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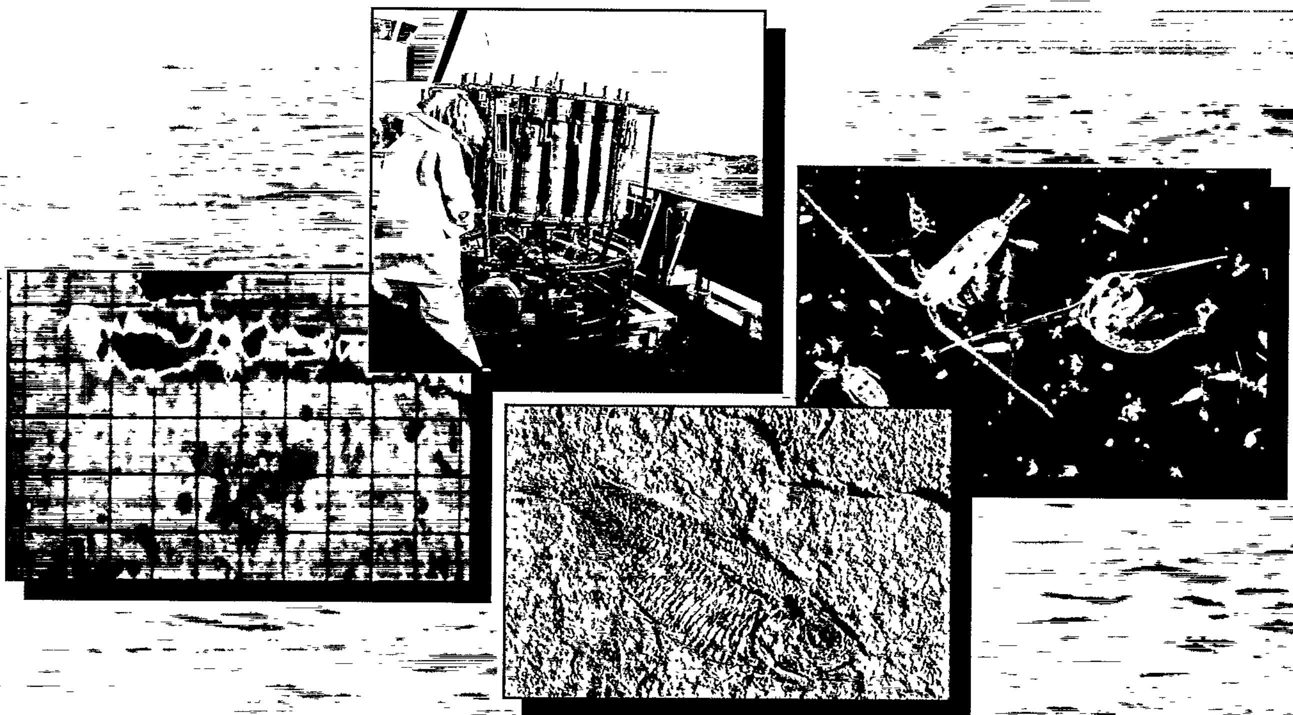

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REPORT No. 4

Report on the maintenance of precision and accuracy of measurements of dissolved nutrients - silicate and nitrate - over 40 days of measurements on WOCE Leg A8, FS *Meteor* Cruise 28/1 29 March to 11 May 1994

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ABSTRACT

An aim of this report is to demonstrate what are the likely precisions and accuracy that can be achieved under the conditions of a WOCE cruise, (i.e. an oceanographic survey on which the order of a hundred samples are being analysed each day for four to eight weeks). Here we define accuracy as a measure of how close the mean of the data is to the true value and precision is a measure of the spread of the data about the mean.

Data obtained on WOCE section A8, for determinations of dissolved nitrate and silicate is reviewed to determine the precision of the data and its likely accuracy. The analyses were carried out using standard (AAII) auto-analyser methods. Most of the procedures recommended by GORDON et al (1993) for obtaining results of good precision and accuracy were followed. Where our methods deviate from these recommendations the reasons are discussed in this document.

KEYWORDS

ACCURACY; ANALYTICAL CHEMISTRY; CRUISE 28/1 1994; *METEOR*/FS; NITRATE; PRECISION; QUALITY CONTROL; SEAWATER; SILICATE; WOCE SECTION A8

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EXECUTIVE SUMMARY

The precision of methods has been assessed on the basis of the variations between duplicate measurements of individual samples, and by the use Quality Control (QC) solutions. The differences between duplicate measurements averaged 0.3% for both silicate and nitrate over the cruise. Four different QC solutions were measured for silicate. The standard deviation was about 0.6% for each of the solutions. For nitrate the results were less satisfactory, the standard deviation of the most stable of the QC solutions was 4.1%.

Accuracy of the calibrations was measured with respect to the available reference standards (Sagami Chemical Co). On A8 the concentration of the Sagami nominally 10μM nitrate standard solutions, was determined to be 9.8 μM (1.5% stdev, n=36), and the nominally 50μM silicate standard, was determined to be 49.7μM (0.8% stdev, n=27).

For the silicate measurements it was possible to compare the results for different QC samples measured each time a set of standards and samples was run through the Auto-Analyser. This comparison indicates the calibration may have varied by up to 1.5%.

Offsets between our results and others measured at 11°S, are greater than the likely errors detected within the A8 measurements themselves. Hydros-4 measurements at 24°W were 2% higher for silicate and 4% higher for nitrate. The corresponding values at 19°W(Knorr) and 1°E(SAVE-3) were 6 and 4% higher for silicate and 5 and 2 % higher for nitrate.

The above suggests there is a problem in accurately calibrating the nutrient measurements. The only way that accuracy and inter-laboratory agreement can be attained is if stable standard reference materials are used to set-up and control the calibration of nutrient analysis systems on all cruises, as is done in the case of the measurement of salinity.

1 INTRODUCTION

The WOCE protocols suggest that certain degrees of precision and accuracy should be attained for the determination of nutrients during cruises undertaken as part of the WOCE cruise programme. Because of the lack of certified reference materials for the determination of nutrients the semantics of WOCE in defining accuracy and precision are not those in common practice in analytical chemistry (see JOYCE, 1991). The suggested values are:- Nitrate 1% accuracy and 0.2% (full scale) precision, Phosphate 1-2% accuracy and 0.4% (full scale) precision and Silicate 1-3% accuracy and 0.2% (full scale) precision (JOYCE, 1991). It was noted that because of the lack of suitable reference material ".... *accuracy* should be taken to mean the *reproducibility* presently obtainable in the better laboratories".

On WOCE leg A11 (RSS Discovery Cruise 199), we started to monitor the day to day performance of the nutrient analyses by using a Quality Control (QC) material. This was to see how consistently the WOCE criteria were met throughout the cruise. In addition we compared our results with those obtained on previous cruises on which the cruise track had crossed our own.

The A11 QC material was simply a bulk sample of sea water, an aliquot of which was determined on each analytical run alongside the water bottle samples. The results of the measurements suggest that although this material was not as stable as a true QC should be, significant changes in the accuracy of the analytical system used on the cruise were detected above the noise in the QC data. Therefore on Meteor Cruise 28/1 (WOCE leg A8) the aim was to improve our ability to monitor the performance of the analytical system by the more rigorous use of QC materials and recording of all relevant data necessary to assess the performance of the system.

There were off sets between the A11 results and previous observations. So we also undertook to monitor the accuracy of our measurements by making measurements of standard reference materials (Sagami Chemical Co. Nutrient reference solutions) at regular intervals throughout the cruise. Additionally by using more than one type of QC material we aimed to asses the likely variation in accuracy of the measurements over the length of the cruise.

2 SAMPLING PROCEDURES

On Meteor Cruise 28/1 two water bottle rosettes where used for the majority of stations for separate deep and shallow depth casts. For data reporting purposes they were termed CTD-2 and CTD-3. Nutrient samples were drawn from all the Niskin bottles closed on the WOCE section stations. Sampling followed that for oxygen and CO_2 on those stations were CO_2 samples when taken. Samples were collected into virgin polystyrene 30ml Coulter Counter Vials (ElKay). These were rinsed three times before filling. Samples were then stored in a refrigerator at 4°C, until analysed. Tests carried out on WOCE leg A11 showed that samples from all depths stored for a week in a refrigerator at 4°C were not detectably affected by storage (see Appendix 1). Actual storage times on Meteor 28/1 varied between 12 hours and being analysed immediately after collection.

3 EQUIPMENT AND TECHNIQUES

The nutrient analyses were performed on a Chemlab AAII type Auto-Analyser, coupled to a Digital-Analysis Microstream data capture and reduction system. Due to problems with noise in the ship's electrical supply the Chemlab Colorimeter was modified at the start of the cruise so that the detectors and light source were driven from stabilised DC supplies.

3.1 Methods

Silicate:

The standard AAII molybdate-ascorbic acid method with the addition of a 37°C heating bath was used (HYDES, 1984). The heating bath increases the precision of the analyses when analysing samples of different temperature (SAUNDERS et al 1991, c.f. JOYCE et al 1991). In order to desensitise the system so that a linear response was obtained from the colorimeter over the concentration range up 0 to 150 µM of silicate, the colorimeter was fitted with a 15mm flow cell and a 660nm filter was used.

Nitrate:

The standard AAII method using sulphanilamide and naphthylethylenediamine-dihydrochloride was used (GRASSHOFF, 1976), with a Cadmium-Copper alloy reduction column (HYDES & HILL 1985). In order to de-sensitise the system so that a linear response was obtained from the colorimeter over the concentration range up 0 to 50 µM of nitrate, the colorimeter was fitted with a 15mm flow cell, and a sample volume of 0.1 ml/min was used. A nitrite standard solution was measured on each analytical run to monitor the relative efficiency of the cadmium/copper reduction column.

Phosphate:

No phosphate data was obtained on this cruise. We had intended to use the standard AAII phosphate method (HYDES,1984) which follows the method of MURPHY & RILEY (1962). However when the apparatus was set up the sensitivity of the method was so low as to make measurements meaningless. We were unable to trace the cause of the problem.

3.2 Calibration

The calibration of all the volumetric flasks and pipettes used on the cruise were checked before packing and were rechecked on return to the laboratory.

3.3 Nutrient standards

Nutrient primary standards were prepared on ship from weighed dry salts. The salts were dried at 110°C for two hours and cooled over silica gel in a desiccator before weighing. Precision of the weighings was better than 1 part per thousand. For **nitrate** 0.510g of potassium nitrate was dissolved in 500ml of distilled water in a calibrated glass volumetric flask. Four different solutions were prepared in three different flasks. No detectable difference could be found between these solutions. Relative to these solution the concentration of nitrate in a nominally 10.0 µM Sagami Standard Solution was 9.76µM stdev 0.14 µM (n=36),. (See below). For **silicate** 0.960g of sodium silica fluoride was dissolved in 500 ml of distilled water in a calibrated plastic (PMP) volumetric flask. No detectable difference could be found between this solution and a standard solution which had been prepared on shore. Relative to these solutions the concentration in a nominally 50.0µM Sagami Standard Solution was 49.70 µM stdev 0.40µM (n=27).

3.4 Analytical Runs

All analytical runs were calibrated on the basis of four mixed secondary standards measured in duplicate at the start of the run. Drift samples and blanks were measured after the standards, half way though the run and at the end of the run. The concentrations of the standards for silicate were 125, 100, 50, 25 µM in the western basin, and 100, 75, 50 and 25 µM in the eastern basin; for nitrate the concentrations were 40, 30, 20 and 10 µM in both basins. Calibration was on the basis of a linear fit by the least squares method forced though the origin. The gains the colorimeter channels were not altered after being established at the start of the cruise. The apparent sensitivity of each run was recorded along with the standard error estimated from the least squares fit (see below).

