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James Rennell Centre
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INTERNAL DOCUMENT No. 19

Report on the maintenance of precision and accuracy of measurements of dissolved nutrients - silicate, nitrate and phosphate - over 40 days of measurement on D213

S E Holley

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WOCE

Institute of
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DOCUMENT DATA SHEET

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PUBLICATION DATE 1995

TITLE

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REFERENCE

James Rennell Centre for Ocean Circulation, Internal Document, No. 19, 20pp., figs & appendices. (Unpublished manuscript)

ABSTRACT

The nutrient data obtained on D213 is reviewed to assess the precision of the data and its likely accuracy. The analyses were carried out using standard (AAII) auto-analyser methods. Throughout this report reference is made to the *Meteor* 28/1 cruise in 1994 (WOCE line A8) where similar procedures were used to measure the nutrients and to assess precision and accuracy.

The method precision was assessed through duplicate sample measurements and through the analysis of quality control (QC) samples. Over the duration of D213 the mean sample duplicate differences were as follows: silicate 0.256 umol/l; nitrate 0.222 umol/l; and phosphate 0.045 umol/l. This is equivalent to 0.17, 0.6 and 1.5% full scale for silicate, nitrate and phosphate respectively. This compares to an average duplicate difference of 0.3% on M28/1 for both silicate and nitrate, phosphate was not measured on M28/1. The QC material used on D213 included a bulk seawater sample collected at the start of the cruise and an external reference seawater sample (prepared by OSI) preserved in mercuric chloride. The mean (and CV%) for the bulk seawater sample (QC1) was: silicate 68.43 umol/l (1.36%); nitrate 26.43 umol/l (2.85%); and phosphate 1.85 umol/l (7.56%). The reproducibility of the OSI standard (QC2) was similar.

The accuracy of the calibrations was measured with respect to certified reference standards (Sagami Chemical Co, Japan). Measurements on D213 were 3% low for silicate (compared with 0.6% on M28/1) and 2.5% low for nitrate compared with 2% on M28/1. Against the Sagami reference material phosphate measurements were 5.3% low. Offsets between the D213 results and those measured on replicate stations on D201 (1993) suggest that the silicate measurements are up to 2% lower than previously and nitrate up to 5% lower. These results are similar to the offsets seen between M28/1 data and historical data sets at 11°S.

The results suggest that there is still a problem in accurately calibrating the nutrient measurements. If better agreement between results is to be attained a stable reference material must be used to set up and control the calibration of the nutrient analysis systems on all cruises, as is the case with salinity.

KEYWORDS

ISSUING ORGANISATION

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1.0 INTRODUCTION

The WOCE requirements for accuracy and precision are silicate 1-3% accuracy (0.2% full scale precision); nitrate 1% accuracy (0.2% full scale precision); and phosphate 1-2% accuracy (0.4% full scale precision) (JOYCE, 1991). The aim of this report is to document the procedures used to assess the accuracy and precision, and to define the levels that can be achieved on a WOCE cruise.

The results obtained are compared to the M28/1 cruise where similar procedures for both the measurement of nutrients and assessment of precision and accuracy were used (HYDES, 1994). Procedures included the rigorous use of quality control (QC) materials and recording of all data relevant to the calibration. The precision of the results on D213 was assessed through the use of quality control materials and duplicate differences between the samples. The QC materials included individual samples of seawater stored at 4°C, taken from a bulk deep water sample at the start of the cruise, and samples of an externally prepared (OSI) QC material preserved in mercuric chloride. Comparisons with historical data and the use of certified reference standards were used to assess the accuracy of the measurements made. The use of more than one type of QC material allowed an estimate to be made on the run to run variation in the accuracy of the measurements.

2.0 SAMPLING

Nutrient samples were collected, after the CFC and oxygen samples had been taken, into new 30 ml plastic 'diluvial' containers that had been rinsed 3 times with the sample. The samples were stored in a refrigerator at 4°C for up to 12 hours then poured into 8 ml analyser cups, that had been rinsed thoroughly with sample, for analysis.

It should be noted that the samples froze on one occasion, station 12683, resulting in a slight increase in the mean duplicate difference for this station compared with the previous and following two stations. After this station the refrigerator temperature was adjusted

3.0 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.

3.1 Methods

Silicate analysis followed the standard AAII molybdate-ascorbic acid method with the addition of a 37°C heating bath (HYDES, 1984). In order to de-sensitise the system, so that a linear response was obtained from the colorimeter over the concentration range up 0 to 150 umol/l of silicate, the colorimeter was fitted with a 15 mm flow cell and a 660 nm filter.

The standard AAII method using sulphanilamide and naphthylethylenediamine - dihydrochloride was used for nitrate analysis (GRASSHOFF, 1976) with a Cadmium-Copper alloy reduction column (HYDES AND HILL, 1985). In order to de-sensitise the system so that a linear response could be obtained from the colorimeter over the concentration range up 0 to 50 umol/l of nitrate, the colorimeter was fitted with a 15 mm flow cell, and a sample volume of 0.1 ml/min was used. A nitrite top standard (40 umol/l) was prepared with each set of working standards and analysed on each run to give an indication of the nitrate cadmium column reducing efficiency. The column was replaced at station 12763.

For phosphate analysis the standard AAII method was used (HYDES, 1984) which follows the method of MURPHY AND RILEY (1962).

All measurements were made in the constant temperature laboratory. Previous cruises suggested that a stable temperature improved precision. The laboratory temperature remained between 23 - 24°C apart from between the first and second station when the temperature increased to 29°C over night.

3.2 Nutrient standards

Primary calibration standards were prepared from nutrient salt material dried at 110°C over night then cooled over silica gel in a desiccator before weighing (the precision of weighing was better than 1 part per thousand). 10 mmol/l stock solutions for silicate were prepared from a known weight of sodium silica fluoride close to 0.960g, dissolution was aided by initially placing the solution in an ultrasonic bath. The primary phosphate standards were prepared from a known weight of potassium dihydrogen phosphate close to 0.681g. Working phosphate standards were prepared from a secondary standard made by diluting 5.00 ml of primary standard to 100 ml in a glass volumetric flask, using a Finnpipette digital 1-5 ml adjustable pipette. The nitrate stock was prepared from a known weight of potassium nitrate close to 0.510g, and nitrite from 0.345g of sodium nitrite.

All primary stock standards were prepared in deionised water and made up in 500 ml plastic volumetric flasks. The flasks were calibrated before the cruise and a correction factor was applied to the calculated primary standard concentration to account for this. During the first half of the cruise the factors shown in Table 1 had to be applied to the final sample data to allow for the calibration of the volumetric flasks and the actual weight of the primary standard material which had been overlooked in the initial calculation.

Table 1. Correction factors applied to the D213 data from calibration of the 500 ml flasks and actual weight of the standard material.

Station	Parameter	Factor multiplied by
12673-12738	nitrate	0.988
12723-12748	silicate	1.0023
12739-12748	nitrate	1.0087

A set of four mixed working standards were prepared daily in 100 ml plastic volumetric flasks with 40g/l Analar grade sodium chloride artificial seawater.

4.0 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 results of this are plotted in Figure 1. This figure shows a shift in the nitrate sensitivity after station 12711 when the analyser pump tubes had been replaced for the first time. A similar shift in the sensitivity was seen on M28/1 and had also been attributed to the retubing of the analyser. The shift in sensitivity may be due to variability in the actual internal diameters of the pump tubes. The nitrate sensitivity returned to previous values after 12727, therefore the nitrate calibration data can be divided into three groups.

The silicate calibration data can also be divided into a number of groups: that leading up to the change in pump tubes at station 12711; data after this change; and data after the correction factors in Table 1 had been applied at station 12749. The calibration coefficient was high again for just 4 stations from 12772 (although it is not clear why this happened).

The phosphate calibration data can be divided into two groups by the first change in pump tubes, which also correlated with a change in the phosphate gain settings. Changing the phosphate pump tubes at the end station 12749 did not result in a change in the calibration coefficient. The variability in the apparent sensitivity is presented in Table 2 with the calibration data divided according to the groups described (note that calibration coefficients calculated for runs that were repeated or recalculated have not been included).

Table 2. Analytical sensitivities grouped by the changes in pump tubes.

Parameter	Stations	mean sensitivity umol/bit	CV%
Silicate	673-711	0.0470	2.44
	712-748	0.0493	2.08
	749-771	0.0484	3.55
	772-775	0.0639	1.47
Nitrate	673-711	0.0144	17.05
	712-727	0.0287	2.92
	728-776	0.0152	5.28
Phosphate	673-711	0.0015	33.16
	712-776	0.0014	17.3

The equivalent results for silicate and nitrate measurements on M28/1 show a higher CV% for nitrate, compared with silicate, but the values are never worse than 2.4% for that dataset.

The gain was changed for each parameter when the tubes were changed on the first occasion. Otherwise the gain setting remained constant for the silicate and nitrate lines. The phosphate gain setting had to be changed on 8 occasions during the cruise to maintain maximum sensitivity. These changes are summarised below in Table 3.

Table 3: Changes in the gain settings used on D213

Parameter	Stations	Gain Setting
Silicate	12673 - 711	5
	12712 - 776	4
Nitrate	12673 - 711	7
	12712 - 776	4
Phosphate	12673 - 675	3
	12676 - 687	1
	12688 - 700	3
	12701 - 707	6
	12708 - 711	1.4
	12712 - 759	4
	12760 - 760	6.5
	12761 - 771	5
	12772 - 776	6

4.2 Precision - Duplicate Measurements

All samples were analysed in duplicate. Overall the mean absolute differences between the duplicate measurements and standard deviations (SD) were: silicate 0.256 umol/l (0.268), n=980; nitrate 0.222 umol/l (0.238), n=967; and phosphate 0.045 umol/l (0.048), n=975. Note that duplicate differences not included in these statistics were 14 values outside of 2 umol/l for silicate, 23 outside of 1.5 umol/l for nitrate and 3 outside of 0.5 umol/l for phosphate as these were all reported as questionable data at the time. There were nearly twice as many duplicate samples as analysed on M28/1 where the duplicate difference for silicate was the same as on D213 but the nitrate duplicate difference and standard deviation was half that seen on D213.

The data presented below in Table 4 has been divided into groups of 10 stations to show the changes in the precision of silicate (Si), nitrate (NO_3) and phosphate (PO_4) measurements over the cruise.

Table 4. Summary of differences between duplicate analyses. Mean taken for groups of ten runs to look for systematic changes over the length of the cruise.

Station	Si mean difff (umol/l)	% full scale (150 umol/l)	NO3 mean diff (umol/l)	% full scale (40 umol/l)	PO4 mean diff (umol/l)	% full scale (2.5 umol/l)
673-682	0.27	0.18	0.17	0.43	0.09	3.6
683-692	0.25	0.17	0.21	0.53	0.03	1.2
693-702	0.29	0.19	0.33	0.83	0.05	2
703-712	0.23	0.15	0.22	0.55	0.04	1.6
713-722	0.24	0.16	0.18	0.45	0.05	2
723-732	0.27	0.18	0.31	0.78	0.03	1.2
733-742	0.22	0.15	0.22	0.55	0.07	2.8
743-752	0.26	0.17	0.17	0.43	0.05	2
753-762	0.27	0.18	0.38	0.95	0.06	2.4
763-776	0.44	0.29	0.18	0.45	0.02	0.8

On M28/1 the standard deviations of the differences were found to be similar to the means of the standard errors of the least squares calculation of the calibration equations. On D213 the mean standard errors were 1.28 umol/l for silicate, 0.58 umol/l for nitrate and 0.15 umol/l for phosphate. In each case this was higher than the mean duplicate differences seen in the dataset (0.268, 0.238 and 0.048 for silicate, nitrate and phosphate respectively). Figure 2 shows the variation in the standard error estimate for the least squares fit of the calibration data.

The correlation coefficient calculated for each run may also provide information on the quality of the data. Figure 3 shows the variation in the quality of the calibration curves across the cruise. The phosphate data is especially variable.

4.3 Precision - consistency of internal QC measurements

A sample of deep water was collected on the first station and stored in a polyethylene carboy. This water was then transferred into rinsed 'diluvials' and stored in the refrigerator. It was analysed throughout the cruise as a 'quality control' sample, referred to here as QC1. Similar water had been used on D199 (SAUNDERS et al., 1993) and on M28/1 and had proved useful in detecting shifts in the data quality. The QC1 data is presented in Figure 4, note that the phosphate data has been multiplied by 20 to keep the scales comparable. There is no discernible trend in the silicate or nitrate QC1 data although there is a downward trend in the phosphate values. This trend is also seen in Table 5 below in which the data has been summarised on the basis of groups of ten stations. The reproducibility of the samples generally deteriorated with time for each parameter.

Table 5: Summary of determinations on QC1 samples. Means and standard deviations calculated for groups of ten stations.

