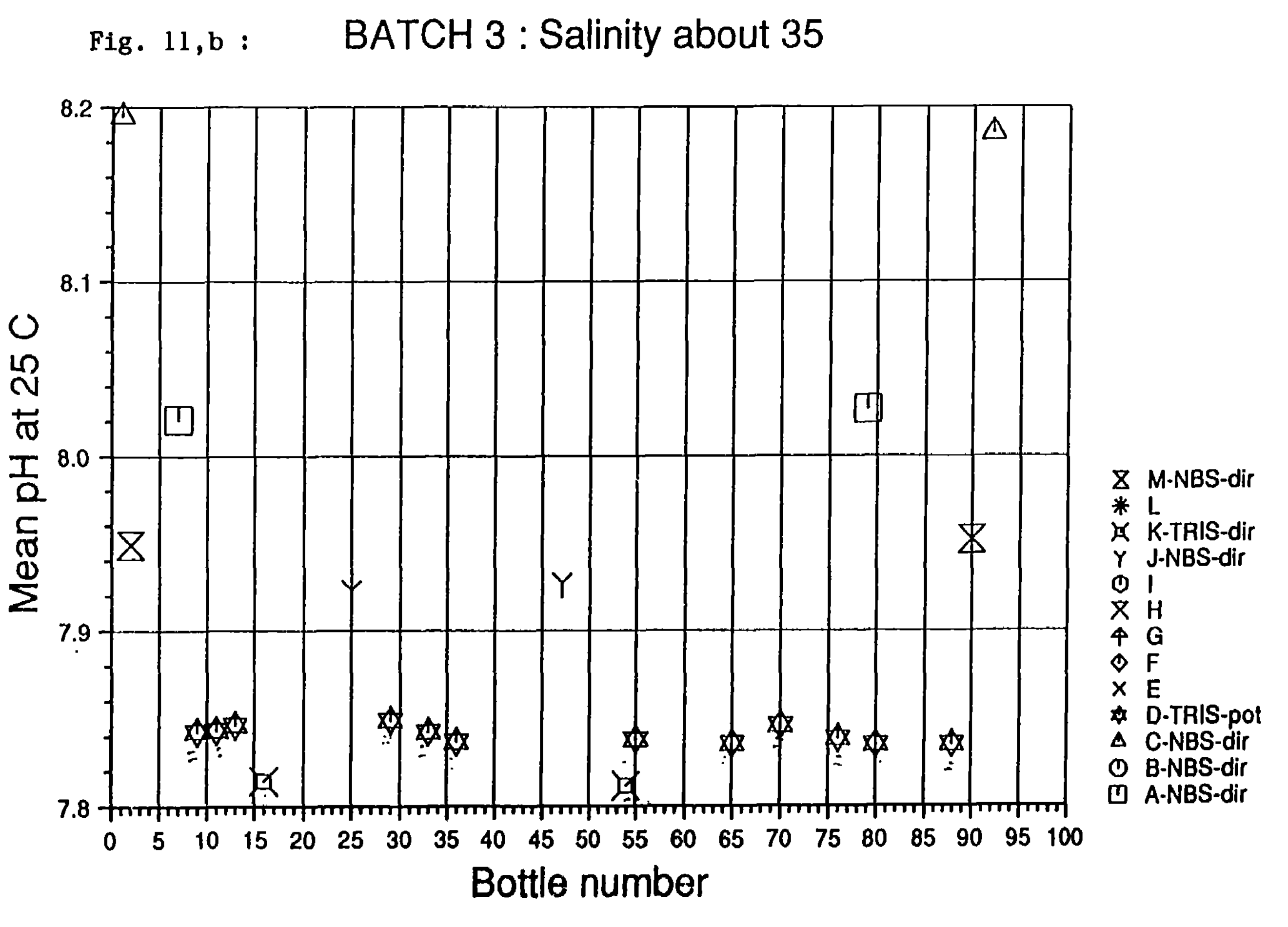


Fig. 11,c : BATCH 3 : Salinity about 35

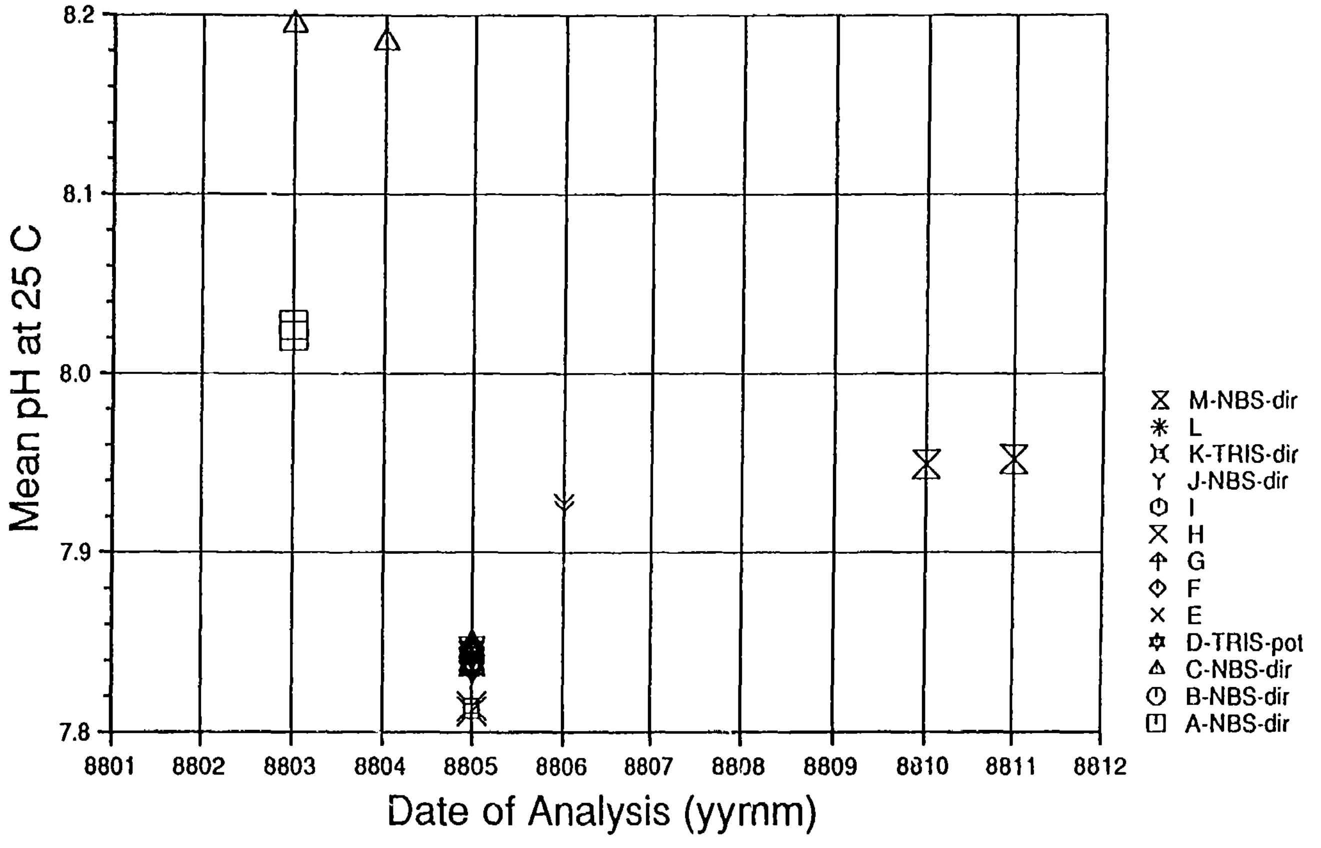


Fig. 12,a : BATCH 4 : Salinity about 38