The secondary standards were prepared in 40g/l Analar Sodium Chloride solution. In auto-analyser work calibration errors can occur if the kinetics of colour development are different between the calibration standards and the actual samples being measured. To check for such an error, the sensitivity of the methods was compared between, a set of standards for the cruise prepared in the our usual way in Sodium Chloride solution, and, a duplicate set of standards prepared in OSI-Low Nutrient Seawater. There was no detectable difference.

The same 40g/l Analar Sodium Chloride solution was used both for the preparation of standards and as the auto-analyser "wash" solution. The "wash" blank was checked daily against OSI-Low Nutrient Seawater. The results are tabulated in Appendix 2. The nitrate blank was undetectable throughout the cruise (less than 0.05µM). The batch of Low Nutrient Seawater we used on this cruise contained a small amount of silicate, determined to be 0.82µM (n=5) against a double distilled water blank, in glass cells using a Pye SP500 spectrophotometer. The mean of 34 pairs of duplicate measurements on Meteor 28/1 was 1.1 µM Si with a standard deviation of 0.1µM.

4 QUALITY CONTROL

4.1 Instrument Stability

For each analytical run the apparent sensitivity of the analyser, was recorded as the calculated first order calibration coefficient. The variability in this measurement is presented in **Table 1** below. The data is divided into three groups corresponding to the re-tubing of the analyser. All the peristaltic pump tubes were replaced routinely each two weeks. Variability in the actual internal diameters of the tubes probably led to the marked change in the nitrate sensitivity on the first tube change. A similar jump in sensitivity occurred for silicate with the second tube change. The apparent shift seen in nitrate sensitivity in the table appears to be part of a more continuous trend in sensitivity when all the results are plotted in **Fig 1.**

Table 1. Mean analytical sensitivities grouped by runs between peristaltic pump tube changes.

Run No.s	Si mean sensitivity µM/bit	Si % stdev	NO3 mean sensitivity µM/bit	NO3 % stdev
14-29	0.0384	0.8	0.0170	0.9
30-73	0.0382	1.2	0.0182	2.4
74-109	0.0331	1.2	0.0170	1.7

4.2 Precision - Duplicate Measurements

Duplicate samples were collected from the deepest four bottles on the deep CTD-3 rosette and the deepest two bottles on the shallow CTD-2 rosette. All samples were then measured once by the analyser. The results for the reproducibility of measurements of the duplicates were assessed on the basis of the variation over groups of ten stations.

Overall the mean differences between the duplicate measurements were for silicate 0.2µM with a standard deviation of 0.3µM(n=594) and for nitrate 0.1µM (stdev 0.1, n=594). The standard deviations on the differences are similar to the means of the standard errors of the least squares calculation of the calibration equations Si-0.28µM and NO3-0.097µM.

There appears to have been no discernible variation in the precision of the data over the length of the cruise. **Fig 2** shows the variation in the standard error estimate for the least squares fit of the calibration data.

Table 2. Summary of differences between duplicate analyses. Mean taken for groups of ten runs to look for systematic changes over length of cruise

Station No.	Silicate Mean µM	mean Diff	mean % Diff	Nitrate Mean µM	mean Diff	% mean Diff
171-180	52.4	0.13	0.25	24.7	0.06	0.25
181-190	87.2	0.27	0.30	32.3	0.10	0.32
191-200	86.5	0.24	0.28	31.9	0.08	0.24
201-210	65.1	0.32	0.49	28.8	0.11	0.38
211-220	35.7	0.12	0.34	21.3	0.07	0.31
221-230	37.1	0.11	0.30	24.4	0.07	0.31
231-240	41.0	0.09	0.22	27.7	0.05	0.17
241-250	46.3	0.12	0.26	27.5	0.07	0.27
251-260	45.5	0.12	0.25	27.9	0.09	0.33
261-270	41.4	0.11	0.27	26.9	0.11	0.41
271-274	28.4	0.11	0.37	26.1	0.13	0.48
287-290	25.1	0.11	0.45	35.4	0.06	0.18

4.3 Precision - consistency of internal QC measurements

Following on from our use of an internal QC standard on WOCE cruise A11, at the first deep station, a bulk sample of water from below 2000m depth was collected from the deeper Niskin bottles into a 25 litre carboy. This water was then placed into 200 ElKay Dilu-Vials (30ml), the same pots used for collection of samples. 50 of these samples were stored Warm (QCW) in the dark at the ambient laboratory temperature (22-25°C), and 150 samples were stored Cold (QCC) in a refrigerator at 4°C. A QCC sample was measured in duplicate on each run and a QCW sample was measured daily. Fifteen pots were opened and analysed the day the pots were filled. Similarly, twenty pots remaining at the end were determined in a single run after the last determination of station samples. The QCC and QCW data are presented in **Fig 3.**

There is no discernible trend in the Si QCC or QCW data. The two data sets are not significantly different. The reproducibility of the nitrate QCC samples deteriorated with time and an increase in the variability is seen when the data is summarised on the basis of groups of ten stations in the **Table 3** below.

An interesting point is that although marked losses of nitrate appear to have occurred in some vials of the QCW samples, the data presented in **Fig 3** suggest that this has not been a steady decrease with time. The loss may depend on the relative sterility of the individual pots.

There may be two sources of noise in the QCC data (1) random noise associated with the short term variability in the flow through the analyser system (2) systematic noise associated with variability in the calibration standards. This latter form of variability if it is significant should show up as a correlation between the observed value of the QC standard and the calculated calibration factor for each run. When these are plotted against one another **Figs 4 & 5** there is no apparent correlation either for silicate or nitrate. The silicate data is divided into two populations by the jump in sensitivity when the pump was re-tubed a second time (see above).

Table 3. Summary of determinations on QCC samples. Means and standard deviations calculated for groups of ten stations

Run No	Si	Si	Si	NO3	NO3	NO3
	mean μM	Stdev	% Stdev	mean μM	Stdev	% Stdev
Start(n=15)	48.18	0.11	0.24	22.13	0.10	0.44
4 to 13	47.99	0.38	0.80	22.10	0.15	0.67
14 to 23	48.33	0.38	0.79	22.10	0.17	0.79
24 to 33	48.24	0.30	0.62	22.04	0.17	0.78
34 to 43	48.13	0.37	0.77	21.68	0.34	1.55
44 to 53	48.12	0.27	0.57	21.69	0.35	1.62
54 to 63	48.09	0.20	0.42	21.32	0.81	3.79
64 to 73	48.00	0.25	0.53	20.63	0.62	3.01
74 to 83	48.14	0.16	0.33	21.13	0.38	1.79
84 to 93	48.07	0.20	0.42	20.58	0.98	4.74
94 to 103	48.31	0.27	0.56	20.75	0.79	3.82
104-109	48.65	0.14	0.29	20.06	0.68	3.38
End(n=20)	48.25	0.13	0.27	20.47	1.01	4.93

As noted above the standard deviation of the difference between the duplicate values for silicate was 0.3μM (n=594), the standard deviation on the QCC measurements for silicate was also 0.3μM (n=222). This would also suggest that the main source of noise in the silicate observations was due to within run variability rather than systematic differences between runs which would be expected to increase the spread of results of the QCC measurement and hence the standard deviation. For nitrate the lower stability of the QCC samples is seen as an increase in the standard deviation of the QCC samples 0.9μM (n=222) relative to the standard deviation and for measurements of duplicate samples nitrate were the standard deviation was 0.1μM (n=594).

Another way of detecting systematic variations between runs is to compare the variation in the values obtained for both the QCC and QCW samples. This can be done for silicate as the two materials seem to have both been relatively stable, this was not the case for nitrate. For silicate the variabilities of the two materials are similar, as shown in **Table 4**.

When the values of the results for the QCC and QCW standards are plotted against one another in **Fig. 6**. a least squares linear fit gives a best fit line with an R^2 value of 0.73. This suggests that variations in QCC and QCW values, do give an indication of measurable variation in the accuracy of the measurements. Inspection of **Fig. 6** suggests this may have been as large as 1.5 % over the course of the measurements. This apparent variability appears to be confirmed when similar comparisons are done of the values of the OSI-QC samples (see below).

Table 4. Summary of QC results for the five QC materials on which Si determinations were made.

	QCC-Si	QCW-Si	OSI-Si	OSI-mix-Si	OSI-LNS
mean µM	48.1	48.4	76.6	77.7	1.1
stdev	0.32	0.36	0.51	0.49	0.15
n	222	68	70	68	68

4.4 Precision - consistency of measurements of an external QC standard

At the NOAA/IOC meeting in Miami in December 1993, on marine analytical standards, Paul Ridout of Ocean Scientific International undertook to investigate the possibility of preparing a "nutrient standard sea water". The idea being that such a standard could be used to provide uniformity in nutrient measurements in a similar way, to that which is provided by OSI-Standard Sea Water for salinity measurements. What would be produced would be a "reference material" rather than an "absolute standard"

The three criteria for the standard were: (1) that it should be packaged in "one-shot" bottles; (2) that the material should be based on real seawater, and (3) that it should be produced and distributed relatively cheaply. The latter two points were decided on to meet two frequently voiced objections to the nutrient standards produced by the Sagami Chemical Co. in Japan, that they are expensive and that they are prepared in sodium chloride solution rather than in sea-water. In circumstances where the analytical set up of an Auto-Analyser has not been optimised the calibration factors can be different between sea water and sodium chloride solution.

The results of recent inter-calibration exercises for nutrients (Si, NO3 and PO4) carried out by ICES-IOC (AMINOT & KIRKWOOD, 1995, KIRKWOOD et al 1991) suggest, that preparation of stable nutrients standards in seawater should be possible. OSI had available surface seawater which has been stored in polythene tanks to prevent contamination with silicate from glass. We decided that in time for Meteor Cruise 28/1, a test QC standards could be prepared by addition of nutrients to this water. The spiked water would be packaged in low density polyethylene bottles of 50ml capacity, fitted with a water tight strip seal caps.

Five different OSI nutrient QC types were taken to Meteor 28/1. These were low nutrient sea water (LNS) without addition of nutrient, LNS plus approximately 75µM silicate (as sodium silica fluoride), LNS plus approximately 30µM nitrate (as potassium nitrate), LNS plus approximately 1.5µM phosphate (as potassium dihydrogen phosphate), and a mixed standard containing approximately the same added quantities of all three nutrients in LNS.

Due to the failure of the phosphate channel on this cruise we only obtained data for silicate and nitrate. The results for nitrate are not satisfactory, this is probably because the LNS is not sterile, and bacterial growth took place in the samples. All the measurements made on the OSI QC samples are shown in **Appendix-Table 3**. The data shows (**Fig 7**) that both the single addition standard and the mixed standard are stable with respect to silicate, the precision appears to be similar to that of the QCC samples (**Table 4** above).

When the results of measurements of QCC and OSI solutions measured on the same analytical runs are compared **Fig 7,** there appears to be a co-variation between the two data sets. This would seem to confirm the suggestion that comparing measurements of QC solutions made on the same run, gives an indication of variation in the calibration between runs which is greater than the within run precision of the measurements. When the two data set are plotted against one another in **Fig 8**, (as in **Fig 6**) the R^2, value is 0.60. Plotting the silicate results for the two OSI materials against one another (**Fig 9**), gives an R^2 of 0.55.

The conclusion from **Figs 6, 8 and 9** is that these plots would suggest that over the length of the cruise there were significant differences in the calibration values. The spread of values suggests that the accuracy of the determinations may have varied within a range of 1.5% over the length of the cruise.