Station	Si mean umol/l	Si CV%	NO3 mean umol/l	NO3 CV%	PO4 mean umol/l	PO4 CV%
673-682	68.31	0.86	26.65	1.30	2.13	10.54
683-692	68.88	0.94	26.48	1.67	1.95	5.21
693-702	68.84	0.84	26.64	2.02	1.83	7.46
703-712	68.14	2.05	26.70	2.74	1.88	4.94
713-722	68.34	3.13	27.34	6.57	1.87	3.84
723-732	67.67	2.81	27.86	13.48	1.84	4.43
733-742	67.62	6.45	25.66	6.25	1.50	13.46
743-752	68.14	2.03	26.49	6.20	1.76	11.42
753-762	67.54	4.44	27.09	9.48	1.81	19.04
763-776	67.87	1.63	26.30	3.88	1.67	6.33

In Figure 4 groups of high nitrate data are seen between stations 12720 and 12722, and 12752 to 12755. The low set of phosphate QC1 values between stations 12734 and 12738 correspond to a set of stations where the data had to be calculated by hand and the QC1 values changed from those calculated by the Microstream software. Obvious shifts in the data have been removed and the summary of the precision obtained after these changes is shown in Table 6.

Table 6: Summary of determinations on QC1 samples, with grouped data removed.

Station	Si mean umol/l	Si CV%	NO3 mean umol/l	NO3 CV%	PO4 mean umol/l	PO4 CV%
673-682	68.31	0.86	26.65	1.30	2.00	4.18
683-692	68.88	0.94	26.48	1.67	1.95	5.21
693-702	68.84	0.84	26.64	2.02	1.83	7.46
703-712	68.43	1.24	26.70	2.74	1.88	4.94
713-722	68.82	0.87	26.75	0.75	1.87	3.84
723-732	68.19	1.74	26.73	2.20	1.84	4.43
733-742	68.37	1.35	26.09	3.89	1.66	5.99
743-752	68.14	2.03	26.02	3.55	1.81	8.00
753-762	68.33	1.64	25.94	1.24	1.83	7.83
763-776	68.16	1.01	26.30	3.88	1.67	6.33

The reproducibility of the QC1 sample was calculated after the grouped data had been removed. The overall mean (and CV%) for each parameter was as follows: silicate 68.43 umol/l (1.36%); nitrate 26.43 umol/l (2.85%); phosphate 1.85 umol/l (7.56%).

4.4 Precision - Consistency of measurements of an external QC standard

On M28/1 a number of samples of spiked seawater were supplied by OSI and tested for use as a reference material. The mixed standards were found to covary with the QC1 material used on the M28/1 cruise confirming that the variation in the calibration between runs was greater than the within run precision of the measurements.

On D213 mercuric chloride preserved seawater was tested again and is referred to here as QC2. This seawater was supplied by OSI in 50 ml sealed vials which were opened on the stations shown in Figure 7 and used until the vials were empty. The precision of the analysis has also been summarised in Table 7 for each bottle of QC2.

Table 7. The mean value and CV% for each bottle of QC2 material. The samples were run over a number of stations, the station number here is the station on which it was recorded that a new bottle was opened.

Station QC2 opened	QC2 bottle	Si mean (umol/l)	CV%	NO_3 mean (umol/l)	CV%	PO_4 mean (umol/l)	CV%
12675	046	74.76	1.02	24.6	1.21	1.87	11.4
12682	085	75.48	1.01	24.37	2.44	1.77	5.5
12691	150	75.34	0.99	24.34	1.98	1.69	6.52
12697	151	74.03	0.43	24.03	1.11	1.52	8.99
12701	153	74.64	1.57	23.94	4.80	1.61	8.72
12704	130	74.85	1.90	24.92	3.03	1.68	4.43
12716	106	75.31	0.84	24.49	0.28	1.6	4.28
12720	023	74.63	2.81	26.73	13.69	1.65	4.65
12730	089	74.8	4.77	25.78	17.85	1.46	10.55
12736	029	74.34	1.97	24.56	5.12	1.48	10.55
12744	019	74.45	1.83	24.43	2.03	1.56	5.11
12750	020	74.63	1.70	26.12	9.50	1.74	17.74
12757	047	70.97	8.18	24.14	3.68	1.58	6.79
12772	021	71.34	3.08	23.62	7.62		

The variability within a set of measurements from one bottle is similar to the variability seen when considering the QC2 data as a whole, as shown in Table 8 where the results have been grouped into sets of ten stations.

Table 8: Summary of determinations on QC2 samples. Means and standard deviations calculated for groups of ten stations.

Station	Si mean umol/l	Si CV%	NO_3 mean umol/l	NO_3 CV%	PO_4 mean umol/l	PO_4 CV%
673-682	74.84	1.03	24.59	1.14	1.86	10.69
683-692	75.45	0.97	24.34	2.47	1.73	5.11
693-702	74.46	1.17	23.76	5.31	1.57	8.72
703-712	75.1	2.21	25.08	3.45	1.69	5.2
713-722	75.21	1.12	25.69	6.56	1.62	4.49
723-732	74.88	2.67	27.0	16.6	1.62	4.9
733-742	74.29	4.12	24.26	6.35	1.42	11.32
743-752	74.29	1.85	24.45	5.87	1.56	11.34
753-762	70.82	9.38	25.78	8.50	1.70	13.91
763-776	72.8	3.18	23.9	4.0	1.56	5.75

As with the QC1 data shifts and groups within the data set can be accounted for and removed as shown in Figure 9.

Table 9: Summary of determinations on QC2 samples with grouped data removed

Station	Si mean umol/l	Si CV%	NO_3 mean umol/l	NO_3 CV%	PO_4 mean umol/l	PO_4 CV%
673-682	74.84	1.03	24.59	1.14	1.77	6.45
683-692	75.45	0.97	24.34	2.47	1.73	5.11
693-702	74.46	1.17	24.07	1.41	1.57	8.72
703-712	75.45	1.43	24.85	1.11	1.69	5.2
713-722	75.21	1.12	24.51	0.41	1.62	4.49
723-732	75.39	1.07	24.82	2.95	1.62	4.9
733-742	75.02	1.41	24.35	1.86	1.55	3.95
743-752	74.39	1.81	24.43	3.23	1.59	8.03
753-762	73.36	2.05	24.24	3.94	1.63	8.05
763-776	73.71	1.91	23.9	4.00	1.56	5.75

Overall the reproducibility of the QC2 results is similar to QC1. The mean (and CV%) overall is: silicate 74.76 umol/l (1.68%); nitrate 24.35 umol/l (2.83%); phosphate 1.65 umol/l (7.43%). The QC2 results are also illustrated in Figure 5, the phosphate data has been multiplied by 20 to put it onto a comparable scale.

The covariation between QC1 and QC2 (comparing the CV% in Tables 5 and 8) is similar to that seen on M28/1, suggested that comparing QC measurements made on the same run gives an indication of the variation in calibration between runs. When the two data sets are plotted against one another, in Figures 6 and 7, the R^2 value for phosphate is high, 0.729, although the R^2 values for silicate and nitrate are lower at 0.118 and 0.481 respectively. The variation around the simple function that has been fitted to the data, illustrated by the error bars, is comparable to the variation between data sets (discussed later in section 4.6). The QC results are compared in Figures 8, 9 And 10, the expanded scale shows the covariation between the QC samples more clearly.

Systematic noise associated with variability in the calibration standards would show up as a correlation between the observed QC value and the calculated calibration factor for each run. This is shown in Figure 11 for the QC1 results for each nutrient parameter. There is no apparent correlation. The nitrate data is divided into two populations by the jump in sensitivity when the analyser was first re-tubed. The four stations with high calibration factors occurred just before the analyser was retubed for the last time. This does not correlate to any factors noted at the time of analysis although there was a fresh batch of working standards prepared on the first and last station within this group which may account for the changes.

4.5 Accuracy - Comparison with Sagami Chemical Co. Standard Solutions

Certified standard reference materials obtained from the Sagami Chemical Company in Japan were run on a number of occasions, from three single batches of standards. Once each of the standards had been opened they were analysed until the contents were used up. The results are summarised below in Table 10.

Table 10. Summary of the results for all determinations made on Sagami standards during D213.

	Si 10 umol/l	Si 50 umol/l	Si 50 umol/l	NO_3 20 umol/l	NO_3 20 umol/l	NO_3 20 umol/l	PO_4 1 umol/l	PO_4 1 umol/l	PO_4 1 umol/l
mean	9.697	48.55	47.19	19.52	19.36	21.98	1.09	0.95	0.81
SD	0.17	0.53	1.01	0.34	0.42	0.27	0.09	0.13	0.04
CV%	0.78	2.42	4.61	1.53	1.91	1.23	0.42	0.61	0.19
% diff	3.03	2.91	5.62	2.41	3.18	9.89	8.5	5.25	18.6
n	7	7	7	8	10	4	4	8	5

The silicate results are all low suggesting a systematic error in the calibration of the results. The nitrate and phosphate results varied either side of the expected value and no systematic error is suggested in the calibration of the nitrate or phosphate data.

The Sagami results reported on D201, measured using the Alpkem Auto-Analyser, were silicate 9.56 umol/l, nitrate 9.64 umol/l and phosphate 1.003 umol/l compared to expected values of 10, 10 and 1 umol/l respectively. The silicate and nitrate results were also low for the M28/1 data where the values reported were 49.7 umol/l for a 50 umol/l silicate standard and 9.8 for a 10 umol/l nitrate standard. The precision of the results, illustrated by the CV%, is similar to that seen on M28/1.

4.6 Accuracy - Comparison with Historical data.

The 45°S line on the D213 section is a repeat of the same line surveyed on D201 (POLLARD, at al., 1994). Out of six D201 station locations reoccupied on D213 the phosphate data was found to be higher on D213 by 0.2 umol/l and the nitrate lower by 0.8 umol/l on one occasion only, generally the data compared very well. The stations compared are listed in Table 11 below.

Table 11. D201 station locations reoccupied on D213.

D201	D213
12393	12684
12396	12686
12402	12693
12405	12694
12409	12697
12410	12698

The full depth profiles have been plotted in sets of three replicate stations. The six stations in Figures 12 and 13 appear to be closely aligned for nitrate and silicate throughout the profile. The phosphate data shows less agreement, especially in Figure 12 which shows that the D213 data is consistently higher than the D201 data. The deep data (over 3000 m) is shown in Figure 14. The deepest of the replicate stations, 12686 and 12396, are considered in Figure 13. The D201 silicate data is lower than the D201 data, within 2% error bars. The nitrate data is low on D213, within 5% error bars and the phosphate data is high (within 10%).

4.7 Implications for the sample data

As each sample run was completed and the data calculated a number of factors were collated onto a hand written table. These included the correlation coefficient, calibration coefficient, gain setting, and quality control sample results. This was used to check the calculations and quality of the data with preceding stations.

The first piece of information recorded was the correlation coefficient. If this was less than 0.999, because of one incorrectly prepared working standard for example, then the data was recalculated.

The shifts in calibration coefficient noted in section 4.1 would be noted at the time and the data examined to see if there was a corresponding change in the measured values. For example between stations 12711 and 12712 when the pump tubes were changed there was a 103% increase in the nitrate calibration coefficient but no corresponding change in the data.

The calibration coefficient changed by 13% between 12768 and 12769, the sample nitrate data also increased by up to 0.7 umol/l. The only factor that had been noted on the logsheets was a change in the working standards. These were prepared daily and did not result in daily changes in the data, for example between 12766 and 12767 there are fresh working standards, and a decrease in the calibration coefficient of 11%, but no apparent change in the sample data.

Changes noted in the calibration coefficient were used to further investigate the following station data:-

1) Phosphate:- on stations 12710-12711 there was a shift of about 0.4 umol/l when the pump tubes were changed.

2) Silicate:- over four stations 12771/72 - 12775/76 there was a 46% change in the calibration coefficient (but no corresponding change in the sample data)

3) Nitrate: It is not clear why the nitrate calibration coefficient shifts back down to the original value between stations 12727/28 . It is likely that the pump tubes were changed but no note was made of this at the time). There is a 39% change in the calibration coefficient and the data changes by about 1 umol/l in the bottom water.

Changes in the gain settings may also have resulted in shifts in the data. For example the gain settings changed for phosphate between 12700 and 12701 and the bottom water data also shifted to higher values. However between 12675 and 12676 there was a change in phosphate gain with no apparent change in the calibration gradient or sample data.

In investigating changes in the sample data changes in the QC values proved useful. The change in the ratio of QC1 from one station to the next can be used as a factor to recalculate data from some of the stations where the whole profile has shifted low or high. The changes that should be made to the D213 data set are summarised in Table 12 below.

Table 12. Changes to be made to the sample data set after calculating the change in QC1 between stations.

Parameter	Station	Shift noted in the data (umol/l)	Factor, based on QC1 changes
Phosphate	12706	0.1 low	1.0958
	12716	0.15 low	1.0554
	12735	0.3 high	0.953
Nitrate	12716	0.7 high	0.9211
	12726	1 low	1.0112

There were two groups of high QC1 and QC2 nitrate results, stations 12720 - 722 and 12752 - 755, noted in sections 4.3 and 4.4. The sample data also shifts high for these stations. The high QC1 values seen for stations 12728 and 12730 was noticed at the time and the sample data as the data was was recalculated .