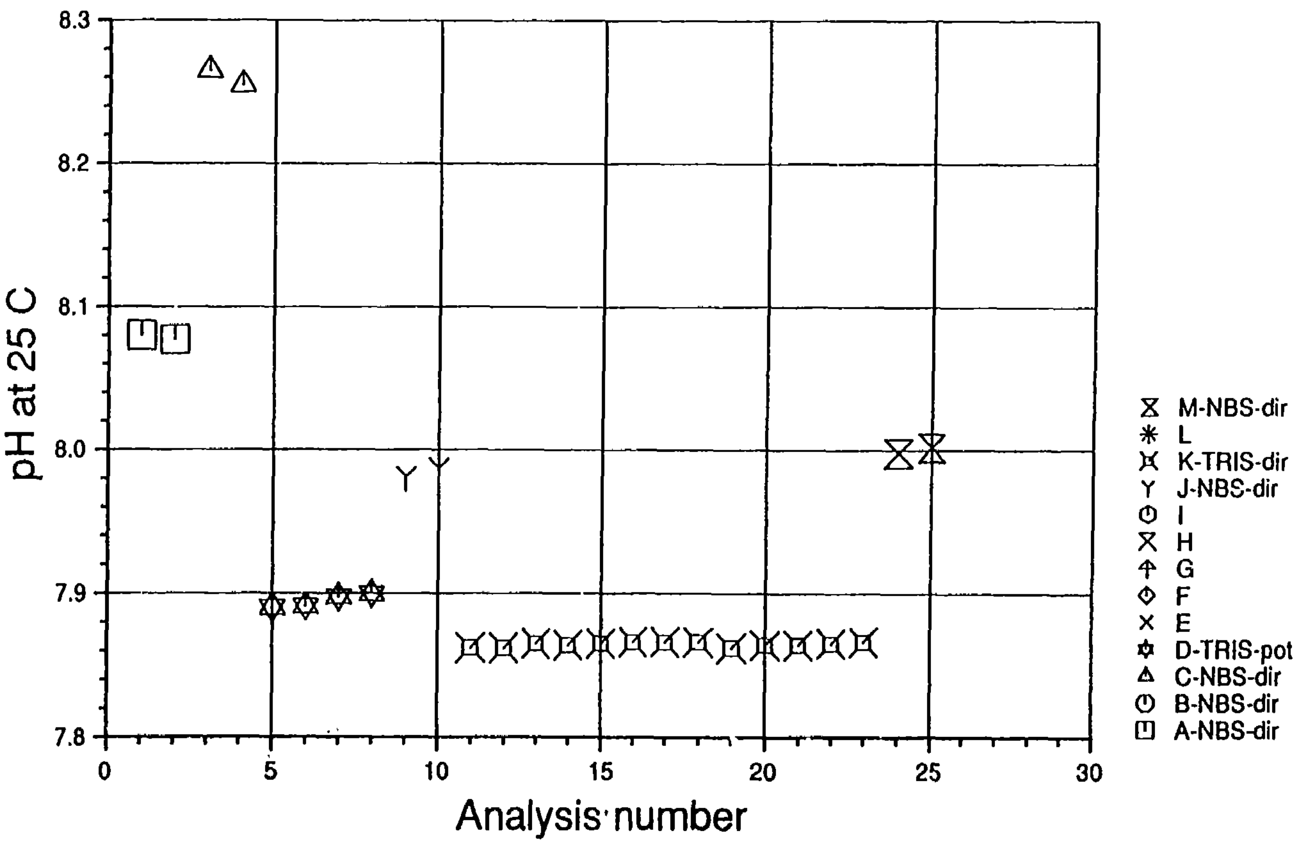


Fig. 12,b : BATCH 4 : Salinity about 38

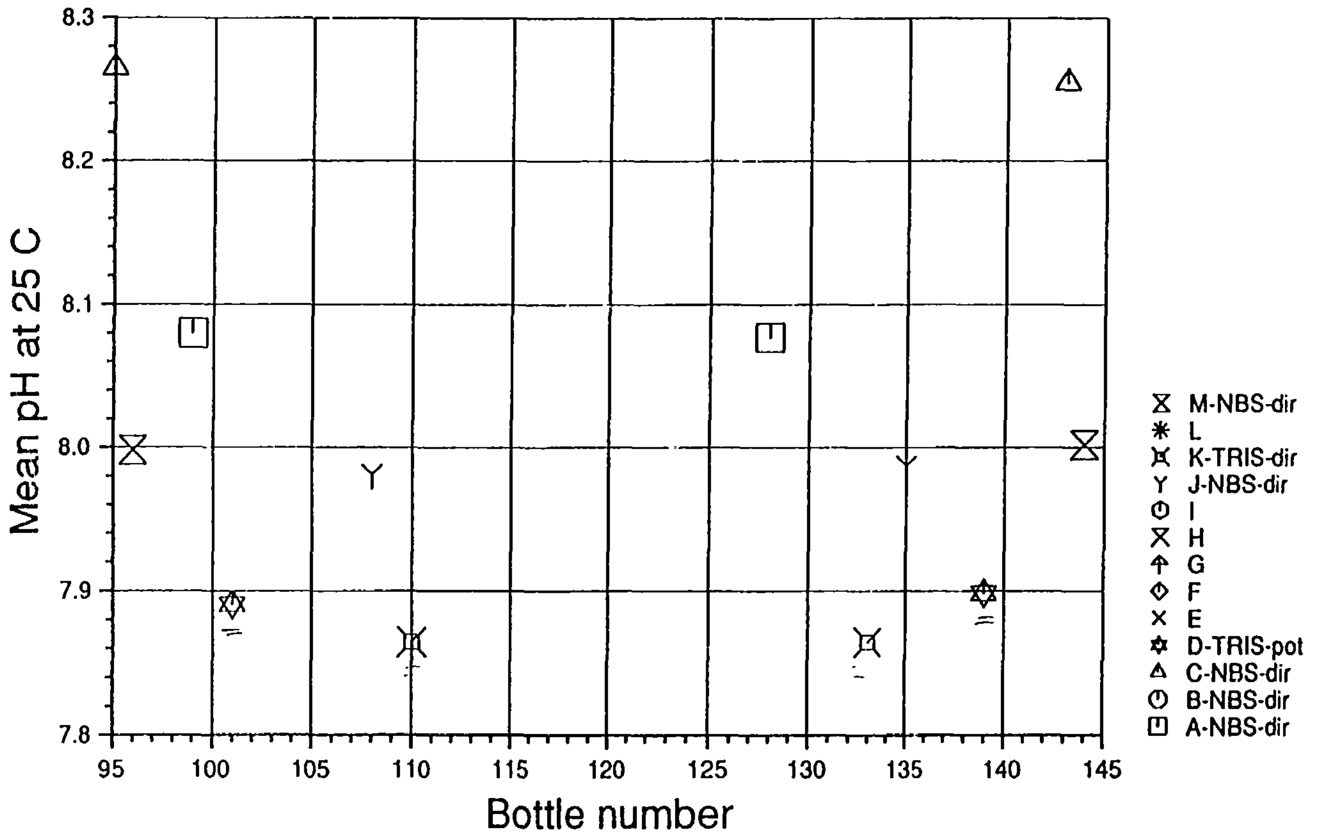