The reason for the variation in R^2 values between the data in **Figs 6, 8 and 9** is not obvious. Shore based measurements of the OSI material suggest that there may have been a lack of homogeneity in the preparation of the OSI standards, which might have contributed to the lower R^2 values. However this was not obvious when the standard deviations are compared to those measured for the QCC and QCW solutions.

4.5 Accuracy - Comparison with Sagami Chemical Co. Standard Solutions

Certified standard reference materials for the measurement of nutrients in sea water are produced by the Sagami Chemical Co. in Japan. These are solutions of nutrients in 30g/litre Sodium Chloride solution. During Meteor Cruise 28/1 we made measurements on two different solutions 1) a 10.0µM concentration of nitrate which is provided in a glass bottle, and 2) a 50.0 µM concentration of silicate which is supplied in a high density polyethylene bottle. Four bottles of each solution were opened and analysed at weekly intervals. All the results are shown in the Appendix-Table 3. The results are summarised in **Table 5** below. These results would suggest that there may be a small systematic error in the calibration of our nitrate results, while the error on the silicate measurements is within the precision of the method.

Table 5. Summary of results for all determination made on Sagami Standards during Meteor 28/1.

	NO3 10.0µM	Si 50.0µM
mean	9.8	49.7
stdev	0.14	0.40
% stdev	1.5	0.8
n	36	27

4.6 Accuracy - Comparison with Historical Data and at the WOCE inter calibration station 11°20'S 19°W.

We have compared our data to that obtained on two North-South sections SAVE-3 and Hydros-4, which crossed our section.

HYDROS-4 stations R/V Melville April 1989

- Station H4-350 at 10°59.2'S 24°59.2'W
- Station H4-351 at 10°24.0'S 24°59.6'W
- Station H4-352 at 09°49.4'S 24°59.9'W

were compared with

- Station A8-195 at 25°20'W
- Station A8-196 at 24°40'W
- Station A8-197 at 24°00'W

SAVE-3 stations R/V Knorr Cruise 134 February 1988

- Station S3-150 at 10°49.1'S 00°59.0'E
- Station S3-151 at 09°14.3'S 01°02.6'E

were compared with

- Station A8-250 at 1°20'E
- Station A8-251 at 2°00'E

Silicate 24° W

When all six profiles are compared **(Fig 10a)** they appear to be closely aligned with an offset which increases to 5µM Si in the deep water (a 2% offset see **Fig 10b**). The A8 measurements are higher than Hydros4 data. At the 1000m intermediate maximum in the concentration of silicate at the three A8 stations agree closely with each other, and are similar to the values at the Hydros-4 Station-352. At this depth there is an offset of about 3µM in concentrations of silicate at all four stations compared to Hydros-4 Station-350, which is the station closest to the A8 latitude.

Nitrate 24° W

When all six profiles are compared **(Fig 11a)** they appear to be closely aligned with an offset which increases to about 1.5µM NO3 in the deep water. The error bars drawn in **Fig 11b** suggest Hydros-4 data is 4% higher than the A8 data.

Silicate 1° E

As at 24°W the shapes of the profiles agree well **(Fig 12a)**, with an offset between the two calibrations equivalent to 2µM silicate in the deep water. The SAVE-3 measurements are 4% higher than the A8 measurements **(Fig 12b)**.

Nitrate 1° E

As at 24°W the shapes of the profiles agree well **(Fig 13a)**. Close inspection shows that in the deep water the SAVE-3 data is 0.5µM (2%) higher than the A8 measurements **(Fig 13b)**.

WOCE inter-calibration station 19° W

Silicate

The profiles from A8-206 and Knorr station 68 show a close correspondence in shape but are offset by about 6% as indicated by the error bars drawn in **Fig 14a and 14b.**

Nitrate

The profiles from A8-206 and Knorr station 68 show a close correspondence in shape but are offset by between 4 and 5% as indicated by the error bars drawn in **Fig 15**.

The percentage offsets in the A8 from other observations are summarised in **Table 6** below.

Table 6 Summary of calibration off sets between results on A8 and previous cruises calculated as a percent difference.

	24°W Hydros-4	19°W Knorr stn 68	1°E SAVE-3	*WOCE* *Criteria*
Silicate	2	6	4	*1-3*
Nitrate	4	5	2	*1*

5 CONCLUSIONS

The precision of the measurements of concentrations of dissolved silicate in the Sagami standards would suggest that any drift in accuracy during the cruise would be of similar magnitude to the standard deviation on these measurements which was 0.8%. The comparison of the results from the different QC measurements indicates that the accuracy of the measurements of silicate could have drifted during the cruise by up to 1.5%. This estimate of the likely accuracy is smaller than observed difference between cruises. A fundamental error in calibration has to have been present to have caused the discrepancy between the Meteor, Knorr SAVE-3 and Hydros-4 data. The same conclusion applies to the determinations of dissolved nitrate.

There is a problem in accurately calibrating the nutrient measurements from cruise to cruise and between different laboratories. This not the first time the problem has been recognised (see AMINOT & KIRKWOOD, 1995). The results of this study add to the conclusion that the only way that accuracy and inter-laboratory agreement can be attained is if stable standard reference materials are used to set-up and control the calibration of nutrient analysis systems on all cruises, as is done in the case of the measurement of salinity.

The results from this cruise, can be taken as defining the likely precision that will be achieved during WOCE hydrographic nutrient surveys. This has been done more clearly than was case with WOCE Operations Manual.

The analysis of the QC data shows the value of making such measurements, as they enable both the precision of the method to be monitored and give an indication of the likely drift in the accuracy of the calibration. Preparation of an adequately stable Si-QC solution appears to straight forward. Either a deep water bulk sample can be used or a surface sea water can be spiked with added silicate. In the case of nitrate a more stable solution than can be achieved by simply taking a bulk deep sea water sample should be used.

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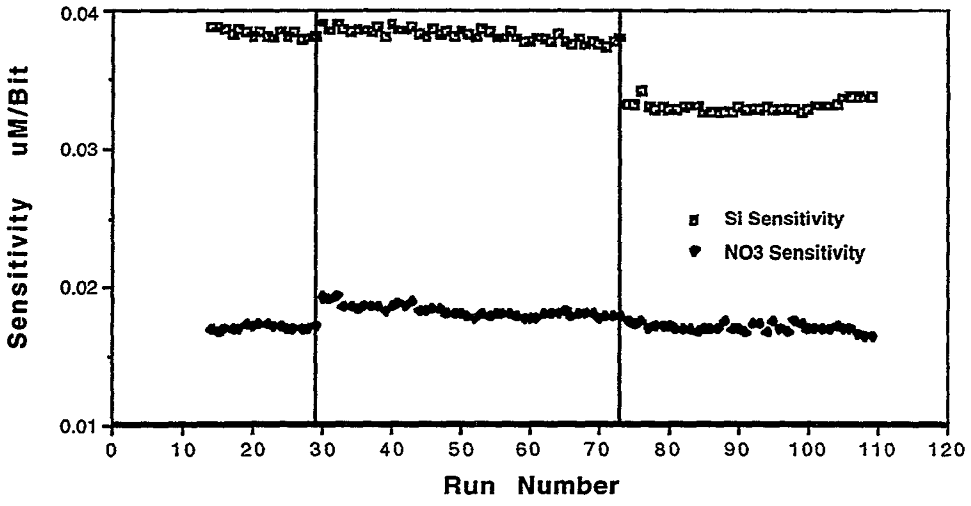
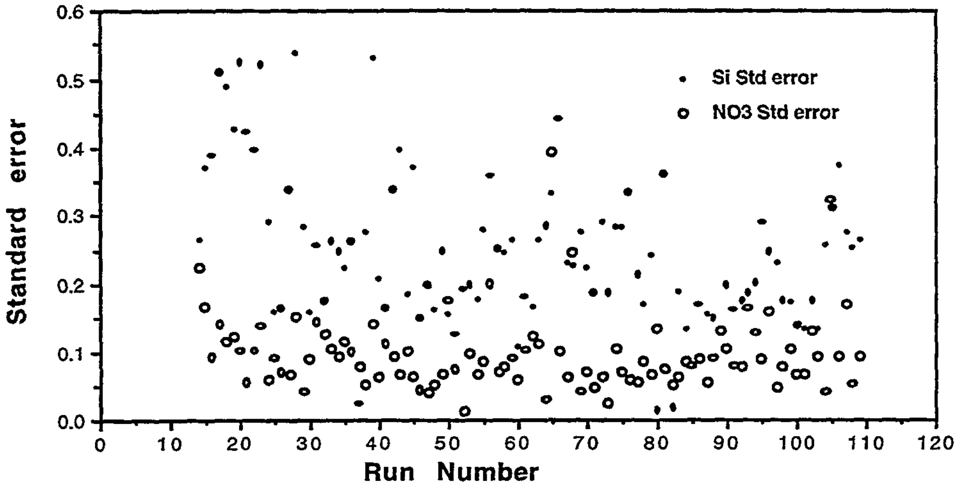
Fig. 1



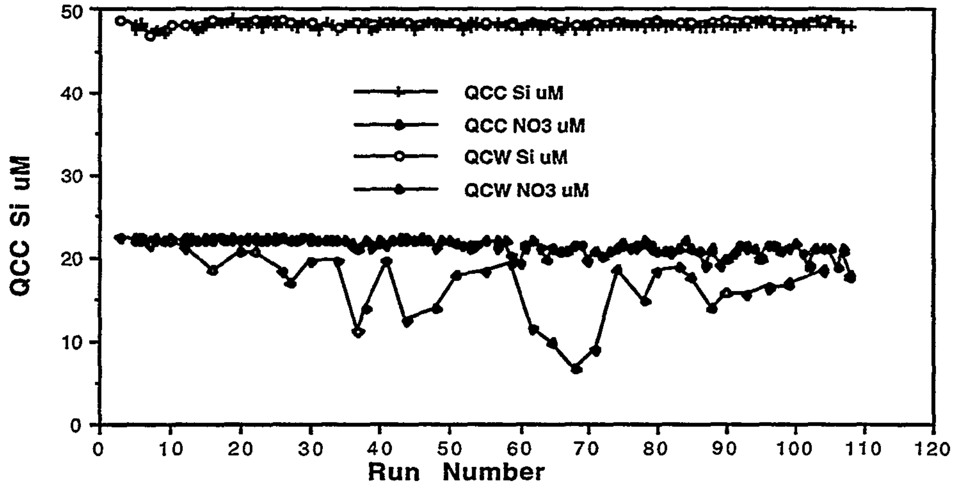
(1) The sensitivity which is the calibration coefficient calculated on each analytical run is plotted against run number. The sharp jumps in sensitivity correspond to times when the tubes on the peristaltic pump were replaced. The size of the jumps are consistent likely changes in actual flow volumes.

Fig. 2



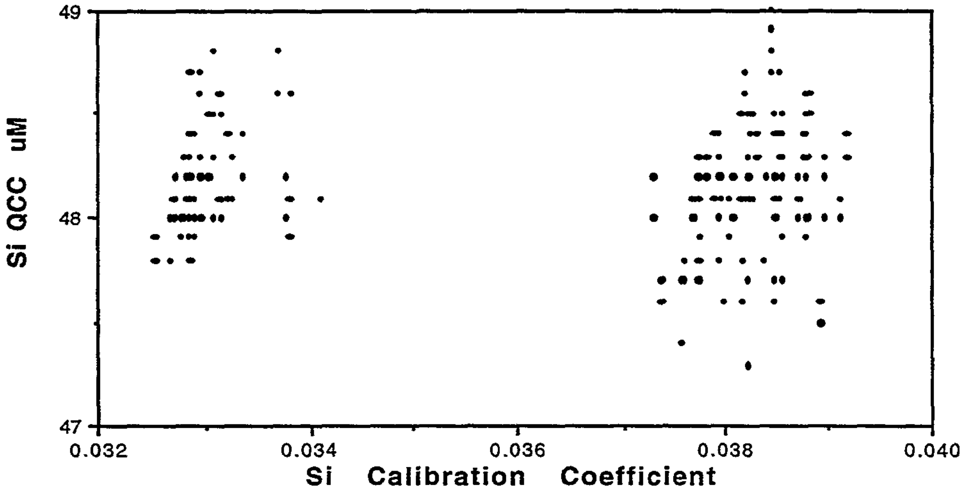
(2) The standard error calculated from the least squares fit of the calibration data for each analytical run are plotted against run number.