4.8 A note on the consistency of the N:P ratio

The nitrate to phosphate ratio for the QC material should be consistent. The relationship between these parameters (Figure 16) shows that this is generally the case. The variation is mostly around the stations where the phosphate QC data was low (where the results had been calculated by hand). There is no real correlation with the NO_2 standard (Figure 17), which was used as a further quality control sample on the nitrate line.

The variation in the N:P parameter across the cruise, plotted in Figure 18, suggests that the high N:P ratio occurs on only four occasions in the cruise (each time over two stations). The surface nitrate is high on these stations but there is no correlation with the QC N:P data. The overall N:P ratio across the cruise, Figure 19, shows extreme low and high ratios which may relate to individual stations where shifts in the data occurred. For example all of the data for station 12763 was low with ratios in the order of 10 when the average ratio was closer to 14.8. Most of the data lies within N:P ratios of 13 to 17.

5.0 CONCLUSIONS

Despite different instruments the D201 and D213 data sets compare well. The silicate data compares better than the South Atlantic data set comparisons with a similar comparison for the nitrate data. However the variability of the D213 data set is greater than that seen on M28/1. This may be due to the air circulation in the constant temperature laboratory of the RRS Discovery as no such problems were encountered on the Meteor. The variation may also be due to problem with the preparation of the working standards.

It has been shown that the variability of the quality control samples is similar with storage at 4°C or in mercuric chloride. Real changes in the data show above the noise of these measurements. It is important that all of the information such as the correlation and calibration coefficients and the values of the QC material be noted and acted upon as soon as possible after a run has been completed. This information can then be used as a basis for looking at the variations in the sample data.

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List of figures

Figure

Appendices:-

Figure 1:- Apparent sensitivity of the analyser - calibration coefficient of silicate, nitrate and phosphate measurements over D213

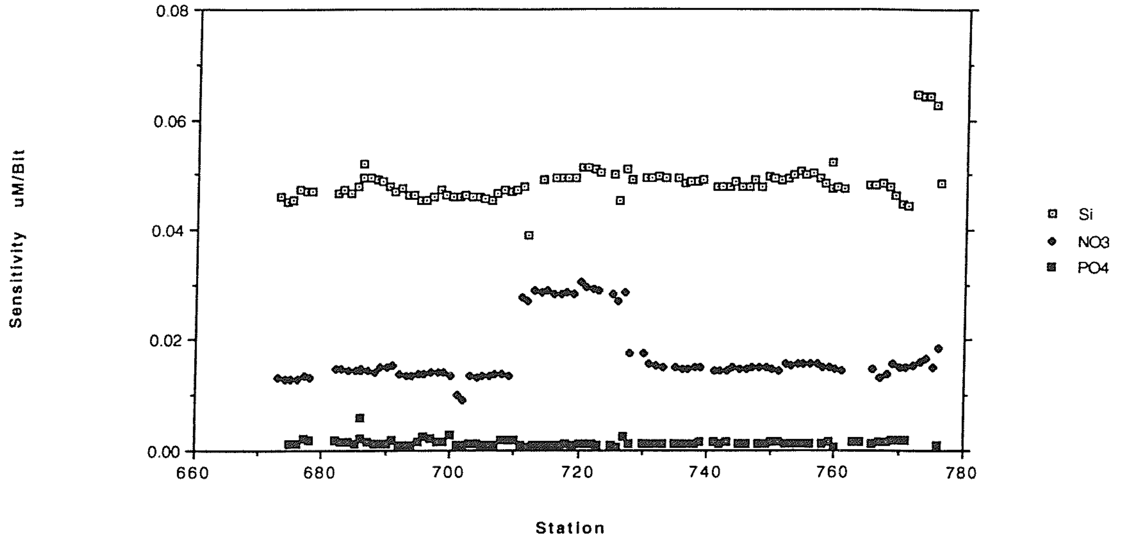


Figure 2:- The variation in the standard error estimate of the least squares fit of the calibration data

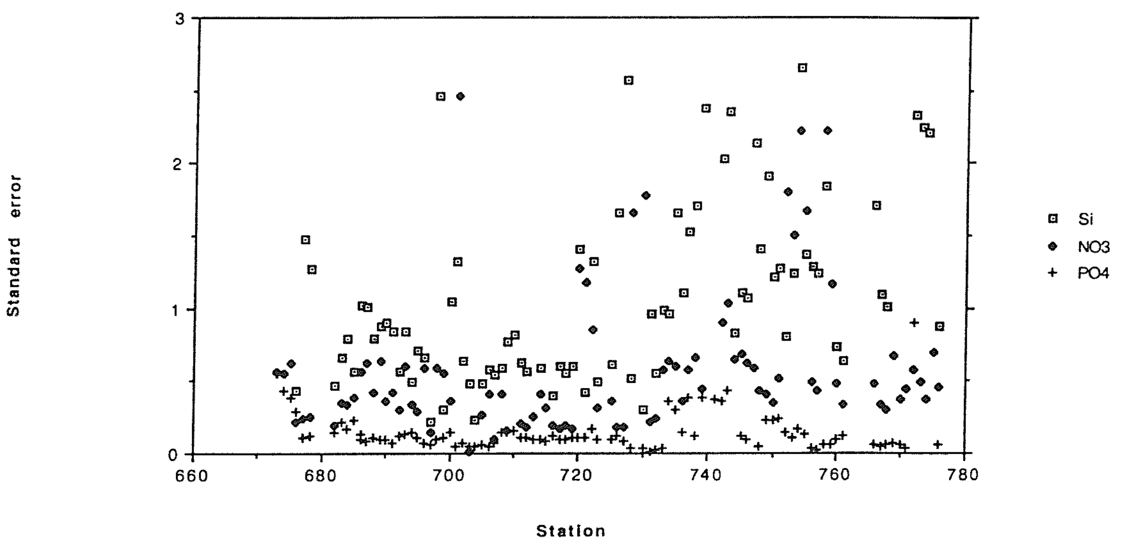


Figure 3:- The correlation coefficient for silicate, nitrate and phosphate calibration

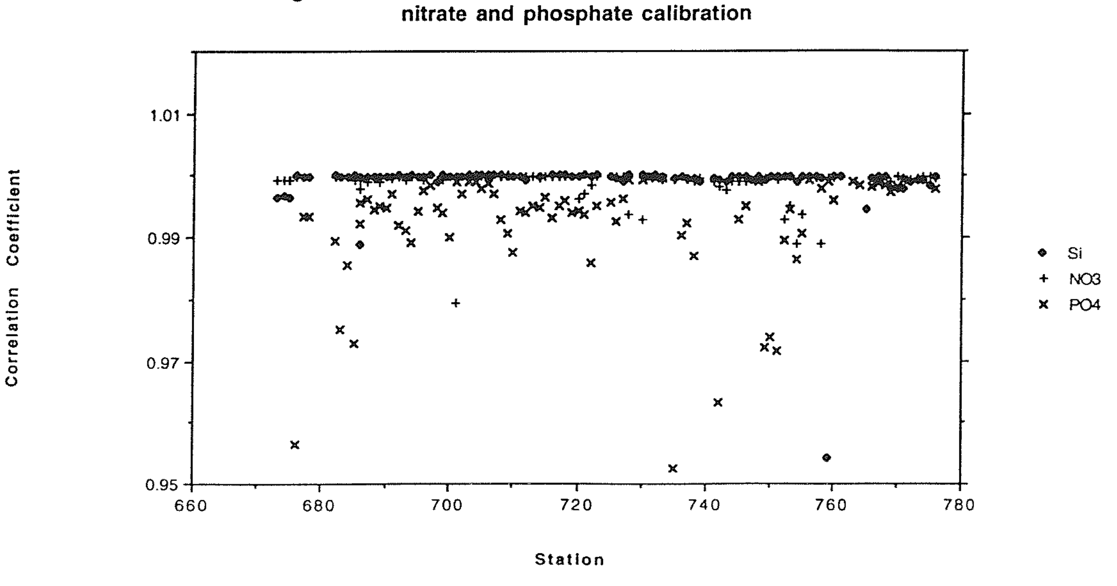


Figure 4:- QC1 data results

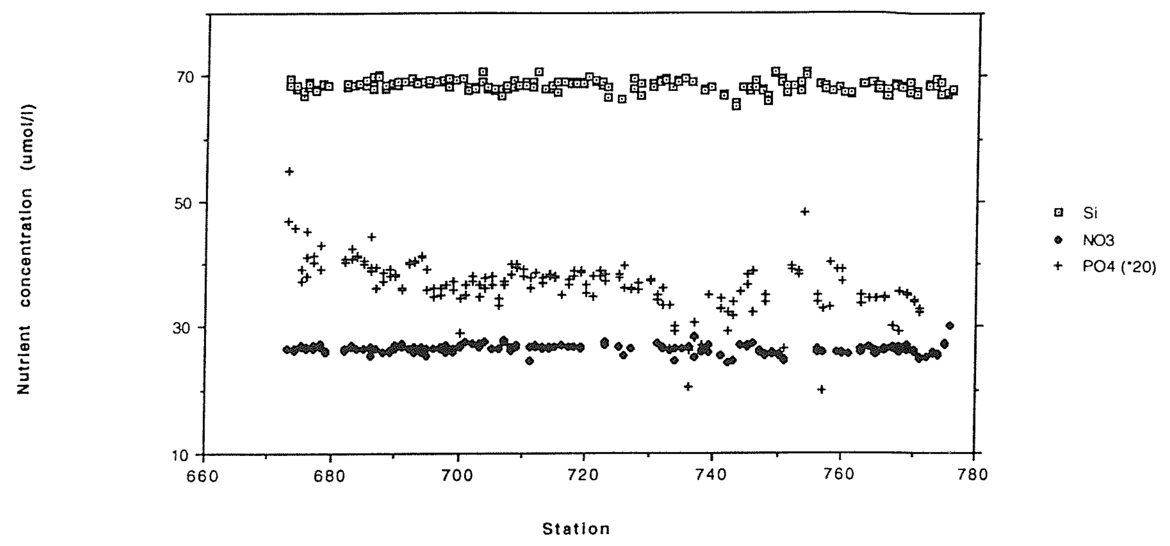


Figure 5:- QC2 data results

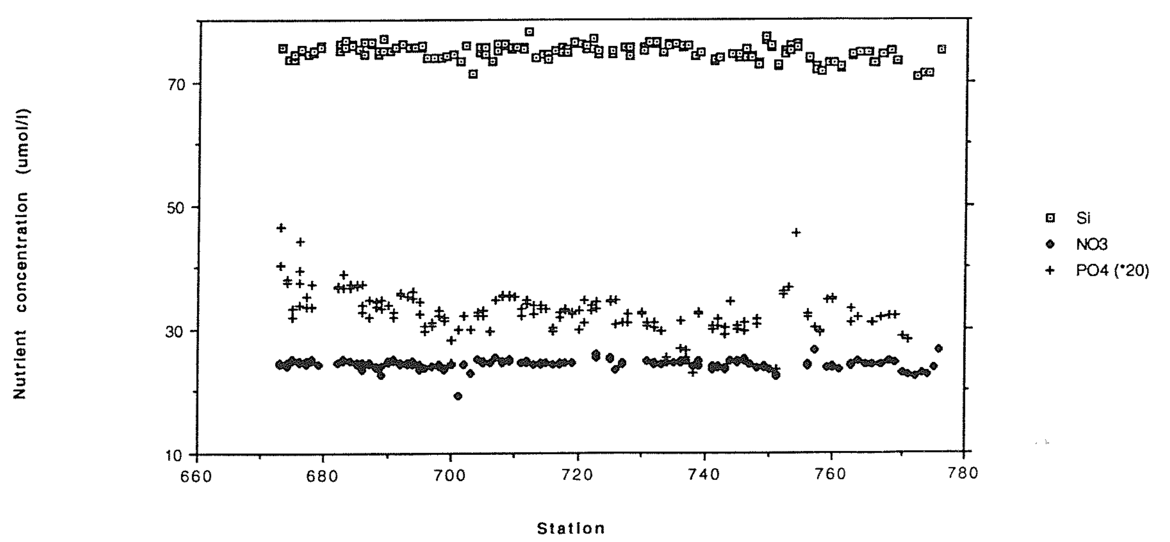
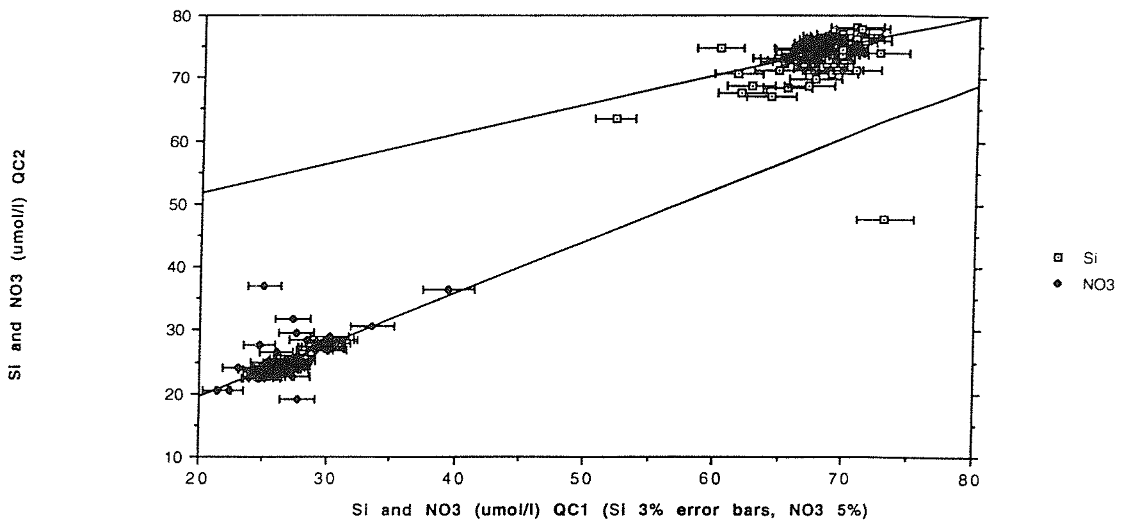