Fig. 12,c : BATCH 4 : Salinity about 38

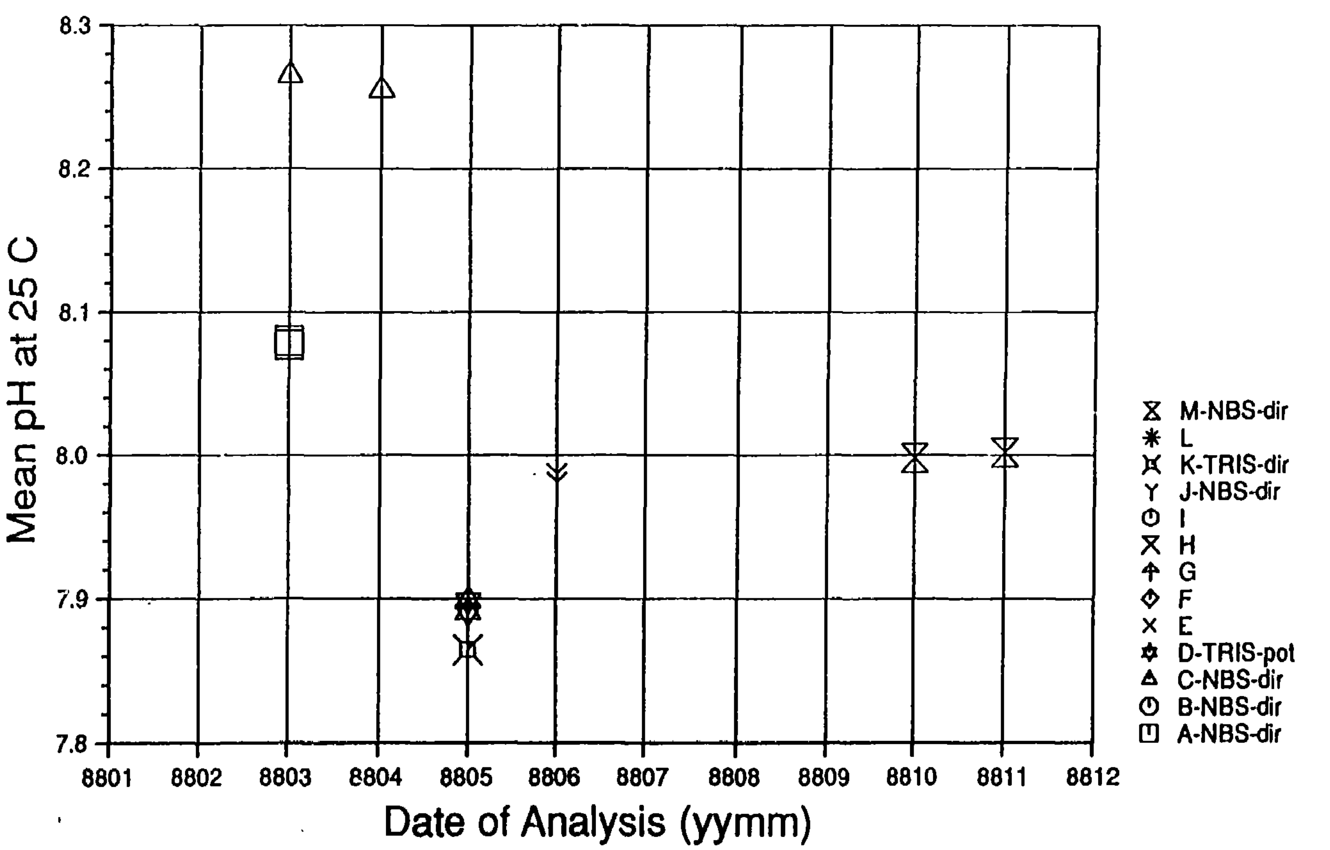


Fig. 13,a : BATCH 1 : Salinity about 8

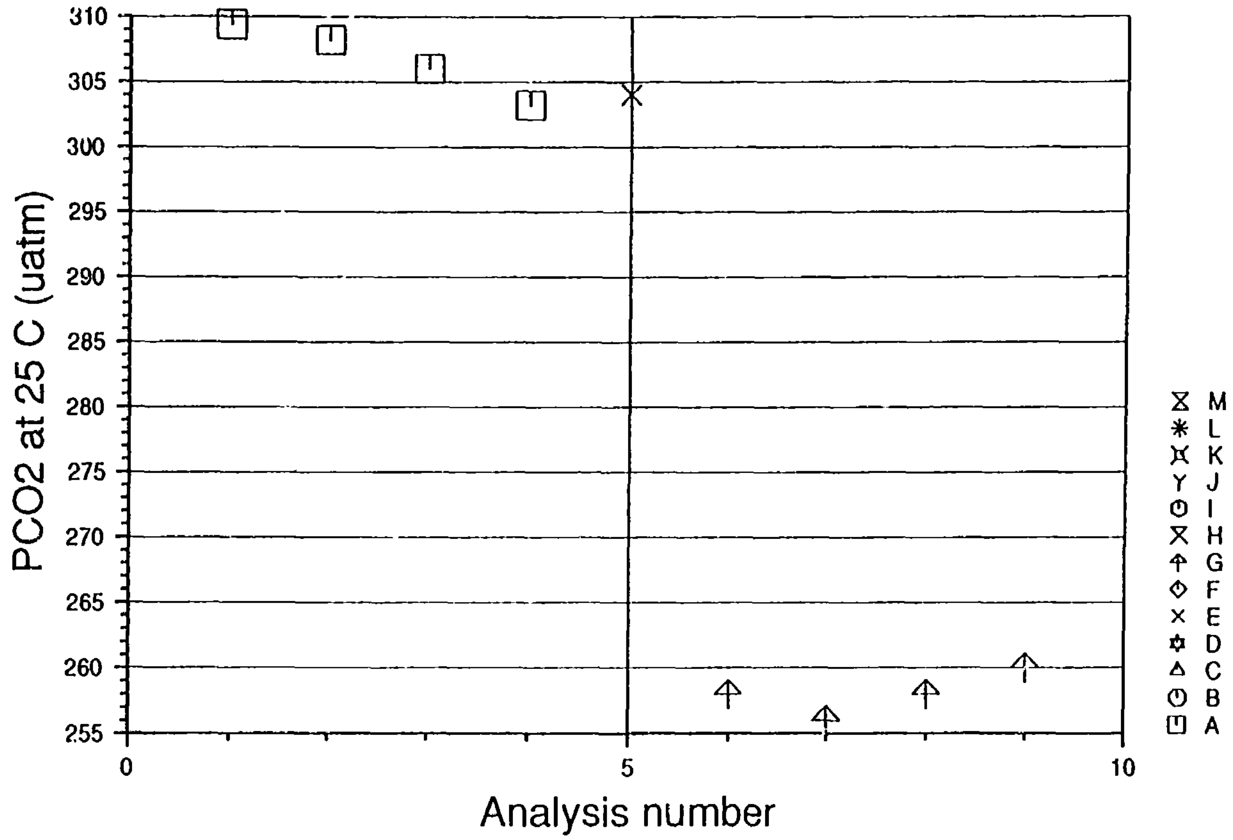