Fig. 3



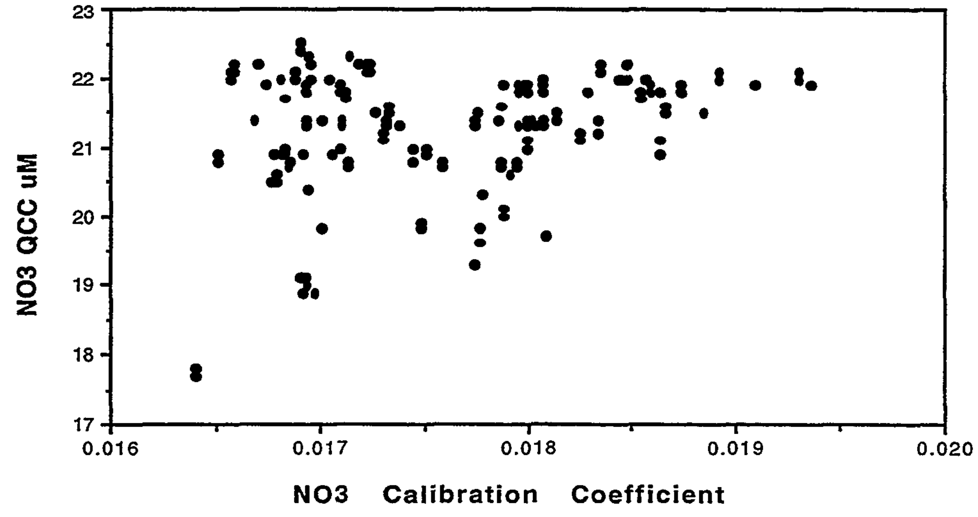
(3) Results for measurements of silicate and nitrate in the quality control samples QCC and QCW. QCC samples where measured on each analytical run QCW were measured daily.

Fig. 4



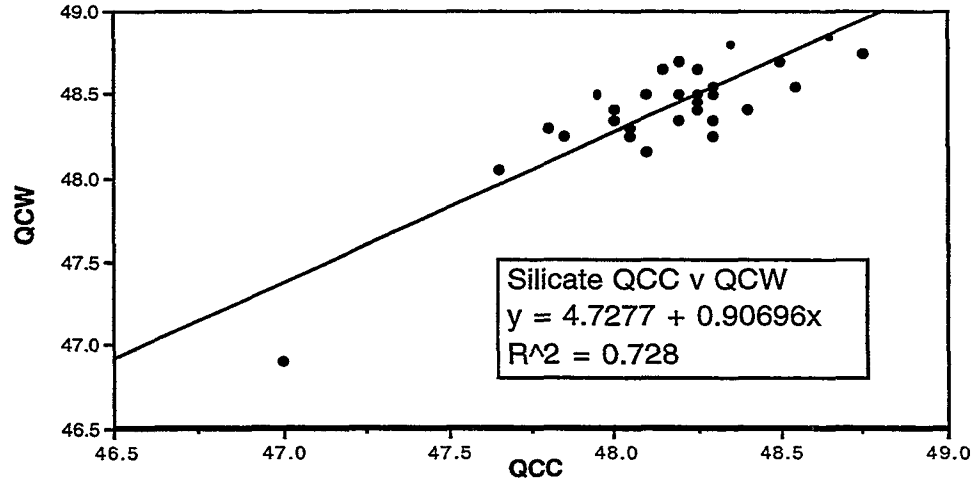
(4) The result for the determination of silicate in the QCC sample plotted against the calibration coefficient calculated for the analytical run on which that QCC sample was measured.

Fig. 5



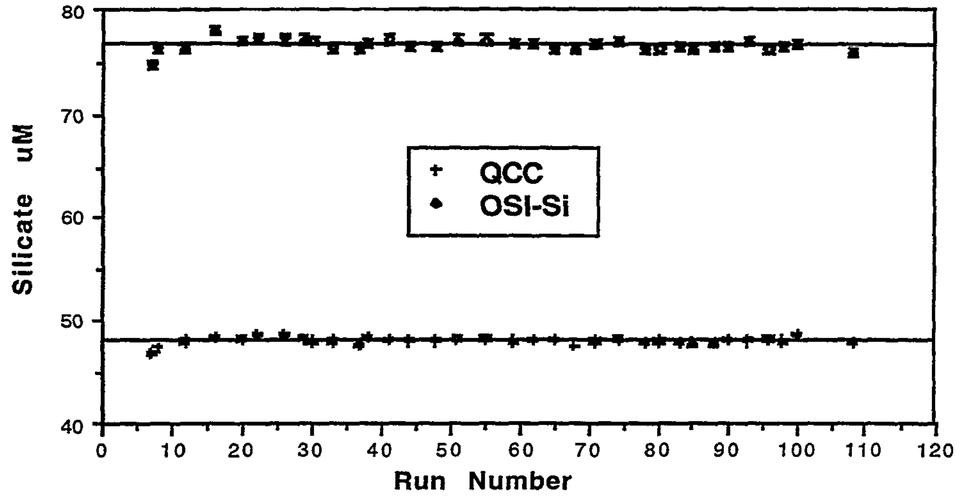
(5) The result for the determination of nitrate in the QCC sample plotted against the calibration coefficient calculated for the analytical run on which that QCC sample was measured.

Fig. 6



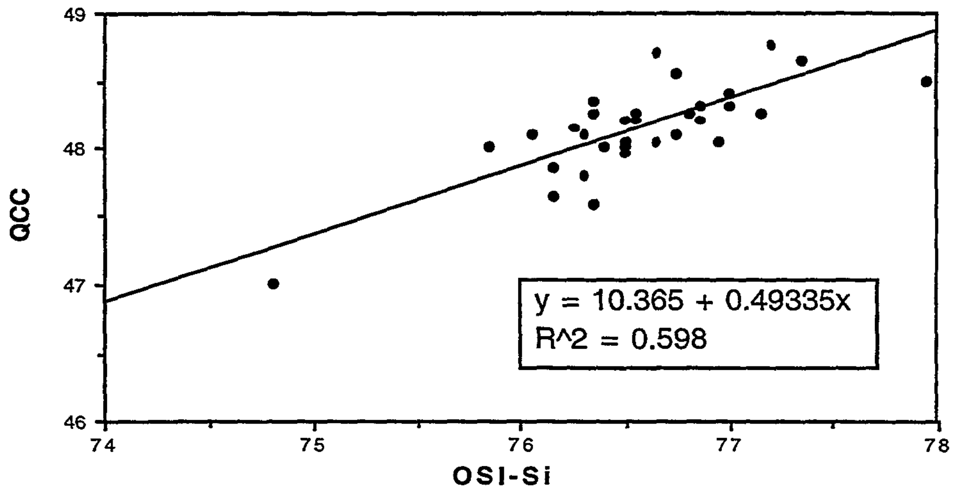
(6) The result for the determination of silicate in the QCC a sample plotted against the result for the QCW sample, for each run on which samples of both quality control materials were analysed.

Fig. 7



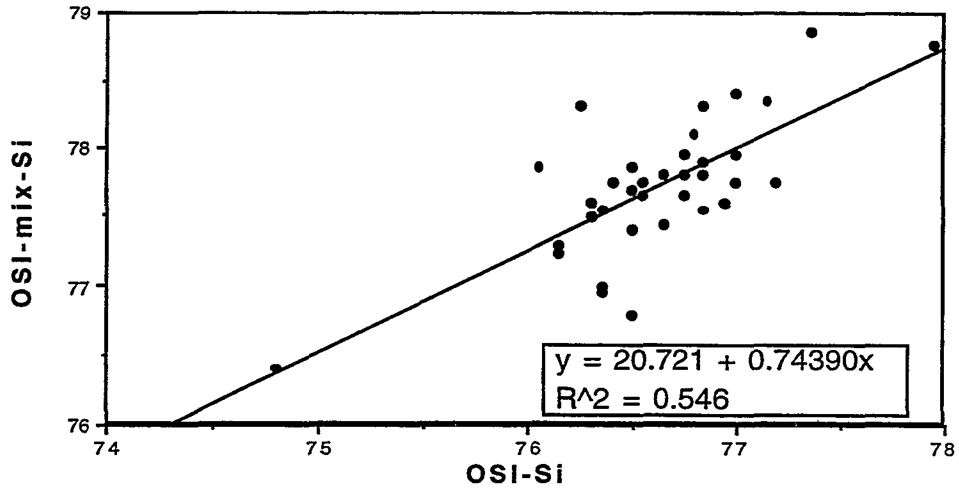
(7) Plot by run number of the results for the determination of silicate in the QCC quality control sample and in the trial quality control solutions prepared by Ocean Scientific International OSI-Si.

Fig. 8



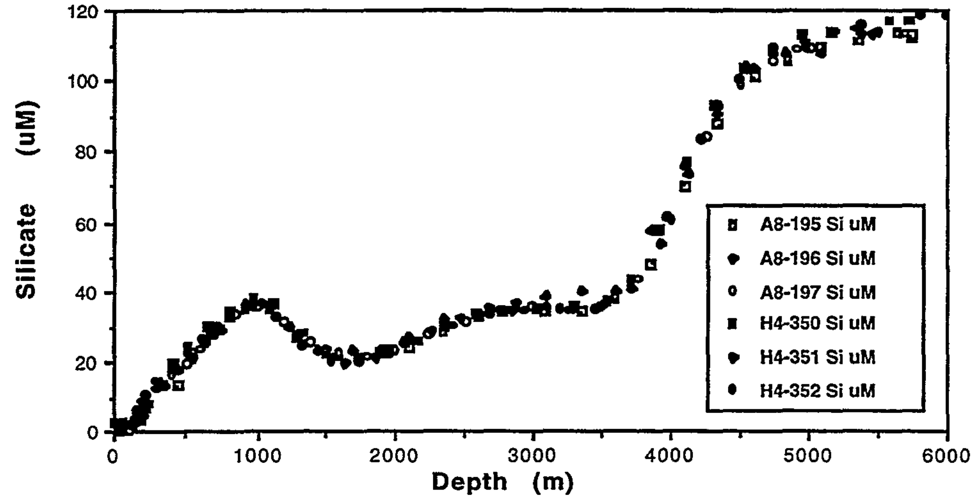
(8) The results for the determination of silicate in the QCC quality control sample and in the trial quality control solutions prepared by Ocean Scientific International OSI-Si

Fig. 9



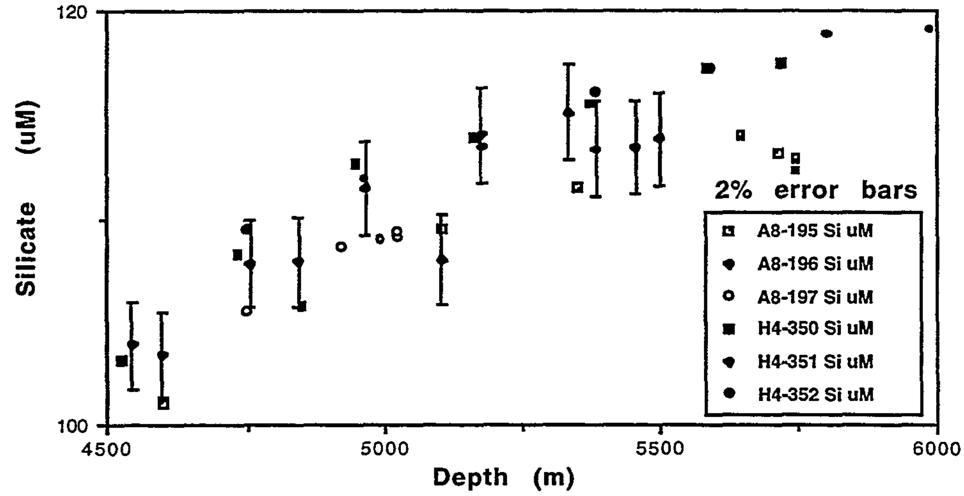
(9) The results for the determination of silicate in the two trial quality control solutions prepared by Ocean Scientific International OSI-Si plotted against one another for runs on which both samples were analysed.