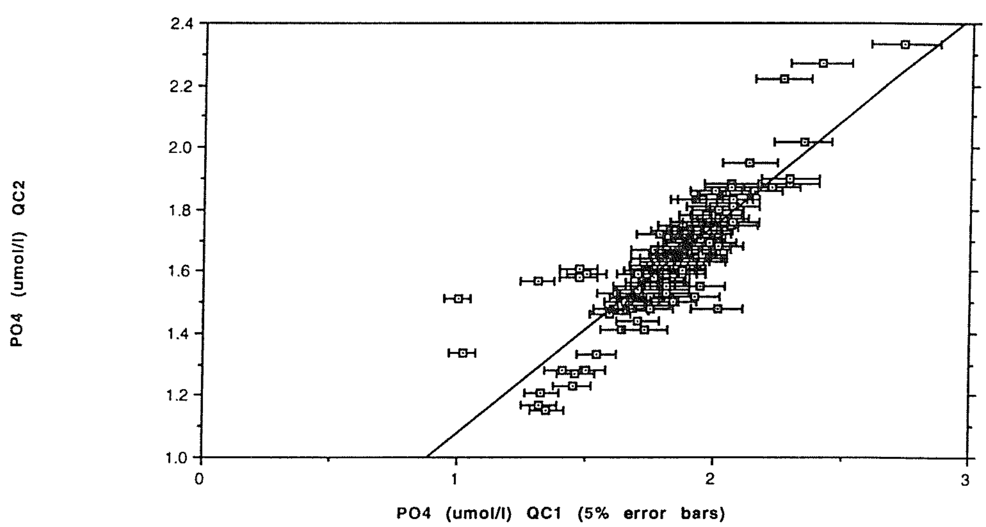
Figure 6:- QC1 and QC2 correlation for silicate and nitrate



y = 42.024 + 0.47280x   R^2 = 0.118

y = 2.6992 + 0.82706x   R^2 = 0.481

Figure 7:- QC1 and QC2 correlation (phosphate)



y = 0.40593 + 0.67016x   R^2 = 0.729

Figure 8:- QC1 and QC2 silicate

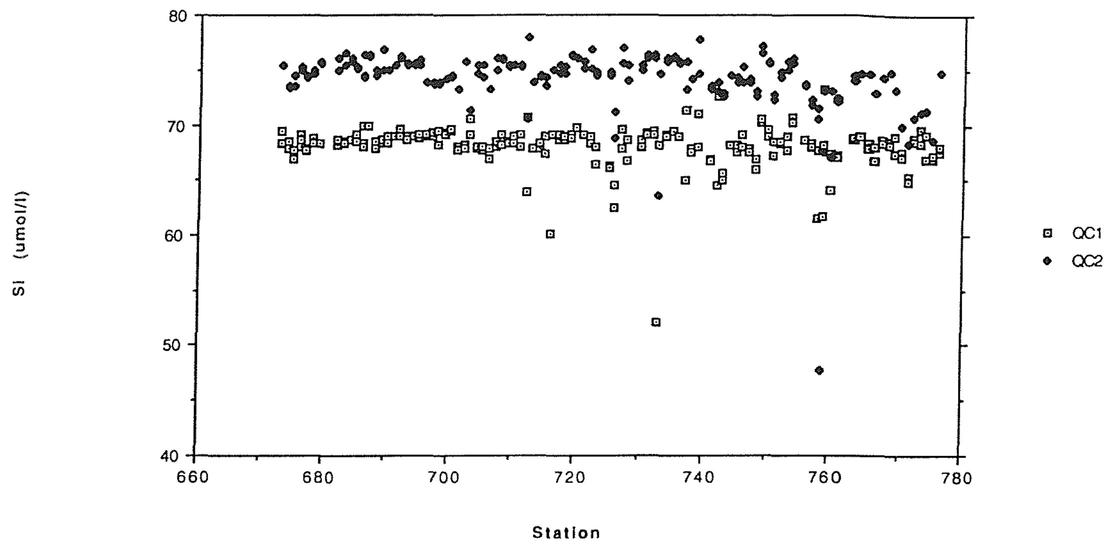


Figure 9:- QC1 and QC2 nitrate

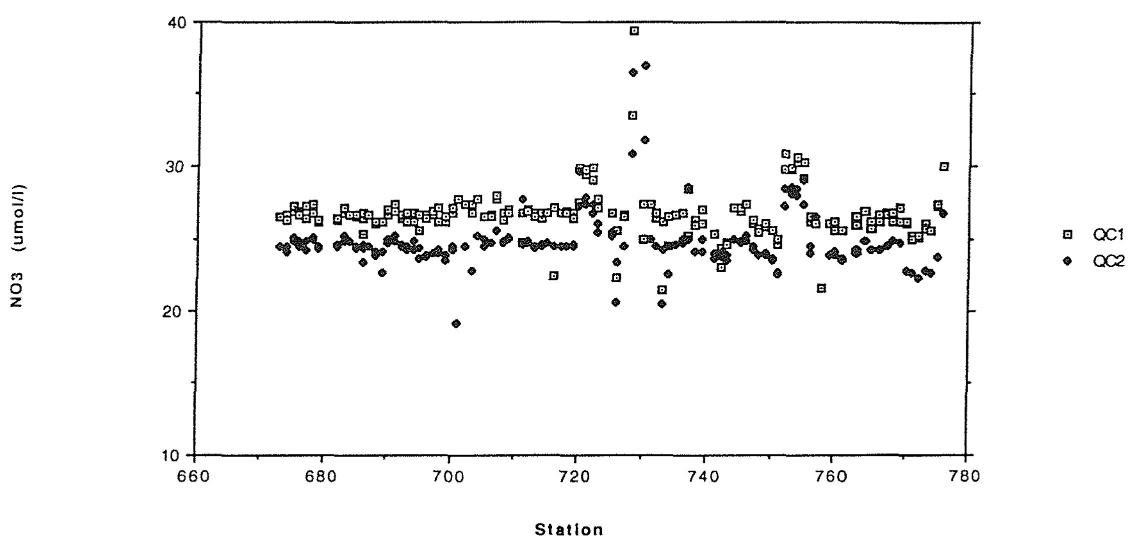


Figure 10:- QC1 and QC2 phosphate

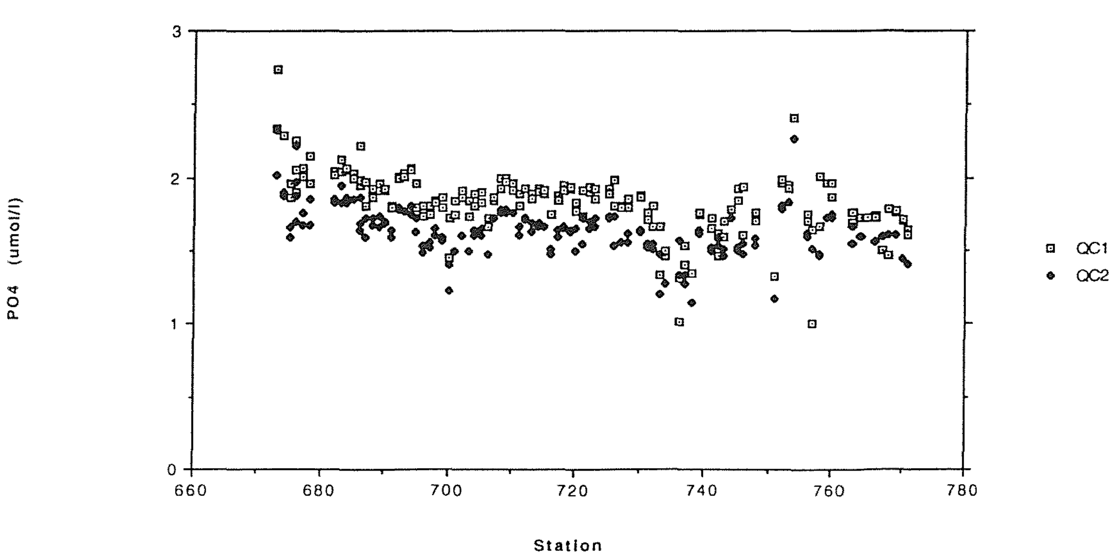


Figure 11 (a):- Correlation of silicate QC1 and the calibration coefficient over D213