Fig. 13,b : BATCH 1 : Salinity about 8

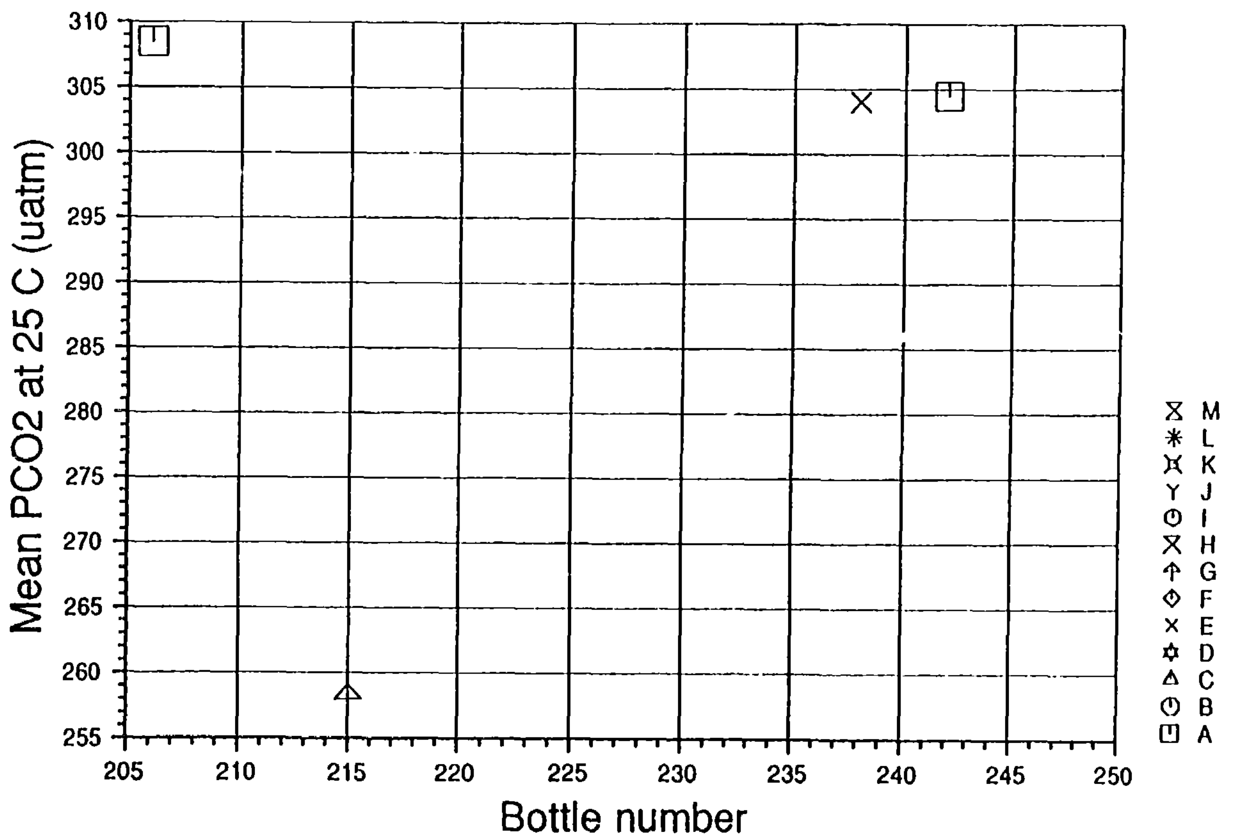


Fig. 13,c :

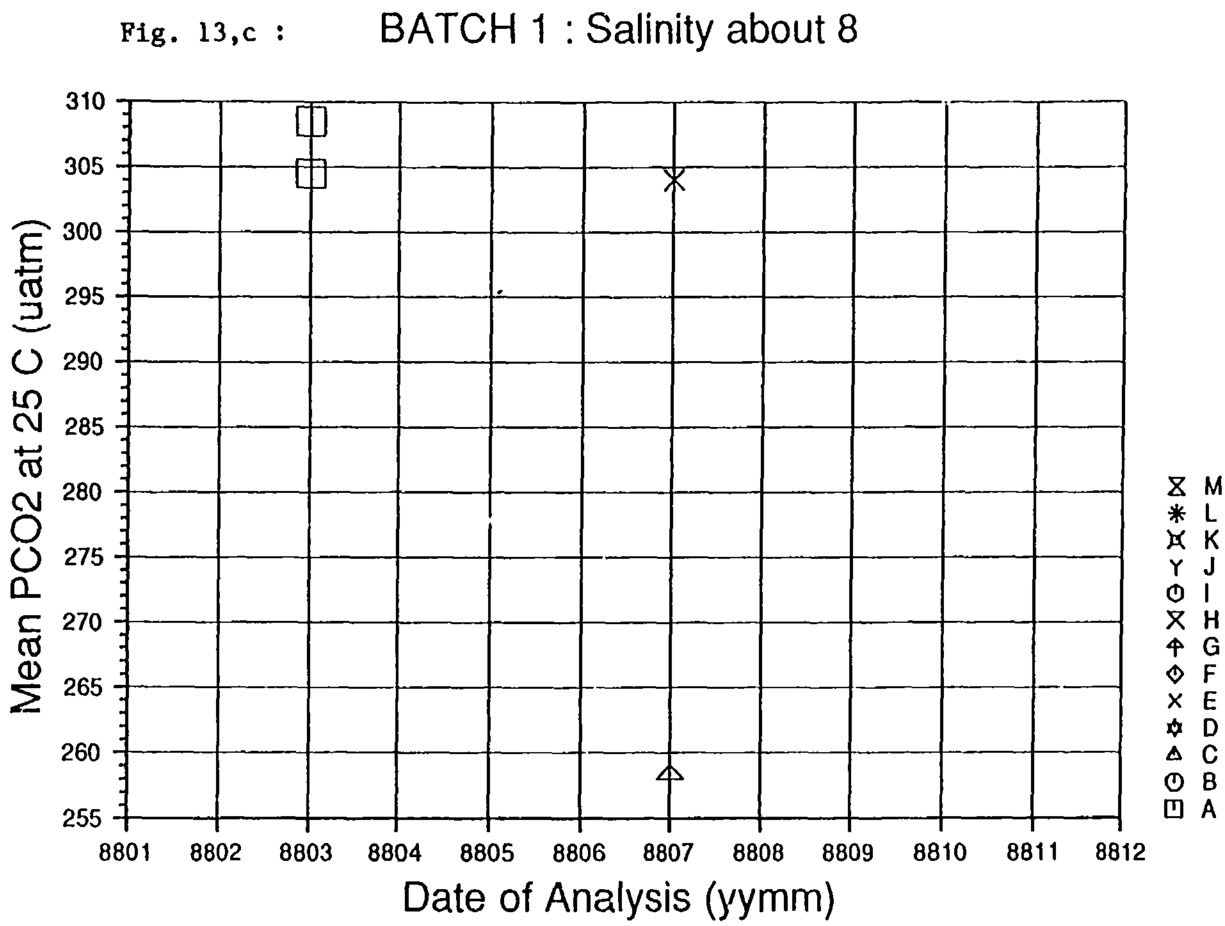


Fig. 14,a :