Fig. 10a



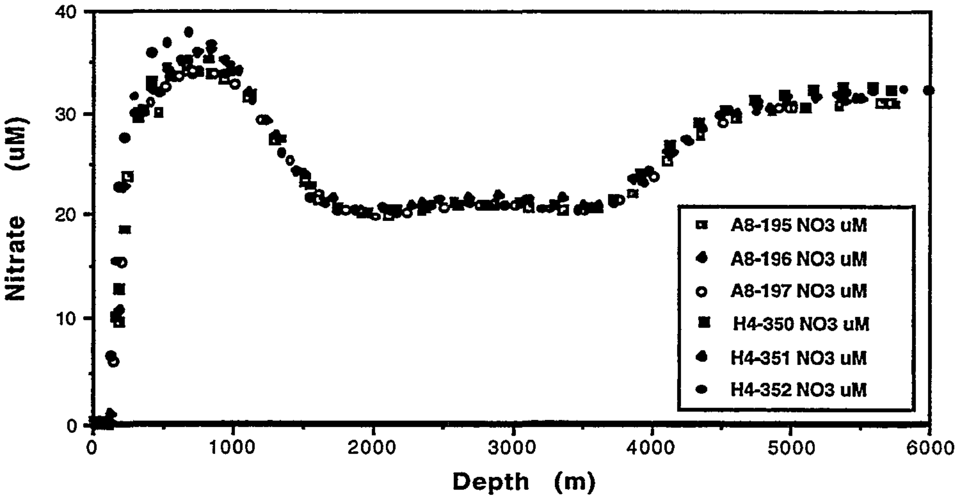
(10a) Plot comparing silicate data obtained on WOCE leg A8 against earlier data collected on the Hydros-4 cruise at geographically similar stations.

Fig. 10b



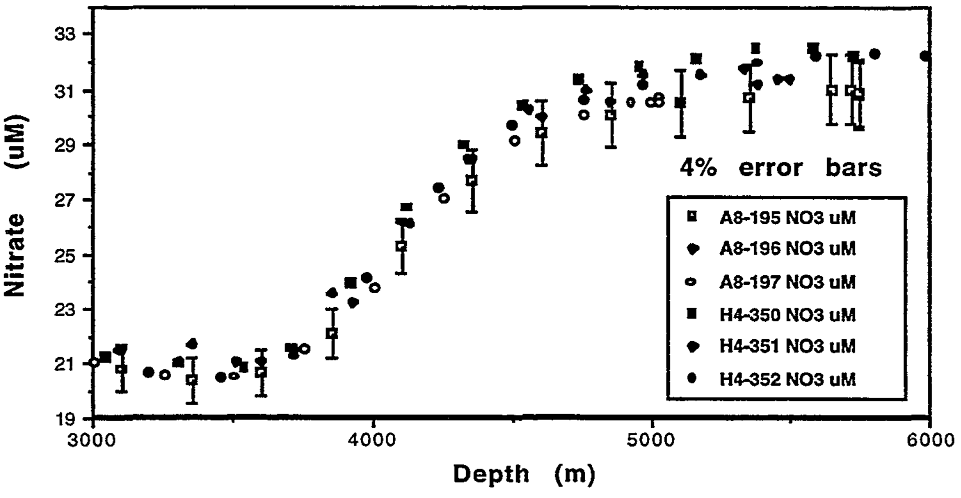
(10b) Plot comparing deep water silicate data obtained on WOCE leg A8 against earlier data collected on the Hydros-4 cruise at geographically similar stations. Error bars drawn only to give an indication of the offset between the data sets.

Fig. 11a



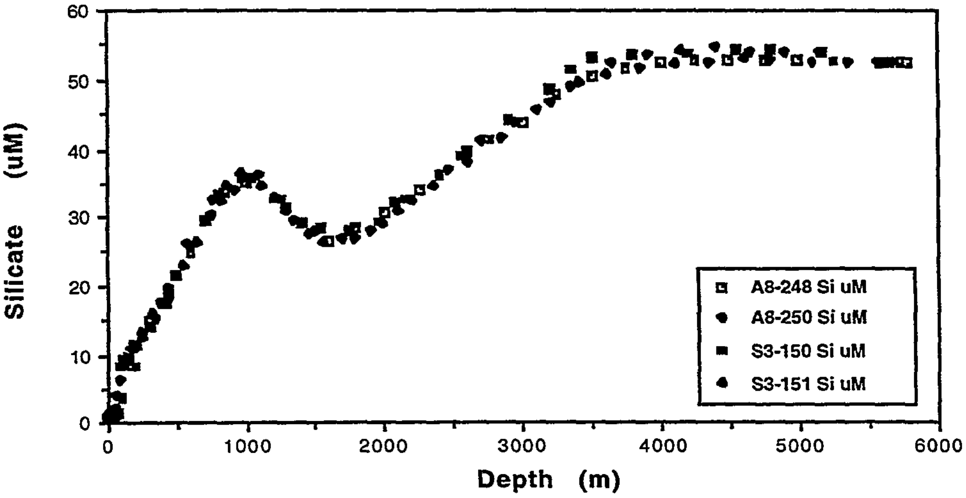
(11a) Plot comparing nitrate data obtained on WOCE leg A8 against earlier data collected on the Hydros-4 cruise at geographically similar stations.

Fig. 11b



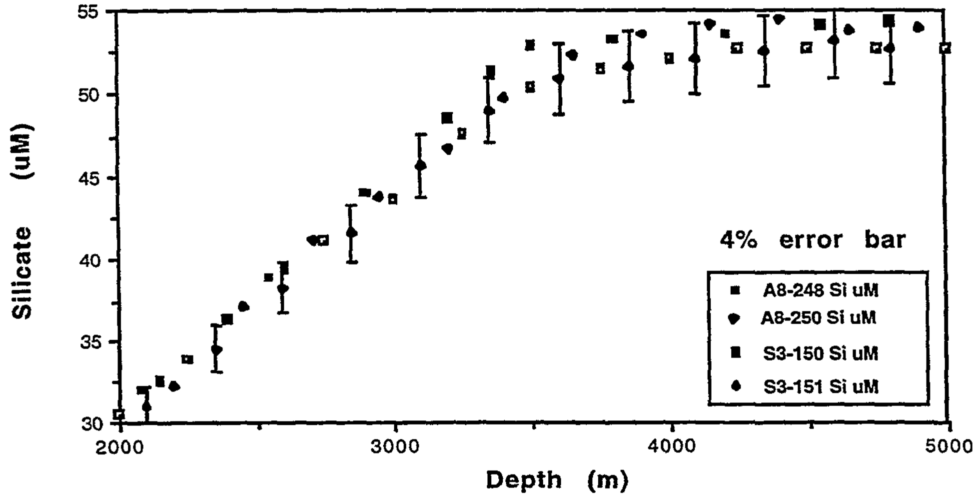
(11b) Plot comparing nitrate data in deep water obtained on WOCE leg A8 against earlier data collected on the Hydros-4 cruise at geographically similar stations. Errors bars are drawn as indicators of the offset between data sets.

Fig. 12a



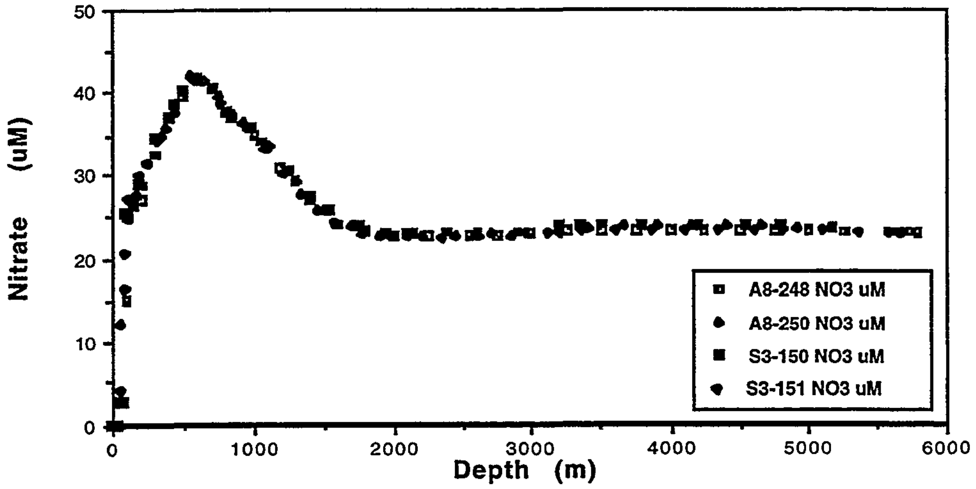
(12b) Plot comparing silicate data obtained on WOCE leg A8 against earlier data collected on the SAVE-3 cruise at geographically similar stations. Errors bars are drawn as indicators of the offset between data sets.

Fig. 12b



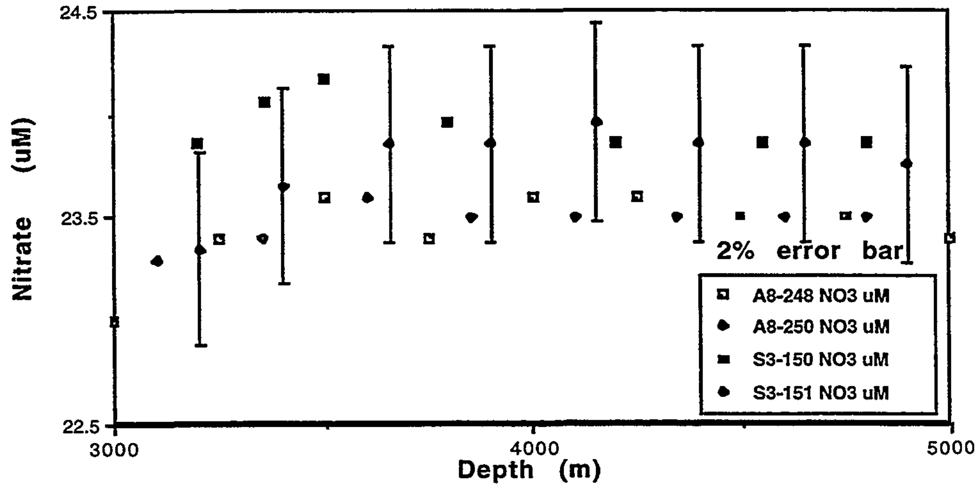
(12b) Plot comparing silicate data in deep water obtained on WOCE leg A8 against earlier data collected on the SAVE-3 cruise at geographically similar stations. Errors bars are drawn as indicators of the offset between data sets.