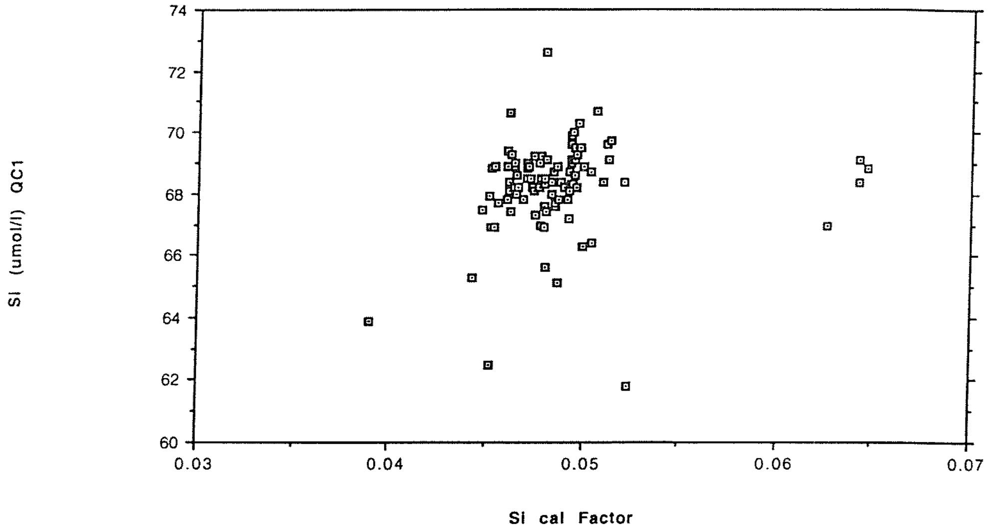


Figure 11 (b):- Correlation of nitrate QC1 and the calibration coefficient

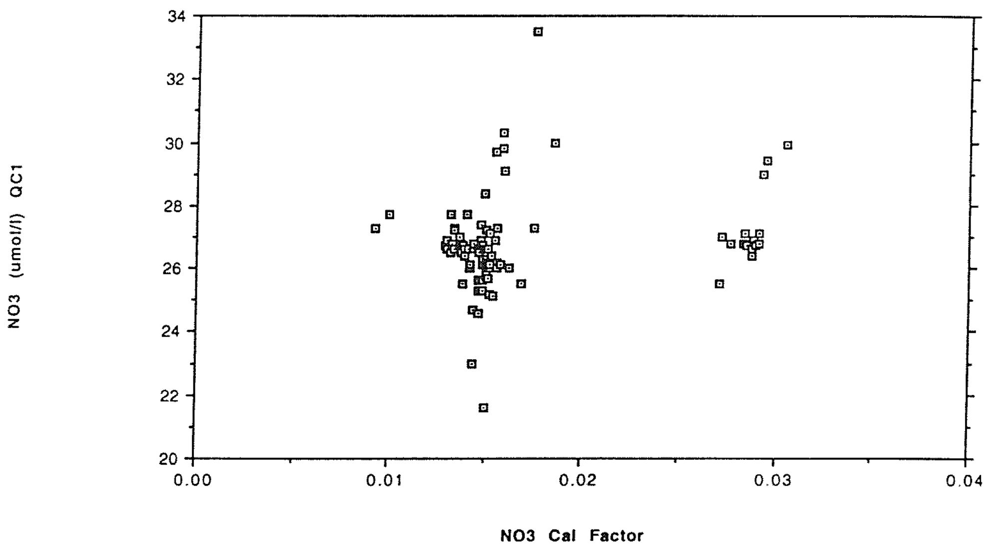


Figure 11 (c):- Correlation of phosphate QC1 and the calibration coefficient

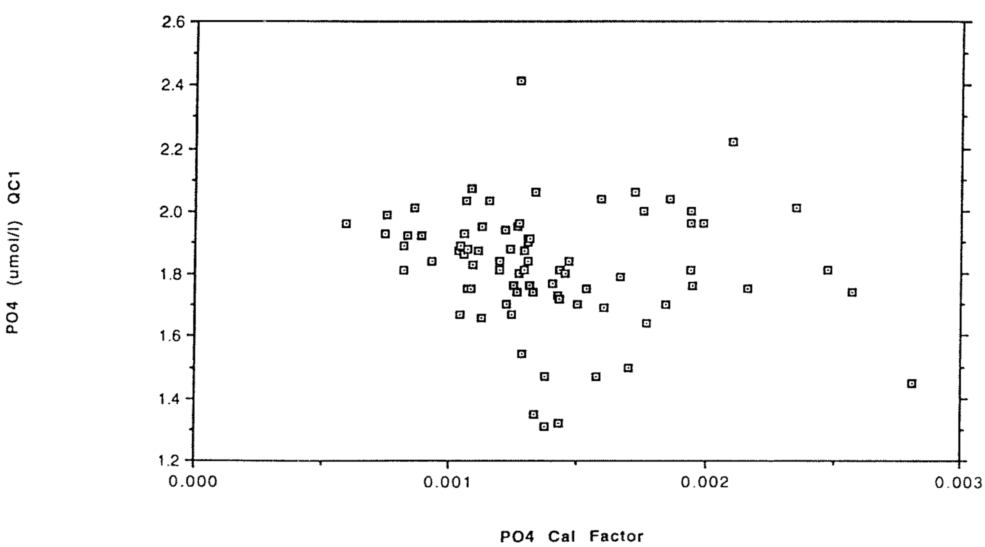


Figure 12 (a):- Full depth silicate profiles

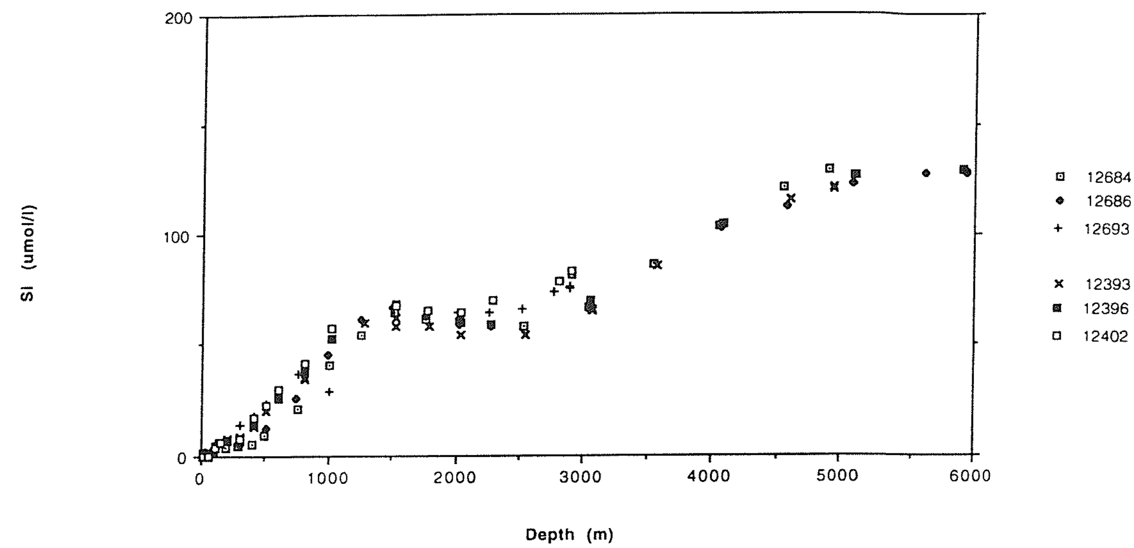


Figure 12 (b):- Full depth nitrate profiles

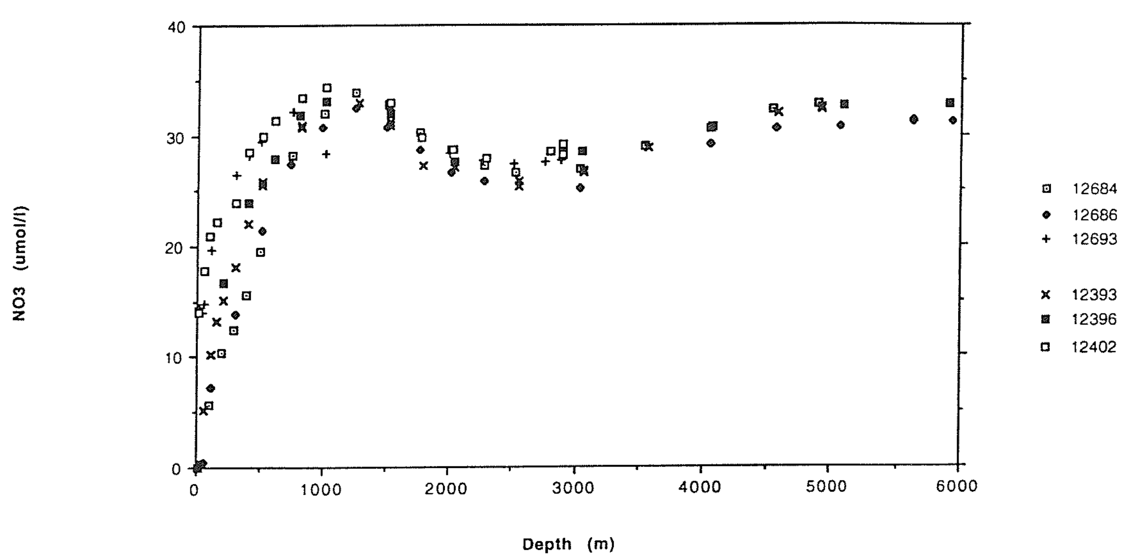


Figure 12 (c):- Full depth phosphate profiles

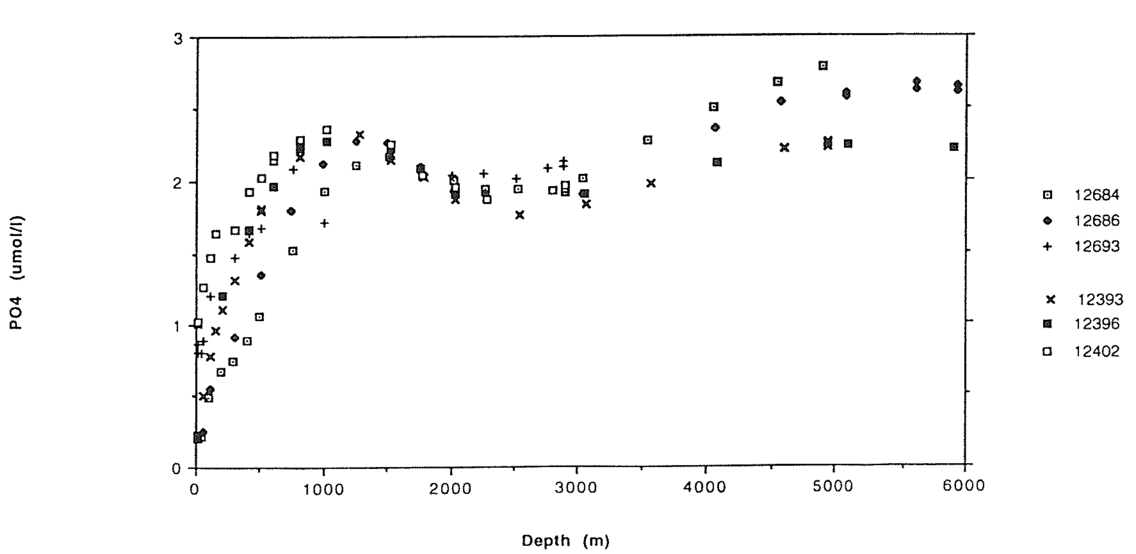


Figure 13 (a):- Full depth silicate profiles

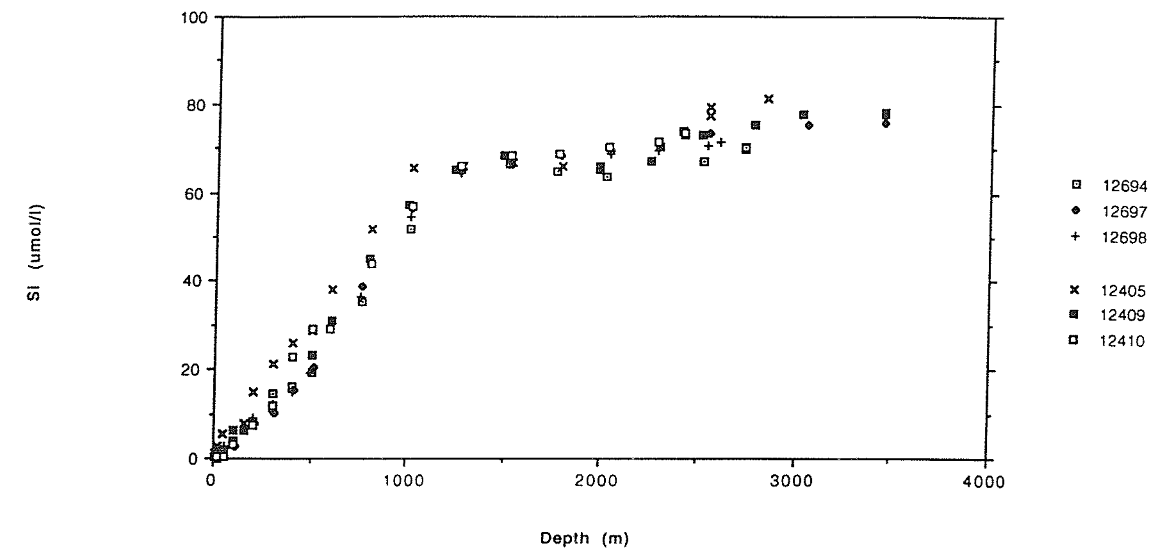


Figure 13 (b):- Full depth nitrate profiles

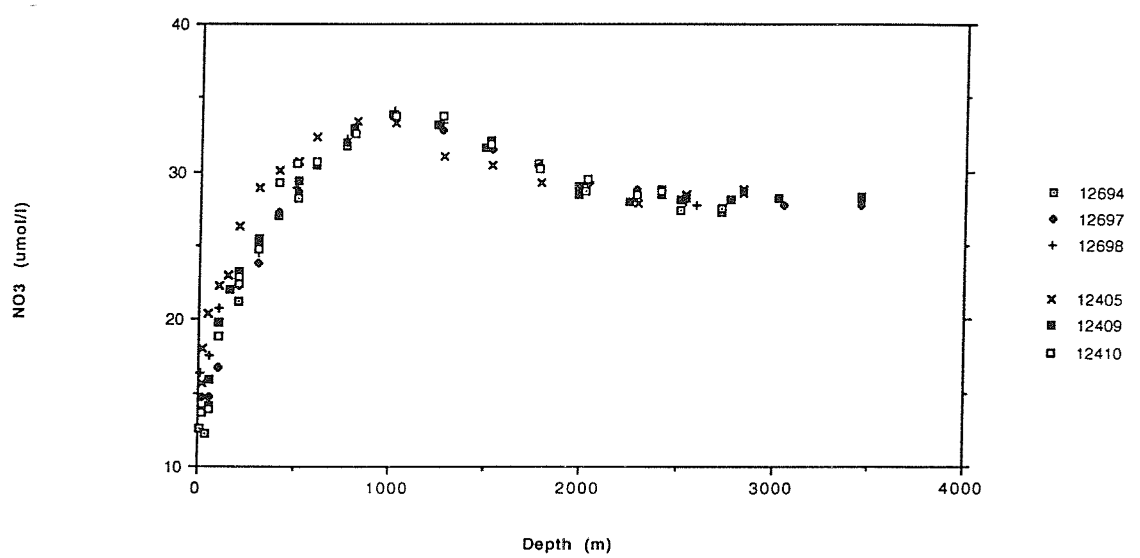


Figure 13 (c):- Full depth profiles phosphate data

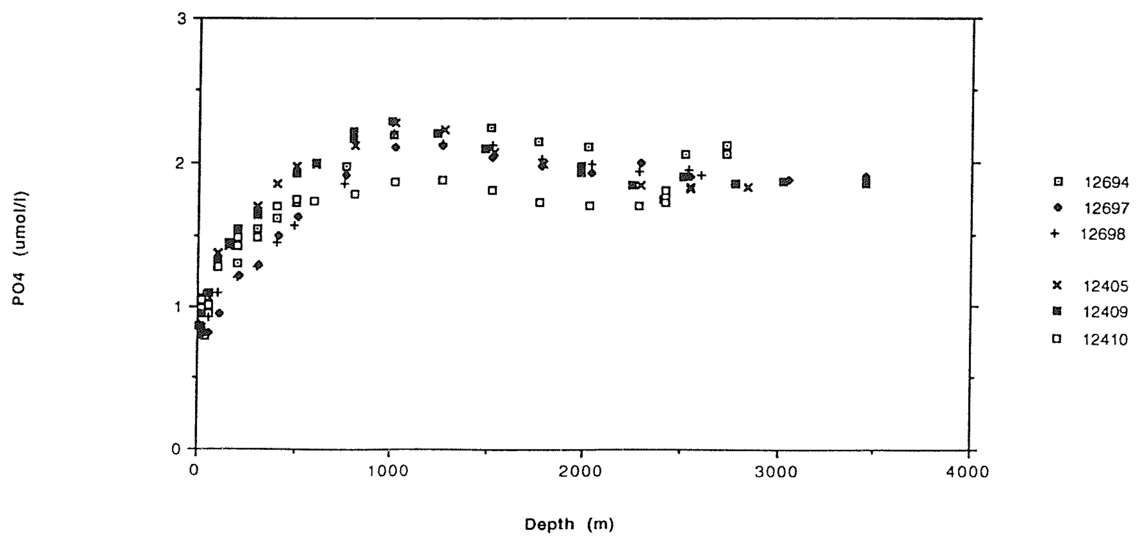


Figure 14 (a) :- Deep station silicate comparisons (>3000m)