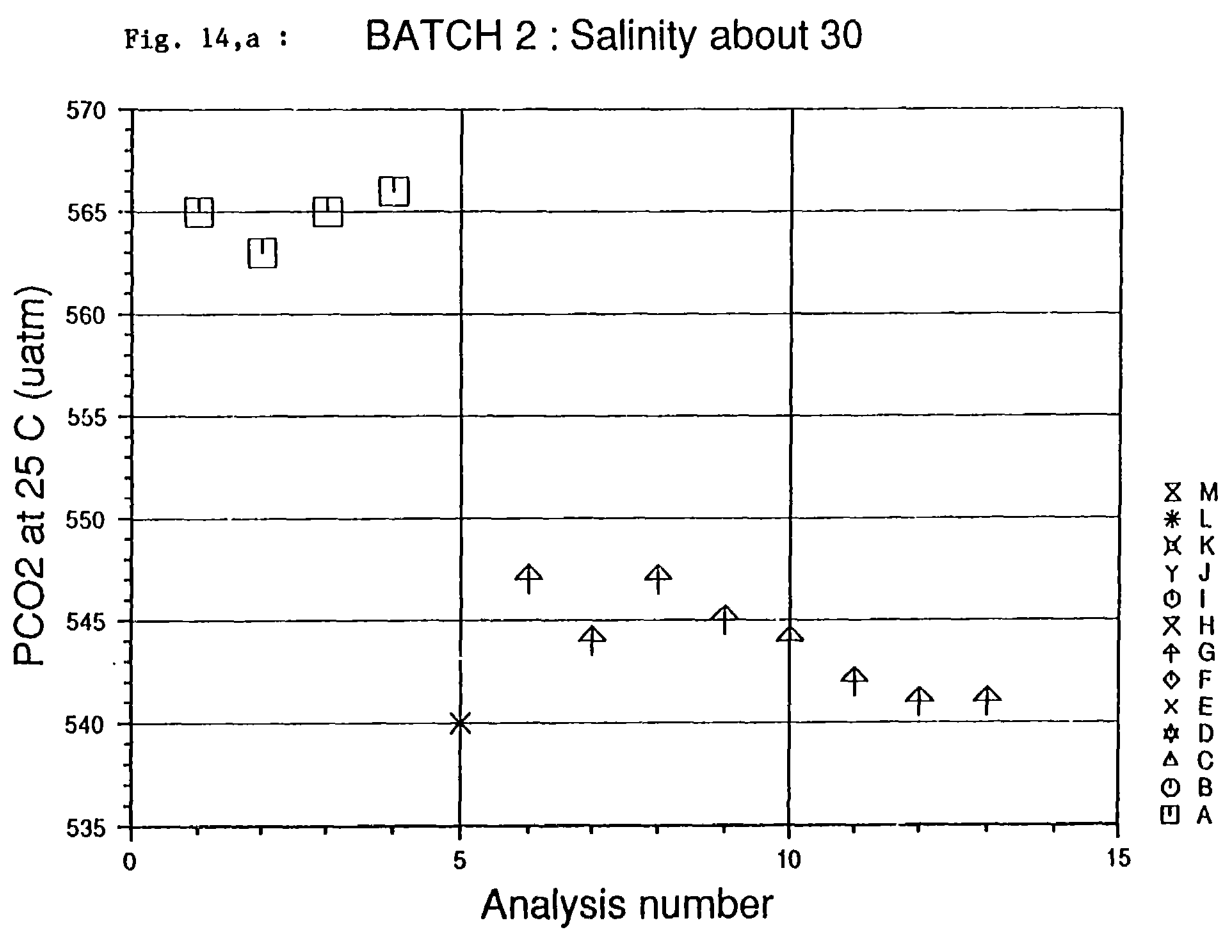


Fig. 14,b : BATCH 2 : Salinity about 30

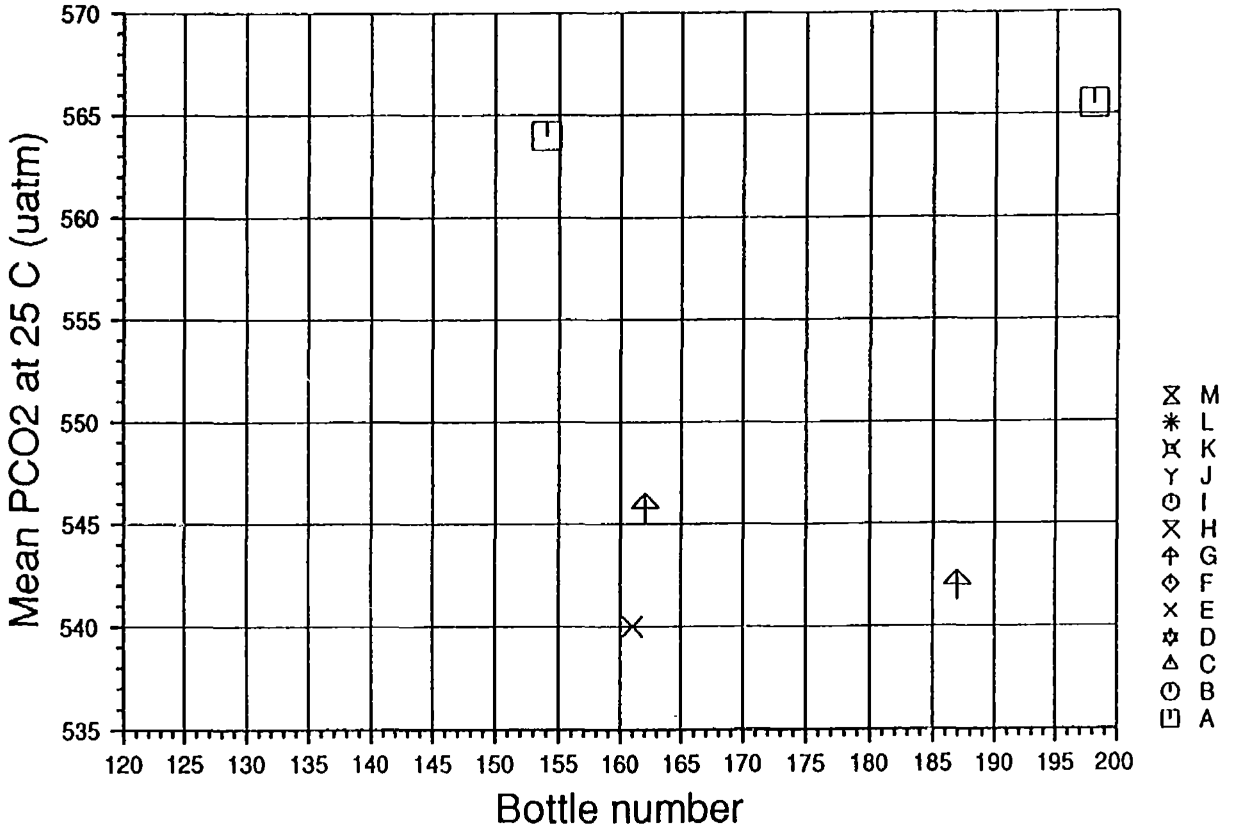