Fig. 13a



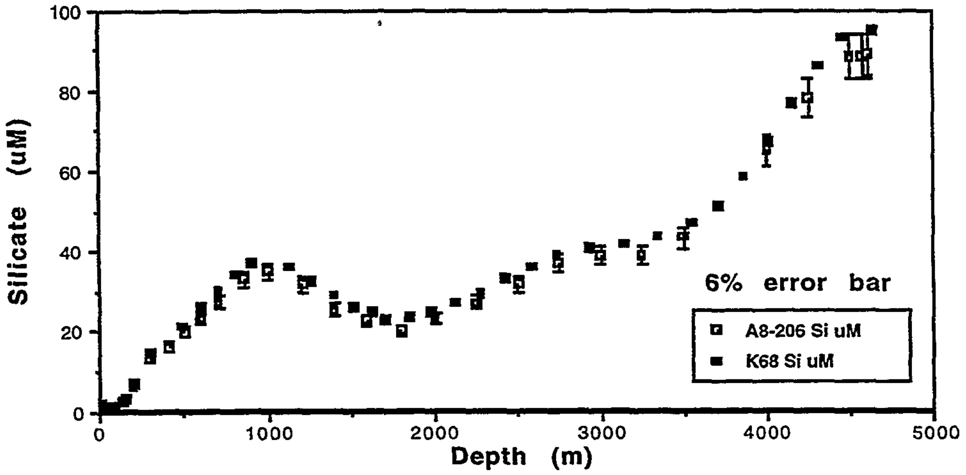
(13a) Plot comparing nitrate data obtained on WOCE leg A8 against earlier data collected on the SAVE-3 cruise at geographically similar stations.

Fig. 13b



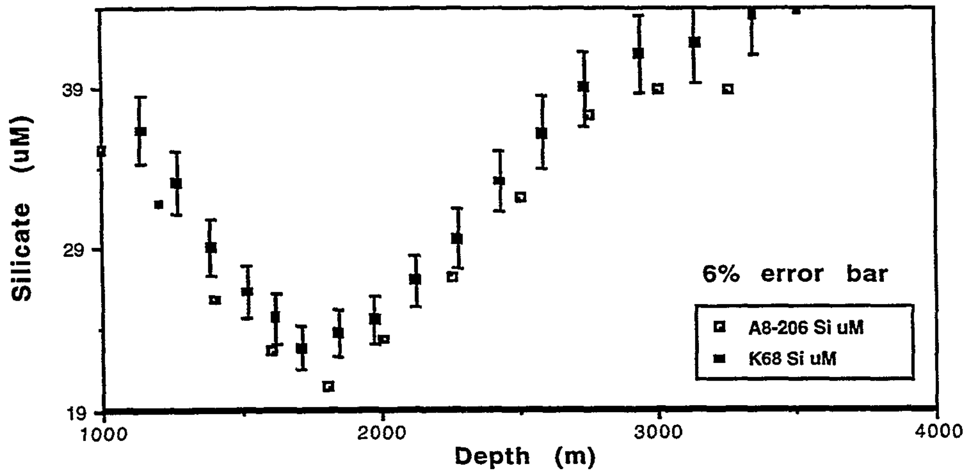
(13b) Plot comparing nitrate data in deep water obtained on WOCE leg A8 against earlier data collected on the SAVE-3 cruise at geographically similar stations. Errors bars are drawn as indicators of the offset between data sets.

Fig. 14a



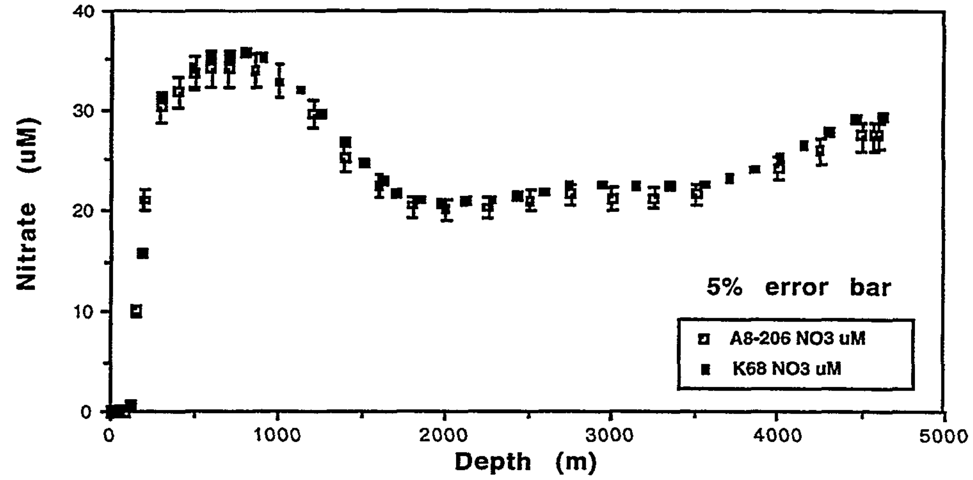
(14a) Plot of the silicate data obtained at the WOCE inter calibration station and determined on board Meteor and Knorr

Fig. 14b



(14b) Plot of the deep water silicate data obtained at the WOCE inter calibration station and determined on board Meteor and Knorr. Error bars are drawn to give an impression of the offset between the data sets.

Fig. 15



(15) Plot of the nitrate data obtained at the WOCE inter calibration station and determined on board Meteor and Knorr. Error bars are drawn to give an impression of the offset between the data sets.

APPENDIX 1. RESULTS OF SAMPLE STORAGE EXPERIMENTS ON CRUISE D199-A11

During cruise D199 (WOCE leg A11) a number of tests were carried out on the storage of samples. This involved repeated measurements at various time intervals after sampling, on the samples collected at stations 12255,12279, 12298 and 12301. We found no changes in sample concentrations greater than differences in the precision of duplicates measured on the same day when samples had been stored in the dark at 4°C before being analysed. When samples had been frozen during storage (accidentally for samples from station 12255, and purposefully for samples from station 12301) the precision of the analyses was less good.

Representative data for precisions of duplicate analyses carried out on the same analytical run on cruise D199 are given below:

Stations 12258,59 and 61 (n=72)

	Si	NO3	PO4
mean uM	77.6	29.9	2.0
% abs diff	0.9	0.6	1.3

Stations 12291,92 and 93 (n=64)

	Si	NO3	PO4
mean uM	52.8	27.4	1.8
% abs diff	0.6	1.0	1.0

These precisions are less good than those recorded on Meteor 28/1. This was probably due to the use of a third generation auto-analyser system an "Alpkem" on Discovery D199. These newer systems seem to be intrinsically less suited to use at sea than the older design AAII (Chemlab) used on Meteor 28/1.

The data for the measurements of the samples from stations 12279, 12298 and 12301 are presented in the attached tables. The results are summarised below.

The samples at station **12279** were measured on the day of collection, one day after and one week later, the mean values for all samples were:

date	8/1/93	9/1/93	16/1/93
silicate	63.75	64.94	63.62
nitrate	29.53	29.78	29.66
phosphate	1.91	1.91	1.91.

The mean absolute differences between duplicates analyses and the subsequent analyses compared to the first analyses were, as percentage of the mean concentration:

date	9/1/93	16/1/93
silicate	2.0	0.9
nitrate	1.3	0.7
phosphate	0.9	0.9

The samples collected at station **12298** were measured on the day of collection and then a week later

date	15/1/93	23/1/93	
	mean uM	mean uM	mean % diff
Si	43.3	43.2	0.4
NO3	27.6	26.4	4.6
PO4	1.80	1.80	1.33

The large difference in nitrate concentrations corresponds to the shift in sensitivity of the nitrate method detected by cruise quality control procedures rather than being the result of a storage problem. The mean percentage difference between duplicates corresponds to mean differences between duplicates measured in the individual runs of:

	15/1/93	23/1/93
	mean % diff	mean % diff
Si	0.60	0.44
NO3	0.65	0.70
PO4	0.78	0.92

The samples collected at station **12301** were measured on the day of collection, and a duplicate set of samples were placed in a -20°C freezer immediately after collection, they were removed one week later and placed in a 4°C refrigerator to defrost slowly for 36 hours before measuring. Replication of the duplicate analyses of the melted samples was poor the percentage mean differences between duplicates were

	Si	NO3	PO4
mean % diff	22.1	18.8	30.6

Conclusions

The sampling vials in which we collect our samples provide a relatively sterile environment, and this coupled with storage in the dark at 4°C sufficiently inhibits algal and bacterial activity in the samples so that high precision analyses can be obtained without the need to analyse samples immediately after collection. This contradicts the WOCE recommended procedure (GORDON et al1993). If the measurements are as usual being made with a continuous flow type auto-analyser system, it is in fact good practice to store up samples so that the machine can be run continuously to analyse a days worth of samples. Auto-analysers are designed to run continuously - their precision tends to be better when they are allowed to settle down rather than being repeatedly switched on and off. Which is what happens when an attempt is made to analyse samples immediately after collection. Taking both these ideas into consideration it seems on balance that the GORDON et al's (1993) assertion that samples should be analysed immediately is if fact recommending **bad** practice.

APPENDIX 2. RESULTS FROM MEASUREMENTS OF OSI QC MATERIALS MEASURED DURING METEOR WOCE LEG A8.

All results are reported here. Listing is by the day on which determinations were made. Duplicate determinations are reported for a silicate solution, a nitrate solution and a mixed silicate, nitrate and phosphate solution all made up in an initially low nutrient natural sea water, and a low nutrient seawater reference material.