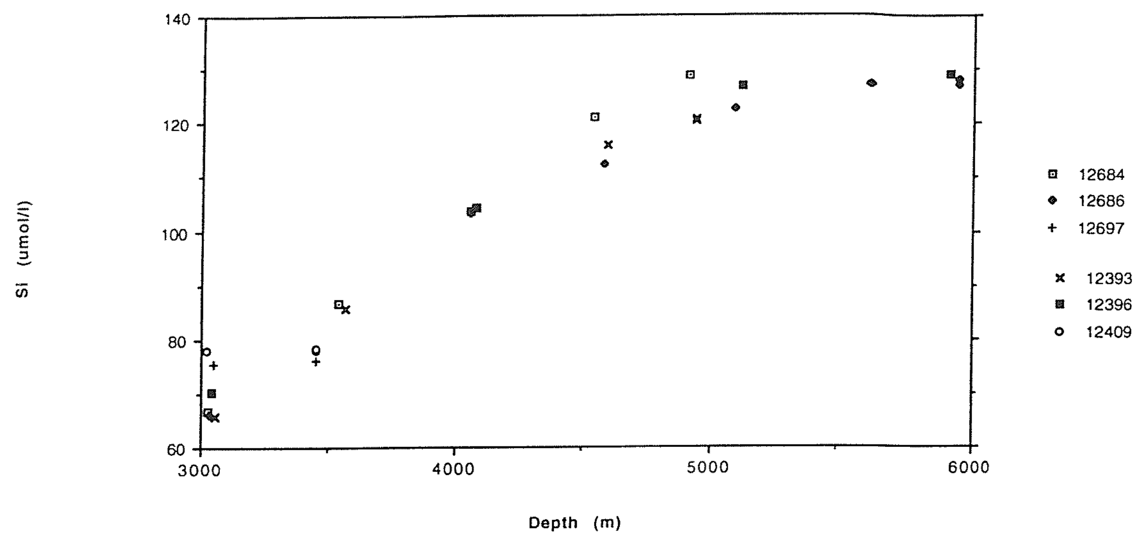


Figure 14 (b):- Deep station nitrate data comparisons (>3000m)

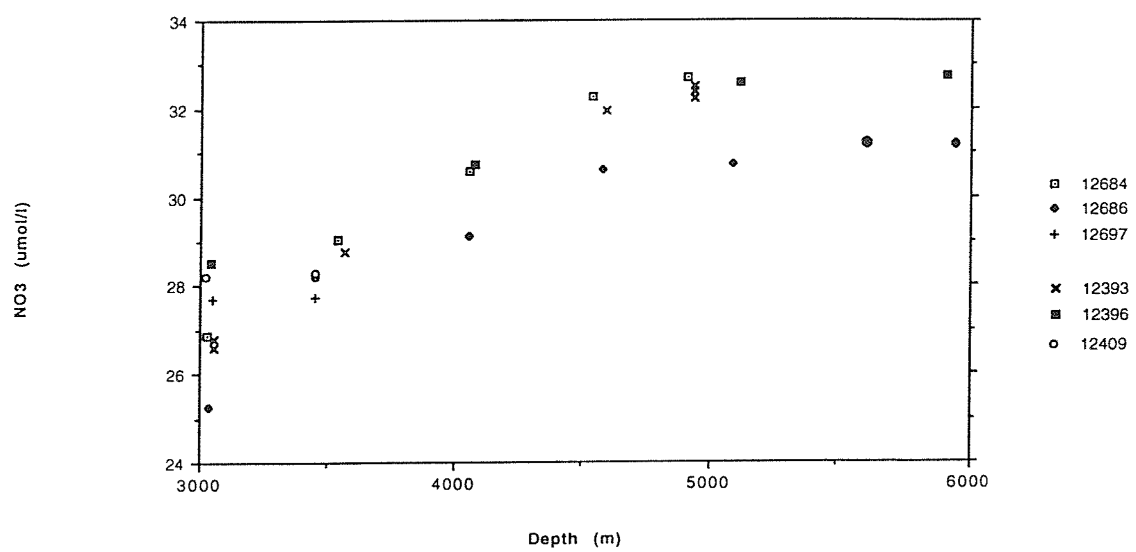


Figure 14 (c):- Deep station phosphate data comparisons (>3000m)