Fig. 14,c : BATCH 2 : Salinity about 30

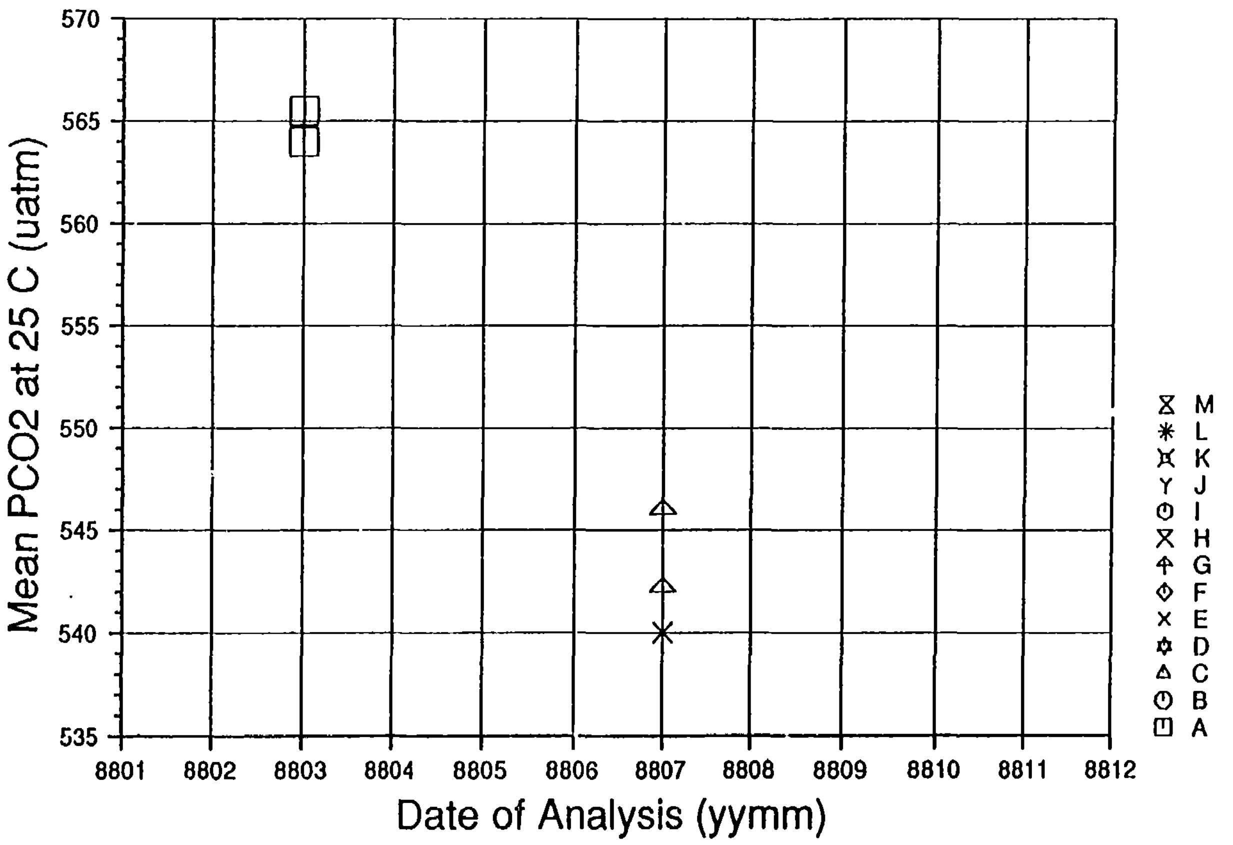


Fig. 15,a :

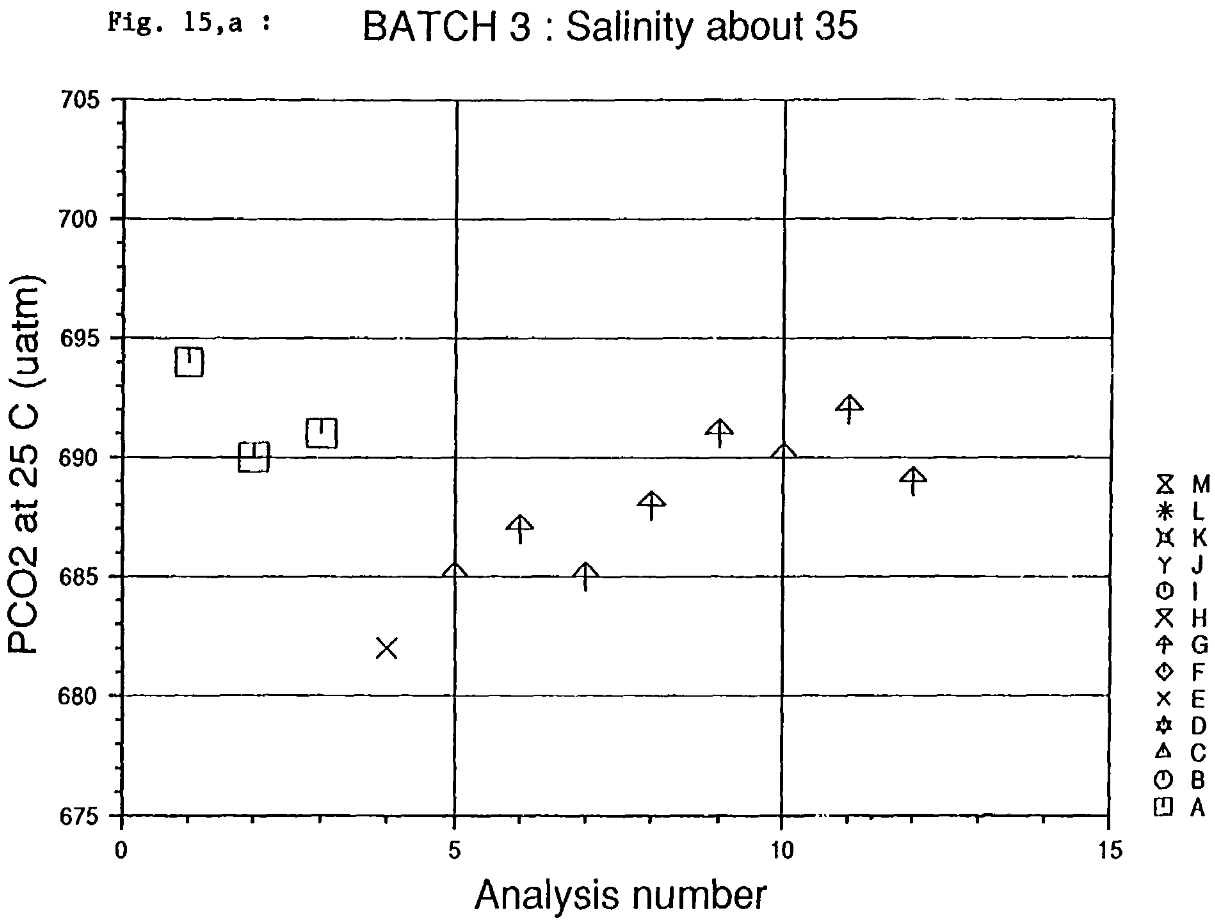


Fig. 15,b :