Date	Si	Si	NO3	NO3	MixSi	MixSi	MixN	MixN	LNSSi	LNSSi	LNSNO3	LNSNO3
1/4/94	76.7	77.0	8.7	8.7	77.8	78.0	2.6	2.5	1.0	0.9	0.0	0.0
2/4/94	74.8	74.8	4.7	4.7	76.4		0.0					
3/4/94	76.2	76.5	5.6	5.6	76.8	77.1	0.0	0.0	0.8	0.8	0.0	0.0
4/4/94	76.2	75.9	0.0	0.0	77.8	77.9	0.2	0.1	1.0	0.9	0.0	0.0
5/4/94	78.0	77.9	9.2	9.2	78.6	78.9	0.0	0.0	1.1	1.0	0.0	0.0
6/4/94	76.8	76.9	0.0	0.1	77.6	78.0	0.0	0.0	1.3	1.1	0.0	0.1
7/4/94	77.2	77.5	2.1	1.9	78.9	78.8	0.0	0.0	1.2	1.0	0.0	0.0
8/4/94	77.2	77.2	2.5	2.3	77.6	77.9	0.0	0.0	1.3	1.2	0.0	0.0
9/4/94	77.0	77.0	8.5	8.4	78.3	78.5	0.0	0.0	1.3	1.1	0.0	0.0
10/4/94	77.0	76.9	13.5	13.4	77.6	77.6	3.3	3.3	1.0	1.0	0.0	0.0
11/4/94	76.0	76.6	0.0	0.0	77.6	77.4	0.0	0.0	1.1	0.9	0.0	0.0
12/4/94	76.1	76.5	0.0	0.0	77.6	77.6	0.0	0.0	1.1	1.0	0.0	0.0
13/4/94	76.5	77.0	0.7	0.6	77.7	77.9	0.0	0.0	1.0	0.8	0.0	0.0
14/4/94	77.0	77.3	0.0	0.0	78.5	78.2	1.3	1.3	1.2	1.0	0.0	0.0
15/4/94	76.4	76.7	8.1	8.1	77.8	77.7	0.0	0.0	1.0	1.0	0.0	0.0
16/4/94	76.4	76.6	1.8	1.7	76.7	76.9	0.0	0.0	1.5	1.4	0.0	0.0
17/4/94	77.0	77.0	0.0	0.0	78.0	77.9	0.0	0.0	1.1	1.0	0.0	0.0
18/4/94	77.0	77.0	0.0	0.0	77.9	77.6	0.0	0.0	1.0	0.9	0.0	0.0
19/4/94	76.8	76.5	0.0	0.0	77.5	77.4	0.0	0.0	0.9	0.8	0.0	0.0
20/4/94	76.9	76.7	0.0	0.0	78.3	77.9	0.0	0.0	1.1	0.9	0.0	0.0
21/4/94	76.3	76.4	0.0	0.0	77.1	76.9	0.0	0.0	1.2	0.9	0.0	0.0
22/4/94	76.0	76.3	0.0	0.0	77.4	77.1	0.0	0.0	1.1	1.0	0.0	0.0
23/4/94	76.6	76.9	5.5	5.4	77.6	77.7	0.0	0.0	1.1	0.9	0.0	0.0
24/4/94	76.9	76.8	0.0	0.0	78.2	78.4	0.0	0.0	1.2	1.0	0.0	0.0
25/4/94	76.3	76.5			77.8	77.7	0.0	0.0	1.1	1.0	0.0	0.0
26/4/94	76.1	76.4			78.2	78.4	0.0	0.0	1.2	1.1	0.0	0.0
27/4/94	76.4	76.6	0.0	0.0	77.8	77.9	0.0	0.0	1.1	0.9	0.0	0.0
28/4/94	76.0	76.3			77.4	77.2	0.0	0.0	1.4	1.3	0.0	0.0
29/4/94	76.6	76.4			77.7	77.7	0.0	0.0	1.2	1.1	0.0	0.0
30/4/94	76.4	76.7			77.7	77.6	0.0	0.0	1.1	1.0	0.0	0.0
1/5/94	76.8	76.9	0.0	0.0	77.3	77.8	0.0	0.0	1.0	1.1	0.0	0.0
2/5/94	76.3	76.4			77.5	77.6	0.0	0.0	1.4	1.2	0.0	0.0

Date	Si	Si	NO3	NO3	MixSi	MixSi	MixN	MixN	LNSSi	LNSSi	LNSNO3	LNSNO3
3/5/94	76.4	76.6	0.0	0.0	77.4	77.4	0.0	0.0	1.2	1.0	0.0	0.0
4/5/94	76.8	76.5			77.8		0.0		1.1	1.0	0.0	0.0
7/5/94	76.7	76.8			77.9	78.0	0.0	0.0	1.3	1.1	0.0	0.0

APPENDIX 3. RESULTS OF THE DETERMINATIONS OF SILICATE AND NITRATE CONCENTRATIONS IN SAGAMI REFERNCE MATERIALS. LISTED BY DATE OF THE DETERMINATION AND THE RUN NUMBER ON WHICH THE DETERMINATION WAS MADE.

date	**run no.**	**Sag 50 Si**	**Sag 10 NO3**
9/4/94	29	50.2	9.8
9/4/94	29	50.1	9.5
9/4/94	29	50.0	9.9
10/4/94	31	48.6	9.7
10/4/94	31	48.8	9.6
10/4/94	32	49.6	9.7
10/4/94	32	49.4	9.6
10/4/94	32	49.6	9.7
11/4/94	34	49.4	9.7
11/4/94	34	49.4	9.7
17/4/94	53	50.3	9.8
17/4/94	53	50.1	9.8
17/4/94	53	49.9	9.6
17/4/94	53	49.8	9.7
17/4/94	53	49.7	9.7
18/4/94	55	49.5	9.7
18/4/94	55	49.6	9.6
18/4/94	55	49.6	9.6
20/4/94	64		9.8
20/4/94	64		9.7
20/4/94	64		9.8
24/4/94	76	49.8	9.9
24/4/94	76	50.3	9.9
24/4/94	76	50	9.9
25/4/94	79		9.8
25/4/94	79		9.9
25/4/94	79		9.9
25/4/94	79		9.9
25/4/94	79		9.9
25/4/94	79		10
2/5/94	96	50	9.8
2/5/94	96	49.9	9.3
2/5/94	96	49.8	9.9
2/5/94	98	49.5	9.9
2/5/94	98	49.5	9.8
2/5/94	98	49.6	9.8

	Si 50.0uM	NO3 10.0uM
mean	49.7	9.8
stdev	0.40	0.14
% stdev	0.8	1.5
n	27	36

APPENDIX 4. ALL DATA FROM MEASUREMNTS OF INTERNAL QCC SAMPLES RUN DURING METEOR WOCE LEG A8.

(QCC are aliquots of deep seawater sample stored in 30 ml dilu-vials in dark at 4°C.)

date	Run No	Type	Silicon	Nitrate	Running mean Si	Running mean NO3	%Difference from starting mean	
							Si	NO3
							48.22	22.22
1/4/94	3	QCC1	48.5	22.4				
1/4/94	3	QCC2	48.6	22.5	48.55	22.45	0.79	1.26
2/4/94	4	QC-bulk	48.1	22.1	48.40	22.33	-0.25	-0.54
2/4/94	4	QC-bulk	48.4	22.3	48.40	22.33	0.37	0.36
2/4/94	4	QC-bulk	48.3	22.3	48.38	22.32	0.17	0.36
2/4/94	4	QC-bulk	48.2	22.2	48.35	22.30	-0.04	-0.09
2/4/94	4	QC-bulk	48.3	22.2	48.34	22.29	0.17	-0.09
2/4/94	5	QCC	48.1	22.2	48.31	22.28	-0.25	-0.09
2/4/94	5	QCC	47.7	21.9	48.24	22.23	-1.08	-1.44
2/4/94	6	QCC1	48	22.1	48.22	22.22	-0.46	-0.54
2/4/94	6	QCC2	48	22.1	48.20	22.21	-0.46	-0.54
2/4/94	6	QCC3	48.4	22.3	48.22	22.22	0.37	0.36
2/4/94	6	QCC4	48.2	22.2	48.22	22.22	-0.04	-0.09
2/4/94	6	QCC5	48.2	22.3	48.21	22.22	-0.04	0.36
2/4/94	6	QCC6	48.1	22.1	48.21	22.21	-0.25	-0.54
2/4/94	6	QCC7	48.1	22.2	48.20	22.21	-0.25	-0.09
2/4/94	6	QCC8	48.3	22.1	48.21	22.21	0.17	-0.54
2/4/94	6	QCC9	48.3	22.2	48.21	22.21	0.17	-0.09
2/4/94	6	QCC10	48.2	22.1	48.21	22.20	-0.04	-0.54
2/4/94	6	QCC11	48.2	22.1	48.21	22.20	-0.04	-0.54
2/4/94	6	QCC12	48.1	22.1	48.20	22.19	-0.25	-0.54
2/4/94	6	QCC13	48.3	22.1	48.21	22.19	0.17	-0.54
2/4/94	6	QCC14	48.2	22.1	48.21	22.18	-0.04	-0.54
2/4/94	6	QCC15	48.1	21.9	48.20	22.17	-0.25	-1.44
2/4/94	7	QCC1	47	21.7	48.16	22.15	-2.53	-2.34
2/4/94	7	QCC1	47	21.8	48.11	22.14	-2.53	-1.89
3/4/94	8	QCC1	47.6	22.2	48.09	22.14	-1.29	-0.09
3/4/94	8	QCC1	47.6	22.1	48.08	22.14	-1.29	-0.54
3/4/94	9	QCC1	47.1	21.8	48.04	22.13	-2.32	-1.89
3/4/94	9	QCC1	47.3	21.9	48.02	22.12	-1.91	-1.44
3/4/94	10	QCC	47.8	22.2	48.01	22.12	-0.87	-0.09
3/4/94	10	QCC1	48.1	22.2	48.01	22.13	-0.25	-0.09

date	Run No	Type	Silicon	Nitrate	mean Si	mean NO3	%Dif from start	
4/4/94	12	QCC1	48	22	48.01	22.12	-0.46	-0.99
4/4/94	12	QCC2	48.2	22.1	48.02	22.12	-0.04	-0.54
4/4/94	13	QCC1	48	22.1	48.02	22.12	-0.46	-0.54
4/4/94	13	QCC2	48.1	22.2	48.02	22.12	-0.25	-0.09
4/4/94	14	QCC1	47.5	22	48.01	22.12	-1.49	-0.99
4/4/94	14	QCC2	47.6	22	47.99	22.12	-1.29	-0.99
4/4/94	15	QCC1	48	22.2	47.99	22.12	-0.46	-0.09
4/4/94	15	QCC2	48.3	22.2	48.00	22.12	0.17	-0.09
5/4/94	16	QCC1	48.4	22	48.01	22.12	0.37	-0.99
5/4/94	16	QCC2	48.6	22.2	48.03	22.12	0.79	-0.09
5/4/94	17	QCC1	48.5	22.4	48.04	22.13	0.58	0.81
5/4/94	17	QCC2	48.4	22.5	48.05	22.13	0.37	1.26
5/4/94	18	QCC1	48.3	22	48.05	22.13	0.17	-0.99
5/4/94	18	QCC2	48.4	22	48.06	22.13	0.37	-0.99
6/4/94	19	QCC1	49	22.2	48.08	22.13	1.62	-0.09
6/4/94	19	QCC2	48.9	22.2	48.10	22.13	1.41	-0.09
6/4/94	20	QCC1	48.1	21.9	48.10	22.13	-0.25	-1.44
6/4/94	20	QCC2	48.5	21.9	48.10	22.12	0.58	-1.44
6/4/94	21	QCC1	48.2	22.1	48.11	22.12	-0.04	-0.54
6/4/94	21	QCC2	48.5	22.2	48.11	22.12	0.58	-0.09
7/4/94	22	QCC1	48.6	22.2	48.12	22.12	0.79	-0.09
7/4/94	22	QCC2	48.7	22.1	48.13	22.12	1.00	-0.54
7/4/94	23	QCC1	47.9	21.8	48.13	22.12	-0.66	-1.89
7/4/94	23	QCC2	48.1	21.9	48.13	22.11	-0.25	-1.44
7/4/94	24	QCC1	48.4	22.2	48.13	22.12	0.37	-0.09
7/4/94	24	QCC2	48.7	22.2	48.14	22.12	1.00	-0.09
8/4/94	25	QCC1	48.2	22	48.14	22.12	-0.04	-0.99
8/4/94	25	QCC2	48.2	22.1	48.15	22.12	-0.04	-0.54
8/4/94	26	QCC1	48.7	22.3	48.15	22.12	1.00	0.36
8/4/94	26	QCC2	48.8	22.3	48.16	22.12	1.20	0.36
9/4/94	27	QCC1	48.1	21.9	48.16	22.12	-0.25	-1.44
9/4/94	27	QCC2	48.4	21.8	48.17	22.11	0.37	-1.89
9/4/94	28	QCC-1	47.8	22	48.16	22.11	-0.87	-0.99
9/4/94	28	QCC-2	48	22	48.16	22.11	-0.46	-0.99
9/4/94	29	QCC1	48.3	22.3	48.16	22.11	0.17	0.36
9/4/94	29	QCC2	48.5	22.3	48.17	22.11	0.58	0.36
10/4/94	30	QCC1	48	22	48.16	22.11	-0.46	-0.99
10/4/94	30	QCC2	48.1	22.1	48.16	22.11	-0.25	-0.54
10/4/94	31	QCC1	47.7	21.9	48.16	22.11	-1.08	-1.44
10/4/94	31	QCC2	47.9	21.9	48.15	22.11	-0.66	-1.44