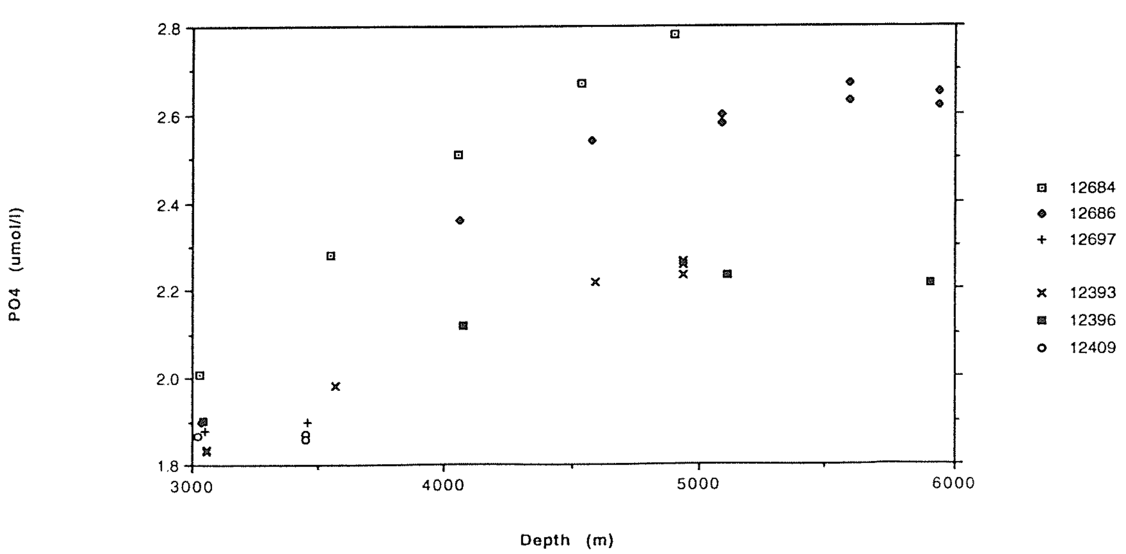


Figure 15 (a) :- Deepest station silicate data comparisons with error bars

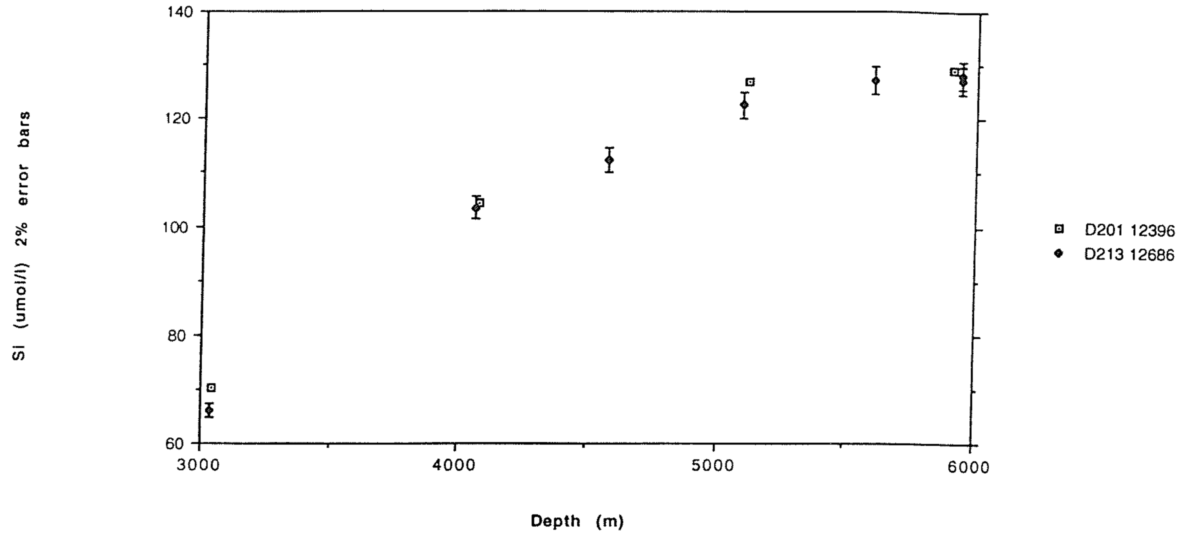


Figure 15 (b) :- Deepest station nitrate data comparisons with error bars

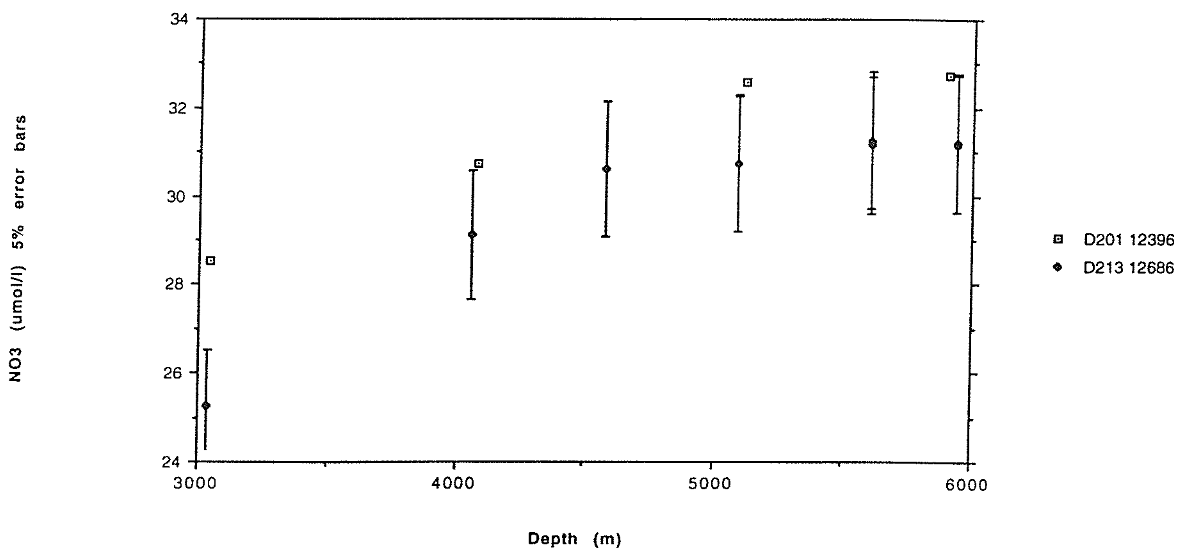


Figure 15 (c) :- Deepest station phosphate data comparisons with error bars

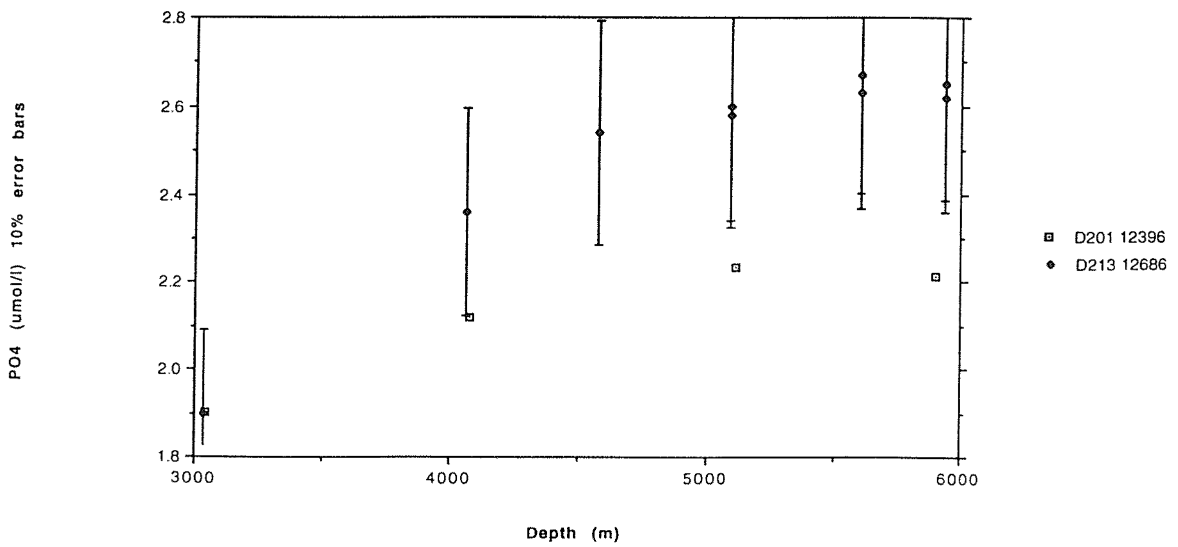


Figure 16 (a):- N:P ratio for QC1 data

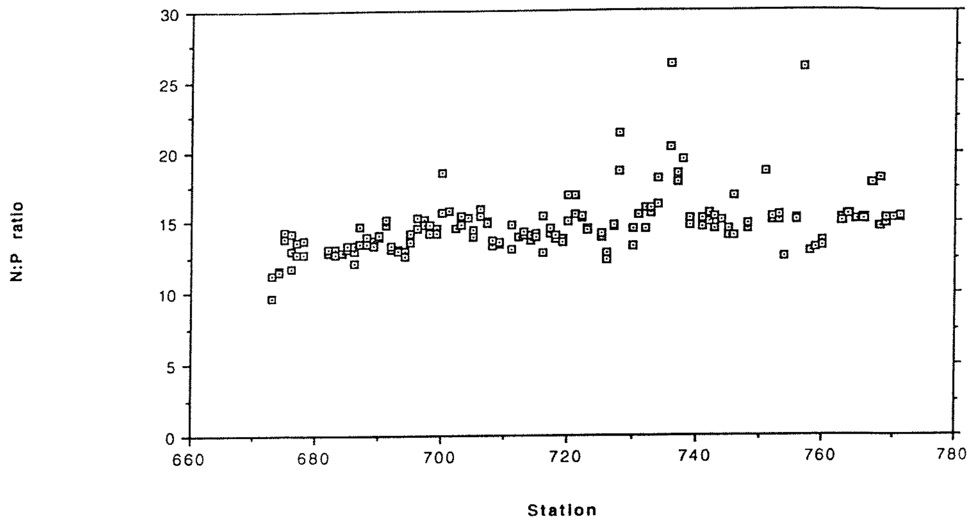


Figure 16 (b):- The N:P ratio for QC2 data

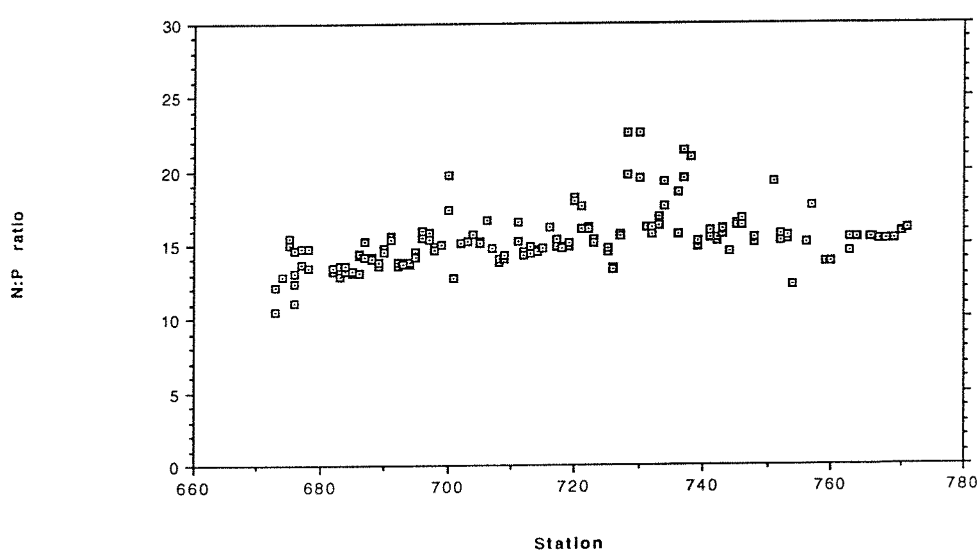


Figure 17:- Variation in the NO2 standard over D213

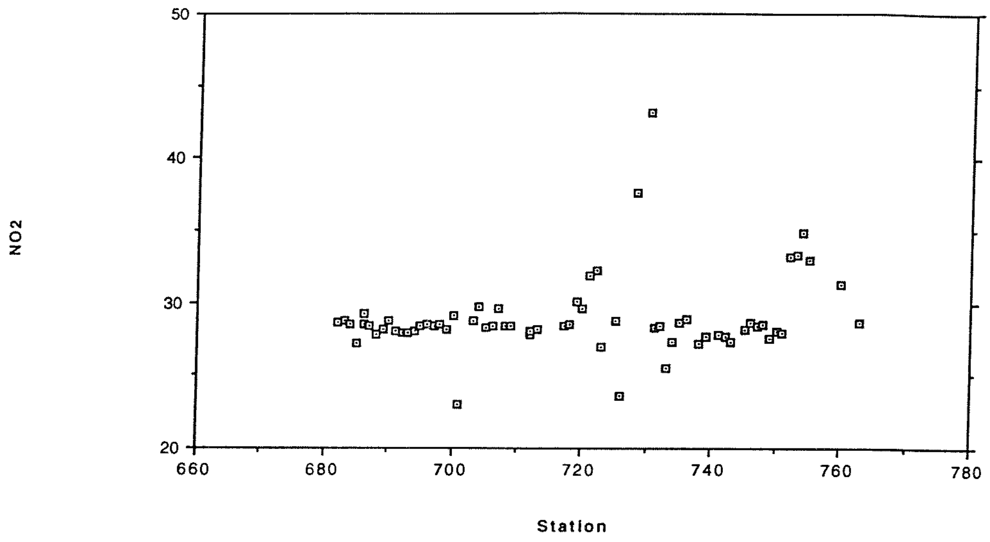


Figure 18:- Variation in the sample N:P ratio over D213

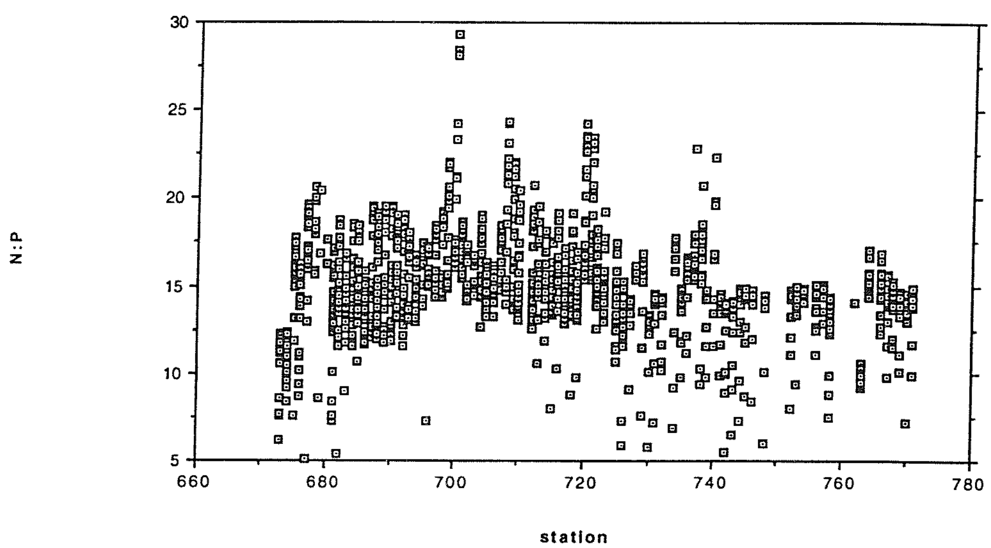
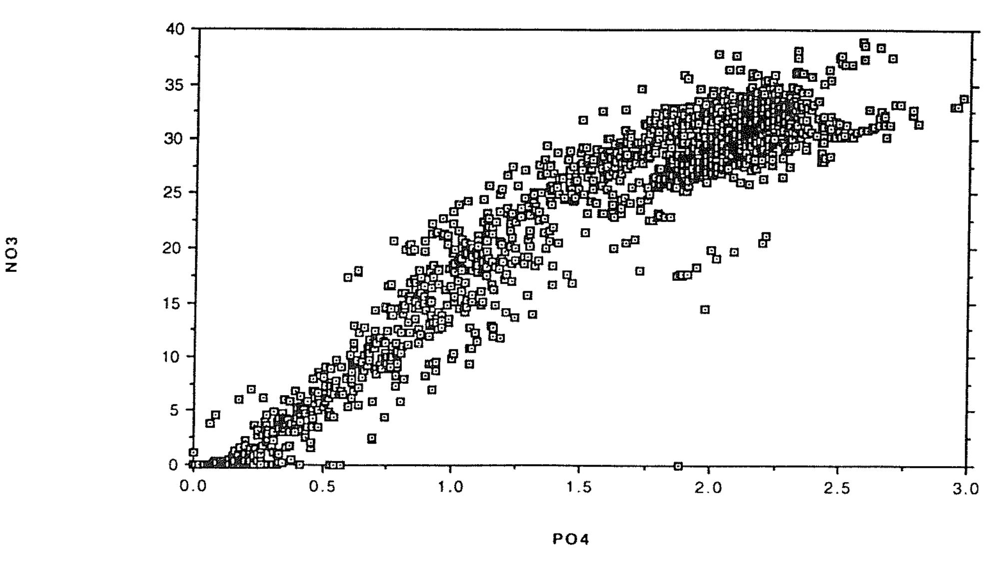


Figure 19:- Overall N:P ratio for D213 sample data



D213 CALIBRATION INFORMATION

The standard error (se), sensitivity (a) and correlation coefficient (r2) is shown here for each run that it was recorded for throughout D213.

	Standard error:-			Sensitivity (uM/bit):-			Correlation coefficient:-		
Station	Si-se	NO3-se	PO4-se	Si-a	NO3-a	PO4-a	Si-r2	NO3-r2	PO4-r2
673	4.72	0.564	0.554	0.0461	0.0132		0.9964	0.9993	
674	4.54	0.556	0.435	0.0451	0.013		0.9967	0.9993	
675	5.35	0.624	0.385	0.0452	0.013	0.0013	0.9966	0.9993	0.9346
676	0.428	0.220	0.292	0.0474	0.0129	0.0013	1.0000	0.9999	0.9564
677	1.47	0.239	0.113	0.0468	0.0134	0.0024	0.9997	0.9999	0.9935
678	1.27	0.252	0.114	0.047	0.0133	0.0019	0.9997	0.9999	0.9934
682	0.471	0.192	0.145	0.0466	0.0148	0.0019	1.0000	0.9999	0.9895
683	0.661	0.352	0.222	0.0472	0.0148	0.0016	0.9999	0.9997	0.9751
684	0.786	0.333	0.170	0.0465	0.0146	0.0017	0.9999	0.9997	0.9855
685	0.566	0.387	0.231	0.0479	0.0146	0.0012	1.0000	0.9993	0.9730
686			0.093	0.0521	0.0148	0.006	0.9890	0.9980	0.9957
686	1.02	0.567	0.133	0.0493	0.0144	0.0021	0.9998	0.9993	0.9924
687	1.01	0.622	0.086	0.0494	0.0144	0.0014	0.9998	0.9991	0.9963
688	0.795	0.425	0.104	0.049	0.0142	0.0011	0.9999	0.9996	0.9946
689	0.879	0.640	0.100	0.0488	0.0152	0.0013	0.9999	0.9991	0.9950
690	0.902	0.364	0.101	0.0479	0.015	0.0013	0.9999	0.9997	0.9949
691	0.835	0.422	0.078	0.047	0.0155	0.0019	0.9999	0.9996	0.9970
692	0.569	0.301	0.126	0.0477	0.0139	0.0009	1.0000	0.9998	0.9921
693	0.841	0.596	0.133	0.0464	0.0136	0.0011	0.9999	0.9992	0.9912
694	0.494	0.330	0.147	0.0464	0.0137	0.0011	1.0000	0.9998	0.9891
695	0.703	0.287	0.107	0.0452	0.0138	0.0015	0.9999	0.9998	0.9942
696	0.657	0.587	0.071	0.0454	0.0139	0.0026	0.9999	0.9992	0.9975
697	0.22	0.143	0.056	0.046	0.0141	0.0022	1.0000	1.0000	0.9984
698	2.46	0.592	0.102	0.0473	0.0142	0.0015	0.9990	0.9992	0.9948
699	0.302	0.553	0.109	0.0462	0.0142	0.0017	1.0000	0.9993	0.9941
700	1.04	0.361	0.140	0.046	0.0136	0.0028	0.9998	0.9997	0.9901
701	1.32	2.460	0.046	0.0461	0.01	0.0011	0.9998	0.9795	0.9991
702	0.639		0.077	0.0464	0.0092	0.001	0.9999		0.9970
703	0.482	0.011	0.043	0.0461	0.0134	0.0013	1.0000	1.0000	0.9991
704	0.228		0.049	0.046	0.0132	0.0012	1.0000		0.9989
705	0.476	0.269	0.064	0.0456	0.0137	0.0011	1.0000	0.9998	0.9980
706	0.578	0.410	0.050	0.0454	0.0134	0.001	1.0000	0.9996	0.9988
707	0.537	0.095	0.076	0.0465	0.014	0.0009	1.0000	1.0000	0.9971
708	0.587	0.404	0.144	0.0474	0.0138	0.0018	1.0000	0.9998	0.9927
709	0.773	0.154	0.148	0.047	0.0136	0.0019	0.9999	1.0000	0.9906
710	0.816		0.157	0.0471		0.002	0.9999		0.9876
711	0.629	0.201	0.107	0.048	0.0276	0.0008	0.9999	0.9999	0.9942
712	0.559	0.179	0.109	0.039	0.0272	0.0007	0.9993	0.9999	0.9940
713		0.255	0.098		0.0289	0.0008		0.9999	0.9952
713									
714	0.59	0.414	0.102	0.0491	0.0287	0.0008	0.9999	0.9996	0.9948
715		0.317	0.085		0.0291	0.001		0.9998	0.9964
716	0.401	0.197	0.122	0.0493	0.0284	0.0011	1.0000	0.9999	0.9931
718	0.553	0.195	0.090	0.0493	0.0288	0.0011	1.0000	0.9999	0.9960
717	0.603	0.167	0.099	0.0495	0.0284	0.0011	1.0000	0.9999	0.9951
719	0.603	0.170	0.109	0.0494	0.0283	0.0011	0.9999	0.9999	0.9940
720	1.4	1.270	0.108	0.0513	0.0305	0.0014	0.9997	0.9963	0.9942
721	0.422	1.180	0.113	0.0512	0.0295	0.0013	1.0000	0.9969	0.9936
722	1.32	0.850	0.168	0.051	0.0293	0.0013	0.9997	0.9984	0.9857
723	0.496	0.311	0.100	0.0504	0.0291	0.0011	1.0000	0.9998	0.9950
725	0.613	0.357	0.095	0.05	0.0285	0.0009	0.9999	0.9997	0.9955
726	1.66	0.183	0.122	0.0452	0.0271	0.0008	0.9996	0.9999	0.9925
727	2.57	0.181	0.089	0.0511	0.0287	0.0025	0.9990	0.9999	0.9961
728	0.516	1.660	0.039	0.0492	0.0175	0.0013	1.0000	0.9938	0.9992