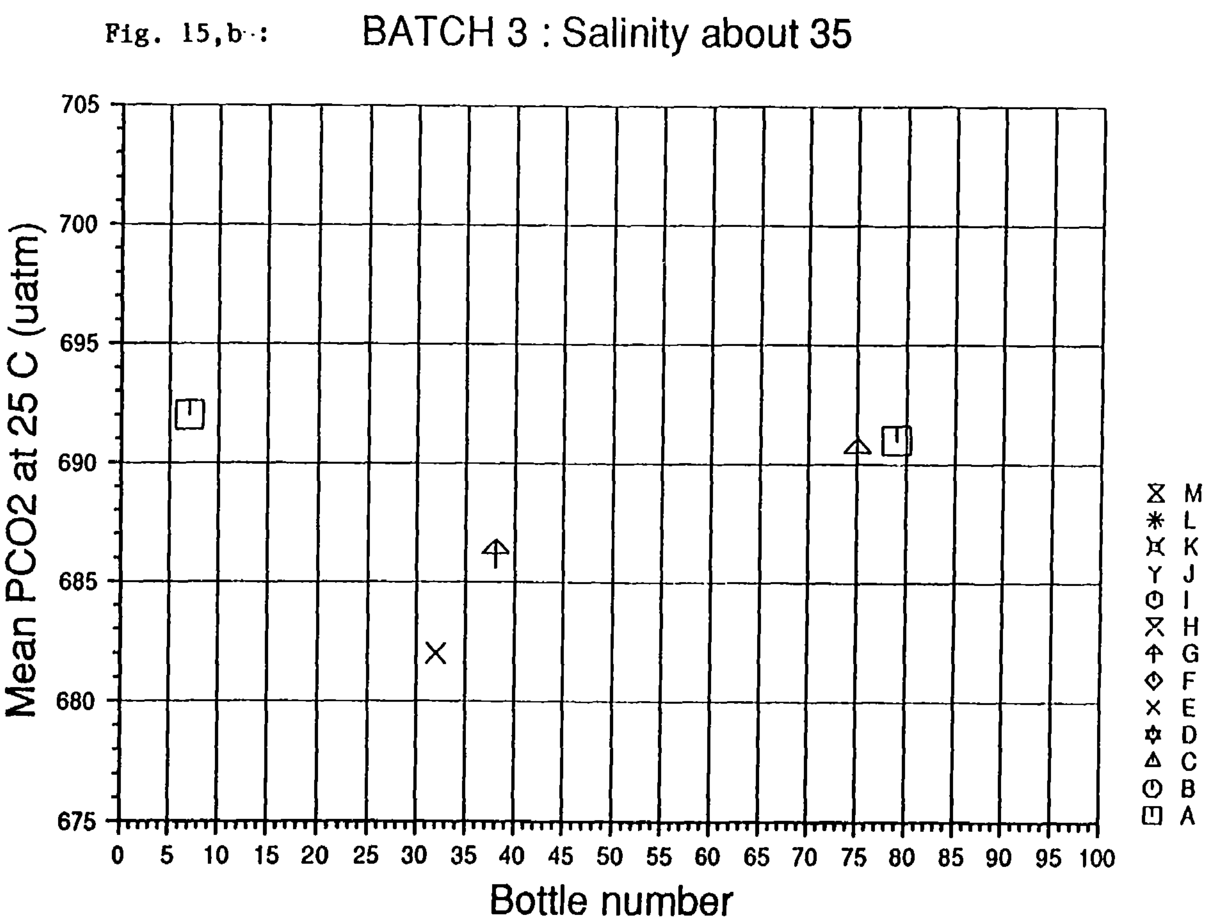


Fig. 15,c : BATCH 3 : Salinity about 35

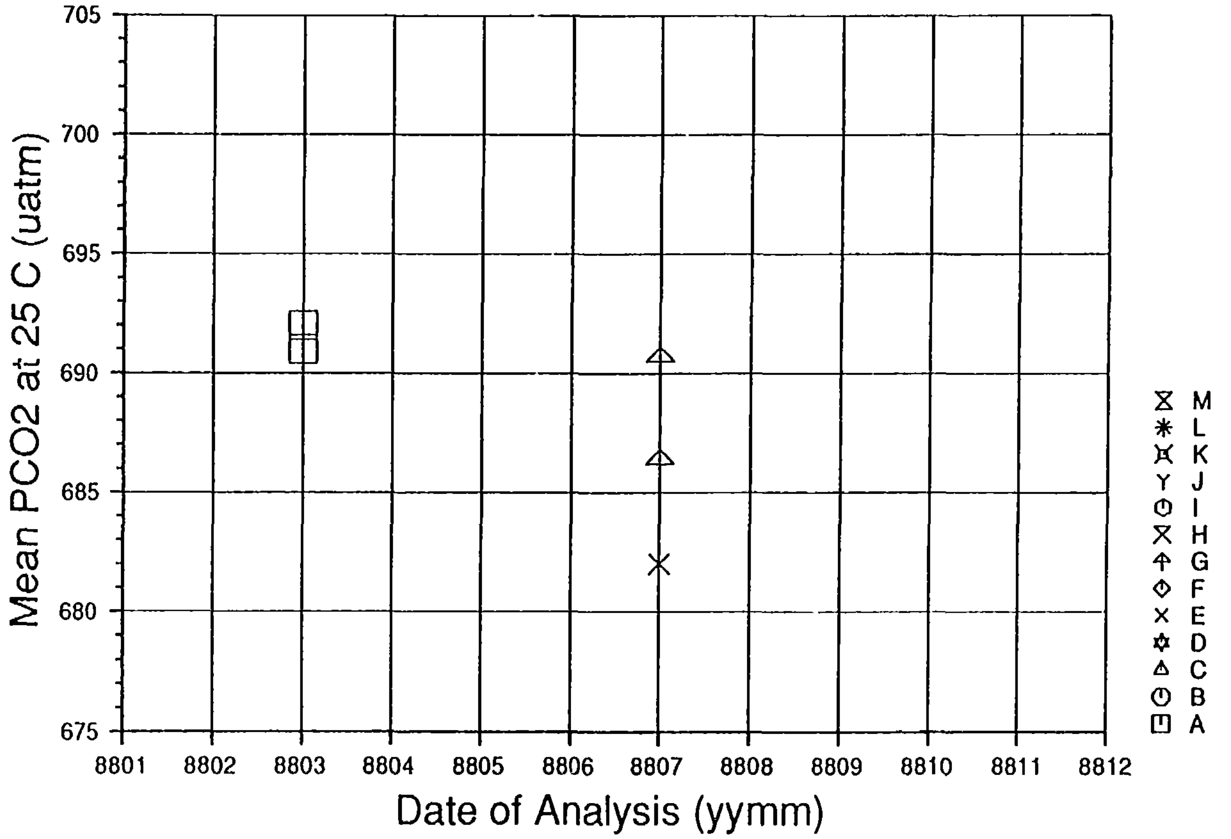


Fig. 16,a : BATCH 4 : Salinity about 38

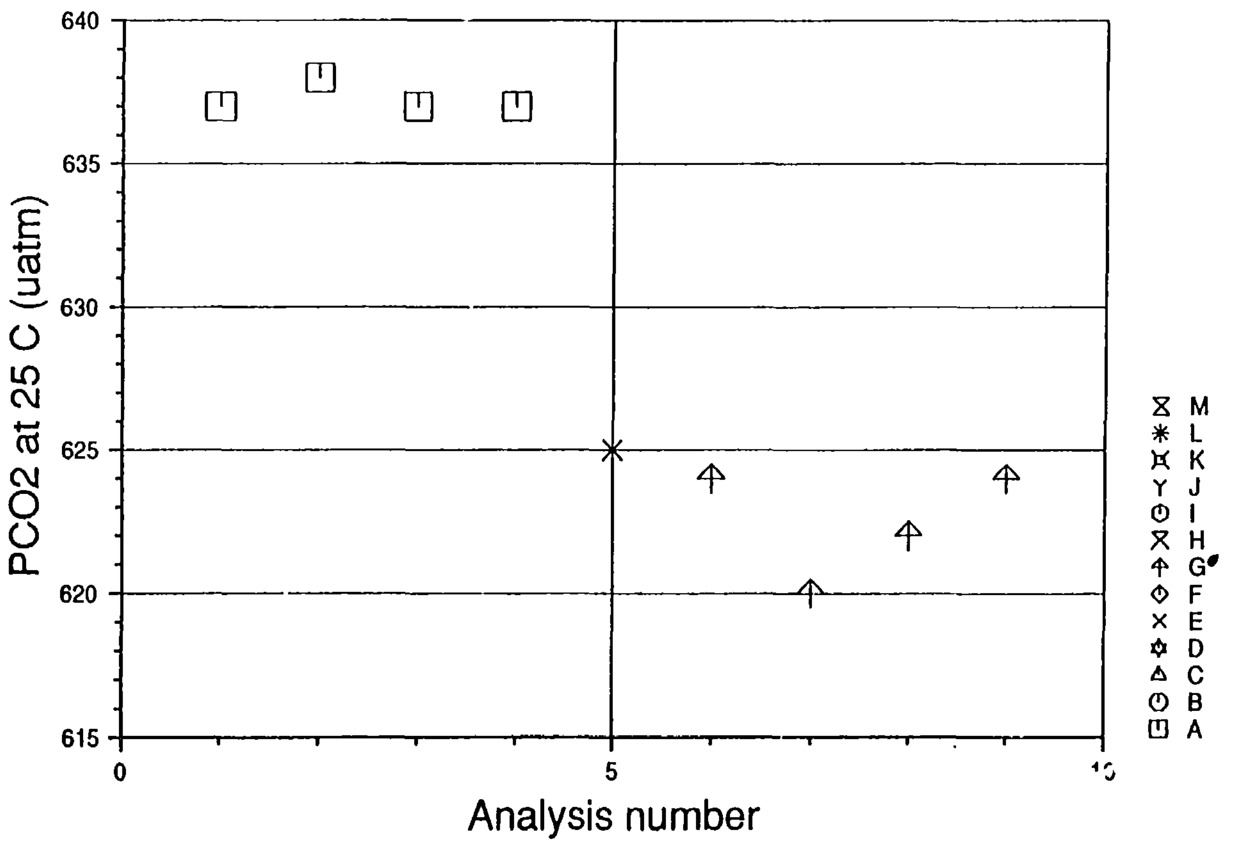