date	Run No	Type	Silicon	Nitrate	mean Si	mean NO3	%Dif from start	
10/4/94	32	QCC-1	48.4	21.9	48.16	22.10	0.37	-1.44
10/4/94	32	QCC-2	48.3	21.9	48.16	22.10	0.17	-1.44
11/4/94	33	QCC1	48	21.8	48.16	22.10	-0.46	-1.89
11/4/94	33	QCC2	48.2	21.9	48.16	22.09	-0.04	-1.44
11/4/94	34	QCC1	47.6	21.8	48.15	22.09	-1.29	-1.89
11/4/94	34	QCC2	47.7	21.8	48.14	22.09	-1.08	-1.89
11/4/94	35	QCC1	48.1	22	48.14	22.09	-0.25	-0.99
11/4/94	35	QCC2	48.1	22	48.14	22.09	-0.25	-0.99
12/4/94	36	QCC1	48.4	21.5	48.15	22.08	0.37	-3.24
12/4/94	36	QCC2	48.5	21.6	48.15	22.07	0.58	-2.79
12/4/94	37	QCC1	47.8	20.9	48.15	22.06	-0.87	-5.94
12/4/94	37	QCC2	47.8	21.1	48.14	22.05	-0.87	-5.04
13/4/94	38	QCC1	48.5	22	48.15	22.05	0.58	-0.99
13/4/94	38	QCC2	48.6	22	48.15	22.05	0.79	-0.99
13/4/94	39	QCC1	47.3	21.2	48.14	22.04	-1.91	-4.59
13/4/94	39	QCC2	47.7	21.4	48.14	22.03	-1.08	-3.69
13/4/94	40	QCC1	48	21.7	48.13	22.02	-0.46	-2.34
13/4/94	40	QCC2	48.3	21.8	48.14	22.02	0.17	-1.89
14/4/94	41	QCC1	48.2	21.5	48.14	22.02	-0.04	-3.24
14/4/94	41	QCC2	48.3	21.5	48.14	22.01	0.17	-3.24
14/4/94	42	QCC1	48.4	21.9	48.14	22.01	0.37	-1.44
14/4/94	42	QCC2	48.1	21.8	48.14	22.01	-0.25	-1.89
14/4/94	43	QCC1	48.6	22.1	48.15	22.01	0.79	-0.54
14/4/94	43	QCC2	48.5	22	48.15	22.01	0.58	-0.99
15/4/94	44	QCC1	48.2	22.1	48.15	22.01	-0.04	-0.54
15/4/94	44	QCC2	48.2	22.2	48.15	22.01	-0.04	-0.09
15/4/94	45	QCC1	47.6	21.8	48.15	22.01	-1.29	-1.89
15/4/94	45	QCC2	47.8	21.8	48.14	22.01	-0.87	-1.89
15/4/94	46	QCC1	48.2	22	48.14	22.01	-0.04	-0.99
15/4/94	46	QCC2	48.2	22.2	48.14	22.01	-0.04	-0.09
15/4/94	47	QCC1	48.4	22	48.15	22.01	0.37	-0.99
15/4/94	47	QCC2	48.3	22	48.15	22.01	0.17	-0.99
16/4/94	48	QCC1	48.2	21.3	48.15	22.00	-0.04	-4.14
16/4/94	48	QCC2	48.2	21.3	48.15	22.00	-0.04	-4.14
16/4/94	49	QCC1	48.1	21.9	48.15	21.99	-0.25	-1.44
16/4/94	49	QCC2	48.1	21.9	48.15	21.99	-0.25	-1.44
16/4/94	50	QCC1	48.3	21.8	48.15	21.99	0.17	-1.89
16/4/94	50	QCC2	48.4	21.9	48.15	21.99	0.37	-1.44
17/4/94	51	QCC1	48.1	21.6	48.15	21.99	-0.25	-2.79
17/4/94	51	QCC2	48.5	21.6	48.15	21.98	0.58	-2.79

date	Run No	Type	Silicon	Nitrate	mean Si	mean NO3	%Dif from start	
17/4/94	52	QCC1	47.6	21.5	48.15	21.98	-1.29	-3.24
17/4/94	52	QCC2	47.6	21.5	48.14	21.98	-1.29	-3.24
17/4/94	53	QCC1	48.3	21.3	48.15	21.97	0.17	-4.14
17/4/94	53	QCC2	48.5	21.4	48.15	21.96	0.58	-3.69
17/4/94	53	QCC3	48	21	48.15	21.96	-0.46	-5.49
17/4/94	53	QCC4	47.9	21.1	48.14	21.95	-0.66	-5.04
17/4/94	54	QCC1	48.1	21.4	48.14	21.94	-0.25	-3.69
17/4/94	54	QCC2	48.4	21.4	48.15	21.94	0.37	-3.69
18/4/94	55	QCC1	48.2	21.9	48.15	21.94	-0.04	-1.44
18/4/94	55	QCC2	48.4	21.9	48.15	21.94	0.37	-1.44
18/4/94	57	QCC1	48	22	48.15	21.94	-0.46	-0.99
18/4/94	57	QCC2	48.1	22	48.15	21.94	-0.25	-0.99
18/4/94	57	QCC3	48.4	21.3	48.15	21.94	0.37	-4.14
18/4/94	57	QCC4	48.2	21.4	48.15	21.93	-0.04	-3.69
18/4/94	57	QCC5	48	21.9	48.15	21.93	-0.46	-1.44
18/4/94	57	QCC6	48	21.8	48.15	21.93	-0.46	-1.89
18/4/94	58	QCC1	48	21.9	48.15	21.93	-0.46	-1.44
18/4/94	58	QCC2	48.2	21.9	48.15	21.93	-0.04	-1.44
19/4/94	59	QCC1	48	20.3	48.15	21.92	-0.46	-8.64
19/4/94	59	QCC2	48.1	20.3	48.15	21.90	-0.25	-8.64
19/4/94	60	QCC1	47.7	19.3	48.14	21.88	-1.08	-13.14
19/4/94	60	QCC2	47.8	19.3	48.14	21.87	-0.87	-13.14
19/4/94	61	QCC1	48	21.4	48.14	21.86	-0.46	-3.69
19/4/94	61	QCC2	48.2	21.3	48.14	21.86	-0.04	-4.14
20/4/94	62	QCC1	48.2	21.9	48.14	21.86	-0.04	-1.44
20/4/94	62	QCC2	48.3	21.8	48.14	21.86	0.17	-1.89
20/4/94	63	QCC1	47.7	21.3	48.14	21.85	-1.08	-4.14
20/4/94	63	QCC2	47.9	21.3	48.14	21.85	-0.66	-4.14
20/4/94	64	QCC1	48.1	19.7	48.14	21.83	-0.25	-11.34
20/4/94	64	QCC2	48.1	19.7	48.14	21.82	-0.25	-11.34
21/4/94	65	QCC1	48.2	21.2	48.14	21.82	-0.04	-4.59
21/4/94	65	QCC2	48.3	21.1	48.14	21.81	0.17	-5.04
21/4/94	66	QCC1	47.4	20.8	48.13	21.80	-1.70	-6.39
21/4/94	66	QCC2	47.7	20.7	48.13	21.80	-1.08	-6.84
21/4/94	67	QCC1	48.2	20.7	48.13	21.79	-0.04	-6.84
21/4/94	67	QCC2	48.3	20.8	48.13	21.78	0.17	-6.39
22/4/94	68	QCC1	47.7	21.5	48.13	21.78	-1.08	-3.24
22/4/94	68	QCC2	47.6	21.4	48.12	21.78	-1.29	-3.69
22/4/94	69	QCC1	48	21.4	48.12	21.77	-0.46	-3.69
22/4/94	69	QCC2	48.1	21.4	48.12	21.77	-0.25	-3.69

date	Run No	Type	Silicon	Nitrate	mean Si	mean NO3	%Dif from start	
22/4/94	70	QCC1	47.7	19.8	48.12	21.76	-1.08	-10.89
22/4/94	70	QCC2	47.8	19.6	48.12	21.75	-0.87	-11.79
23/4/94	71	QCC1	48	20.6	48.12	21.74	-0.46	-7.29
23/4/94	71	QCC2	48.2	20.6	48.12	21.73	-0.04	-7.29
23/4/94	72	QCC1	48.1	20	48.12	21.72	-0.25	-9.99
23/4/94	72	QCC2	48.1	20.1	48.12	21.71	-0.25	-9.54
23/4/94	73	QCC1	48.1	20.7	48.12	21.70	-0.25	-6.84
23/4/94	73	QCC2	48.2	20.7	48.12	21.70	-0.04	-6.84
24/4/94	74	QCC1	48.2	20.9	48.12	21.69	-0.04	-5.94
24/4/94	74	QCC2	48.4	21	48.12	21.69	0.37	-5.49
24/4/94	75	QCC1	48.1	21.5	48.12	21.69	-0.25	-3.24
24/4/94	75	QCC2	48.3	21.6	48.12	21.69	0.17	-2.79
24/4/94	76	QCC1	48.1	21.3	48.12	21.68	-0.25	-4.14
24/4/94	76	QCC2	48.1	21.3	48.12	21.68	-0.25	-4.14
24/4/94	77	QCC1	48.2	21.4	48.12	21.68	-0.04	-3.69
24/4/94	77	QCC2	48.2	21.3	48.12	21.68	-0.04	-4.14
25/4/94	78	QCC1	47.9	21.8	48.12	21.68	-0.66	-1.89
25/4/94	78	QCC2	48.1	21.7	48.12	21.68	-0.25	-2.34
25/4/94	79	QCC1	48.2	21.3	48.12	21.68	-0.04	-4.14
25/4/94	79	QCC2	48.5	21.4	48.12	21.67	0.58	-3.69
26/4/94	80	QCC1	48	20.8	48.12	21.67	-0.46	-6.39
26/4/94	80	QCC2	48.3	20.7	48.12	21.66	0.17	-6.84
26/4/94	81	QCC1	47.9	20.8	48.12	21.66	-0.66	-6.39
26/4/94	81	QCC2	48	20.8	48.12	21.65	-0.46	-6.39
27/4/94	82	QCC1	48	20.5	48.12	21.65	-0.46	-7.74
27/4/94	82	QCC2	48.2	20.6	48.12	21.64	-0.04	-7.29
27/4/94	83	QCC1	48	21	48.12	21.64	-0.46	-5.49
27/4/94	83	QCC2	48	20.9	48.12	21.63	-0.46	-5.94
27/4/94	84	QCC1	48.1	21.9	48.12	21.64	-0.25	-1.44
27/4/94	84	QCC2	48.5	21.9	48.12	21.64	0.58	-1.44
28/4/94	85	QCC1	47.8	20.9	48.12	21.63	-0.87	-5.94
28/4/94	85	QCC2	47.9	20.9	48.12	21.63	-0.66	-5.94
28/4/94	86	QCC1	47.9	20.7	48.12	21.62	-0.66	-6.84
28/4/94	86	QCC2	48	20.8	48.12	21.62	-0.46	-6.39
28/4/94	87	QCC1	47.8	19	48.12	21.61	-0.87	-14.49
28/4/94	87	QCC2	48	19.1	48.11	21.59	-0.46	-14.04
29/4/94	88	QCC1	47.9	21.0	48.11	21.59	-0.66	-5.49
29/4/94	88	QCC2	48.0	20.8	48.11	21.58	-0.46	-6.39
29/4/94	89	QCC1	48.1	19.1	48.11	21.57	-0.25	-14.04
29/4/94	89	QCC2	48.2	19.1	48.11	21.56	-0.04	-14.04

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