Fig. 16,b : BATCH 4 : Salinity about 38

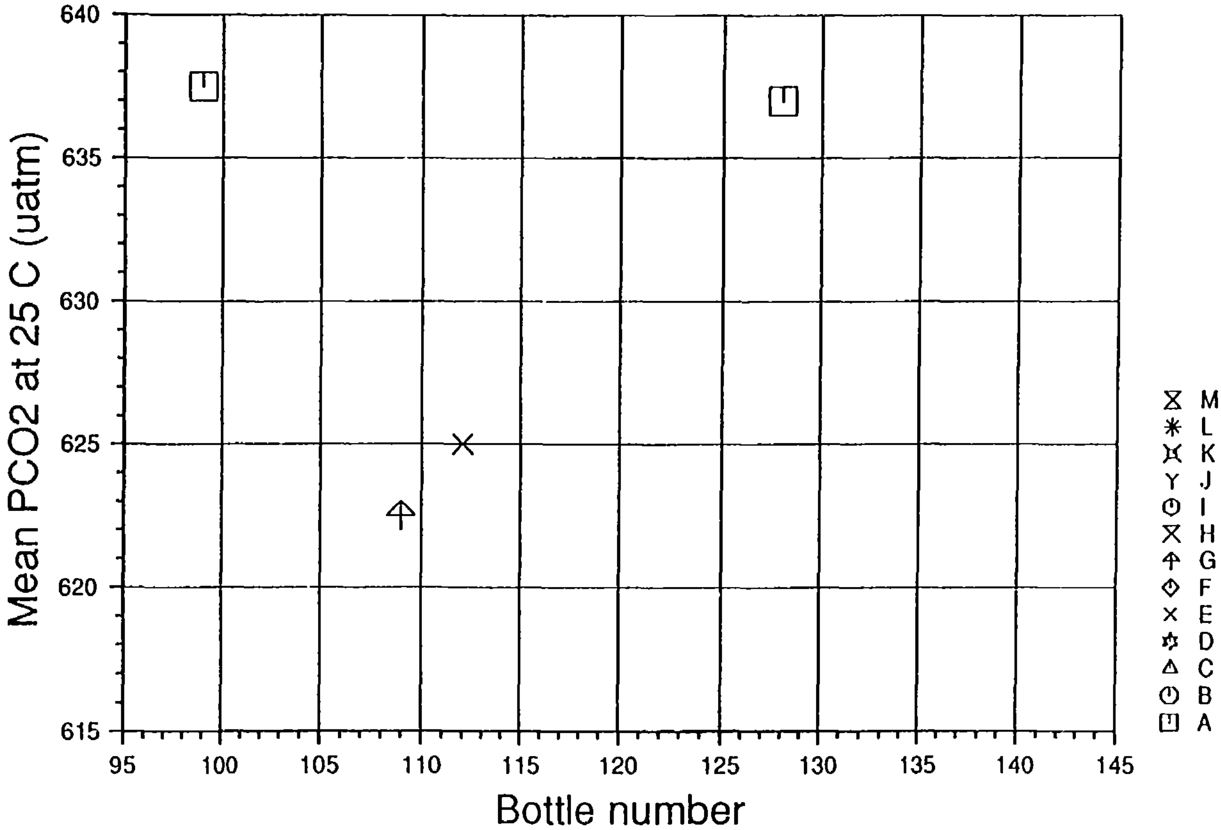
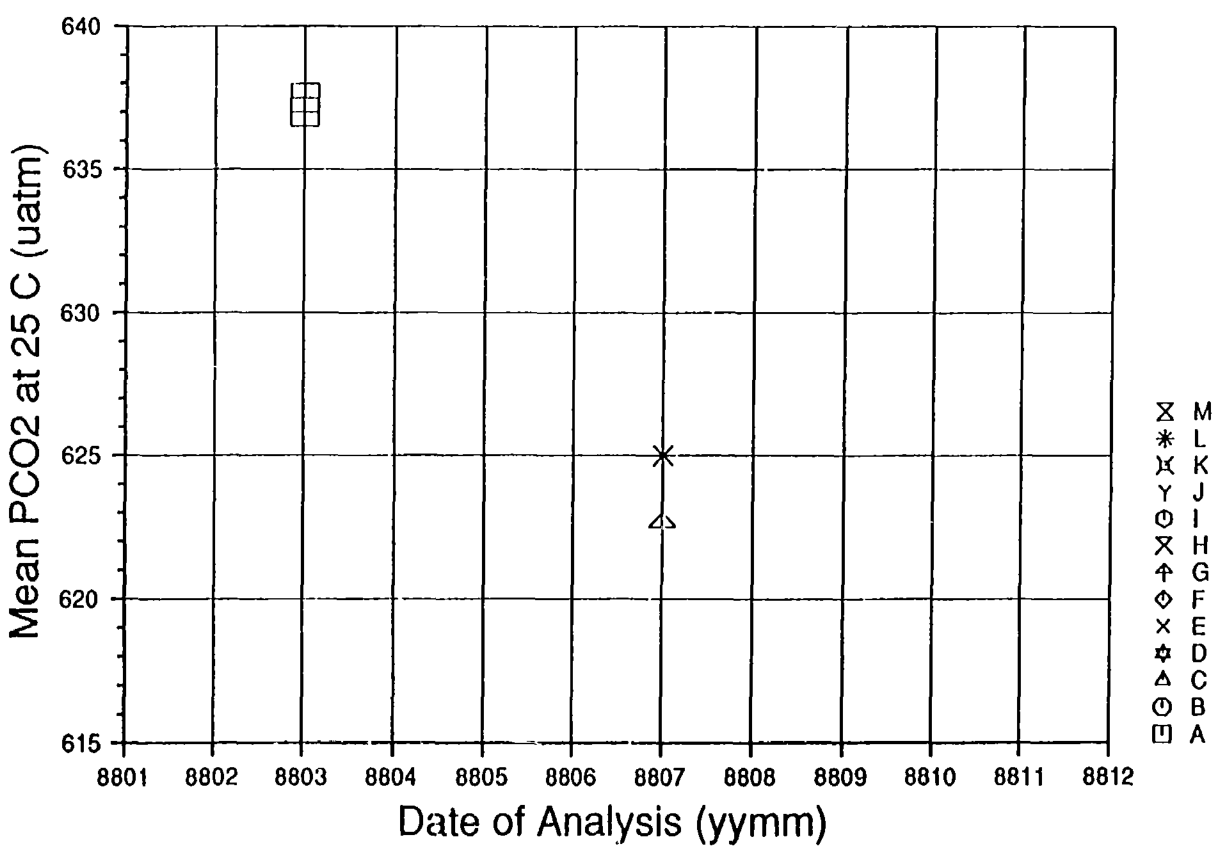


Fig. 16,c : BATCH 4 : Salinity about 38



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