	Standard error:-			Sensitivity (uM/bit):-			Correlation coefficient:-		
Station	Si-se	NO3-se	PO4-se	Si-a	NO3-a	PO4-a	Si-r2	NO3-r2	PO4-r2
730	0.302	1.770	0.040	0.0495	0.0175	0.0012	1.0000	0.9929	0.9992
731	0.956	0.211	0.012	0.0496	0.0156	0.0013	0.9999	0.9999	0.9999
732	0.547	0.238	0.029	0.0498	0.0153	0.0013	1.0000	0.9999	0.9996
733	0.978	0.581	0.032	0.0496	0.0151	0.0012	0.9999	0.9992	0.9995
734	0.965	0.631	0.365						
735	1.65	0.596	0.304	0.0495	0.0151	0.0014	0.9996	0.9992	0.9525
736	1.1	0.363	0.139	0.0486	0.0147	0.0014	0.9998	0.9997	0.9903
737	1.52	0.575	0.385	0.0487	0.0149	0.0013	0.9996	0.9993	0.9922
738	1.7	0.662	0.125	0.0487	0.015	0.0013	0.9995	0.9990	0.9869
739	2.37	0.439	0.378	0.0492	0.015	0.0015	0.9991	0.9996	0.9257
741			0.368	0.0478	0.0146	0.0014	0.9996	0.9991	0.9297
742	2.03	0.898	0.363	0.0479	0.0144	0.0014	0.9994	0.9982	0.9632
743	2.35	1.030	0.434	0.048	0.0144	0.0015	0.9991	0.9977	0.9008
744	0.83	0.651		0.049	0.0152		0.9999	0.9991	
745	1.1	0.687	0.117	0.0479	0.0147	0.0012	0.9998	0.9989	0.9927
746	1.07	0.628	0.099	0.0478	0.0147	0.0012	0.9998	0.9991	0.9951
747	2.13	0.591		0.049	0.0151		0.9993	0.9992	
748	1.4	0.428	0.044	0.0479	0.0151	0.0013	0.9997	0.9996	0.9990
749	1.91	0.406	0.233	0.0497	0.015	0.0014	0.9994	0.9996	0.9722
750	1.21	0.344	0.228	0.0493	0.0148	0.0015	0.9998	0.9997	0.9737
751	1.27	0.518	0.236	0.0492	0.0146	0.0014	0.9997	0.9994	0.9717
752	0.801	1.800	0.145	0.0494	0.0158	0.0013	0.9999	0.9928	0.9894
753	1.24	1.500	0.104	0.05	0.0155	0.0013	0.9998	0.9950	0.9946
754	2.65	2.220	0.163	0.0506	0.0158	0.0013	0.9989	0.9890	0.9865
755	1.37	1.670	0.135	0.0501	0.0159	0.0014	0.9997	0.9938	0.9907
756	1.28	0.494	0.035	0.0503	0.0157	0.0012	0.9997	0.9995	0.9994
757	1.24	0.431	0.028	0.0493	0.0156		0.9998	0.9996	
758	1.84	2.220	0.065	0.0485	0.015	0.0011	0.9995	0.9890	0.9979
759		1.160	0.062	0.0523		0.0017	0.9543		
760	0.729	0.486	0.090	0.048	0.0148	0.0006	0.9999	0.9995	0.9959
761	0.637	0.342	0.114	0.0475	0.0146		0.9999	0.9997	
759				0.0477	0.015			0.9996	0.9991
766	1.7	0.484	0.058	0.0483	0.0149	0.0013	0.9995	0.9995	0.9983
767	1.09	0.338	0.048	0.0484	0.0133	0.0017	0.9998	0.9998	0.9988
768	1.01	0.299	0.056	0.0478	0.0138	0.0016	0.9998	0.9998	0.9984
769		0.666	0.074	0.0462	0.0156	0.002	0.9980	0.9990	0.9973
770	3.75	0.369	0.062	0.0447	0.0152	0.0018	0.9978	0.9997	0.9981
771	3.76	0.443	0.040	0.0443	0.0152	0.0018	0.9978	0.9996	0.9992
772	2.33	0.580	0.903	0.0647	0.0154		0.9991	0.9993	
773	2.24	0.490		0.0642	0.0162		0.9992	0.9995	
774	2.21	0.374		0.0642	0.0168		0.9992	0.9997	
775	3.2	0.694		0.0626	0.015		0.9984	0.9997	
776	0.874	0.457	0.062	0.0485	0.0185	0.001	0.9999	0.9995	0.9980

SAGAMI RESULTS D213

Results of measurements made on external QC standards (Sagami chemical Co. Japan) during D213. The expected concentration, and the percentage difference of the mean of the measurements made from that value, is recorded.

	Silicate:-			Nitrate:-			Phosphate:-		
Conc.	10.00	50.00	50.00	20.00	20.00	20.00	1.00	1.00	1.00
umol/l									
	9.90	49.30	47.74	19.46	19.94	22.09	1.17	1.19	0.86
	9.70	48.33	47.19	19.19	19.56	21.69	1.07	0.96	0.86
	9.97	48.61	48.51	19.98	19.32	22.30	0.96	0.97	0.79
	9.53	47.86	47.20	19.32	18.92	21.83	1.14	1.08	0.78
	9.61	49.21	46.64	19.16	18.71			0.82	0.78
	9.58	48.20	45.31	20.02	19.34			0.92	
	9.59	48.32	47.73	19.66	20.07			0.81	
				19.35	19.46			0.83	
					19.12				
					19.20				
mean	**9.70**	**48.55**	**47.19**	**19.52**	**19.36**	**21.98**	**1.09**	**0.95**	**0.81**
SD	0.17	0.53	1.01	0.34	0.42	0.27	0.09	0.13	0.04
CV%	0.78	2.42	4.61	1.53	1.91	1.23	0.42	0.61	0.19
% diff	3.03	2.91	5.62	2.41	3.18	9.89	8.50	5.25	18.60

D213 QUALITY CONTROL RESULTS

Results from the measurement of quality control samples (QC1 and QC2) and nitrite (NO2) standards over D213.

Station	Si - QC1	Si - QC2	NO3 - QC1	NO3 - QC2	PO4 - QC1	PO4 - QC2	NO2
673	68.4	75.4	26.5	24.5	2.34	2.02	
673	69.5	75.5	26.5	24.4	2.74	2.33	
674	67.9	73.5	26.6	24.5	2.29	1.9	
674	68.5	73.4	26.3	24.1	2.29	1.88	
675	66.9	73.5	26.9	24.8	1.87	1.6	
675	67.7	74.5	27.2	25.1	1.96	1.67	
676	68.1	74.9	26.7	24.6	2.06	1.88	
676	69.1	75.3	26.9	24.8	1.9	1.7	
677	67.8	74.3	27.2	24.8	2.01	1.68	
677	67.7	74.5	26.4	24.2	2.07	1.76	
678	68.8	75	26.8	24.9	1.96	1.68	
678	68.4	74.7	27.3	25.1	2.15	1.86	
679	68.3	75.7	26.1	24.3			
679	68.3	75.6	26.3	24.4			
676	68.6	75.2	26.6	24.6	2.26	2.22	
676	68.7	75.2	26.7	24.5		1.97	
682	68.2	75	26.3	24.5	2.04	1.85	28.63
682	68.6	76	26.4	24.6	2.02	1.83	
683	68.5	75.5	26.7	24.8	2.04	1.83	28.8
683	68.4	76.6	27.1	25.2	2.13	1.95	
684	68.6	76	26.6	24.8	2.06	1.87	28.56
684	68.7	75.8	26.6	24.8	2.07	1.83	
685	68.5	75.1	26.5	24.3	2.03	1.85	27.16
685	69.2	75.2	26.6	24.5	2	1.86	
686	68.4	74.5	25.3	23.4	1.95	1.64	28.49
686	68	74.3	26.4	24.3	1.98	1.69	
686	69.9	76.3	26.8	24.6	2.22	1.87	29.24
687	70	76.2	26.6	24.4	1.81	1.6	
687	69.9	76.4	26.6	24.5	1.97	1.73	28.41
688	67.8	74.5	26	23.9	1.87	1.68	27.76
688	68.5	75	26.1	24.1	1.93	1.72	
689	68.4	76.8	26.1	22.6	1.91	1.66	28.19
689	68.6	75	26.2	24.1	1.96	1.74	
690	68.3	75	26.6	25	1.91	1.69	28.71
690	69	75	27	24.7	1.92	1.7	
691	69	75.4	26.9	24.8	1.81	1.59	28.04
691	69	75.4	27.3	25.2	1.8	1.64	
692	69	76	26.4	24.4	2.01	1.8	27.87
692	69.6	76.2	26.6	24.6	2	1.78	
693	69	75.4	26.7	24.5	2.03	1.77	27.87
693	68.7	75.6	26.1	24.2	2.01	1.77	
694	68.9	75.5	26.8	24.8	2.07	1.81	28.06
694	69	75.6	26.1	24.2	2.06	1.75	
695	68.8	75.4	25.5	23.6	1.8	1.63	28.34
695	69.2	75.9	26.6	24.3	1.96	1.72	
696	68.9	73.8	26.6	23.8	1.74	1.49	28.55
696	69.1	73.9	26.4	23.7	1.81	1.53	
697	68.9	73.7	26.6	24	1.75	1.52	28.41
697	69.3	73.8	26.9	24	1.81	1.56	
698	68.2	73.8	26.1	24	1.84	1.61	28.49
698	69.5	73.7	27.1	24.2	1.83	1.65	
699	69.3	74.2	26.1	23.5	1.79	1.57	28.17
699	69.2	74.1	26.5	23.9	1.87	1.59	
700	69.4	74.5	26.8	24.2	1.45	1.23	29.17
700	69.6	74.4	27.1	24.4	1.73	1.41	

Station	Si - QC1	Si - QC2	NO3 - QC1	NO3 - QC2	PO4 - QC1	PO4 - QC2	NO2
701	68.1	73.3	27.7	19.2	1.75	1.5	23.05
701	67.7				1.84		
702	68.2	75.8	27.3	24.4	1.87	1.61	
702	67.9				1.91		
703	70.6	71.3	27.3	22.8	1.84	1.5	28.71
703	69.1		26.8		1.74		
704	67.8	74.6	27.7	25.2	1.81	1.61	29.76
704	68.1	75.4			1.89	1.64	
705	67.7	74.3	26.5	24.5	1.83	1.61	28.32
705	68	75.4	26.5	24.9	1.9	1.65	
706	66.9	73.3	26.6	24.7	1.67	1.48	28.41
706	67.9		26.5		1.72		
707	68	74.9	27.7	25.5	1.84	1.73	29.62
707	68.5	76.1	27.9		1.87		
708	69.2	75.9	26.7	24.7	2	1.78	28.34
708	68.2	76.1	26.3	24.8	1.92	1.76	
709	68.5	75.3	27	25	2	1.78	28.36
709	68.4	75.4	26.7	25.1	1.97	1.76	
710	68.9	75.5			1.96	1.76	
710	68.3				1.91		
711	69.1	75.4	26.8	24.6	1.81	1.61	
711	68.1	75.2	24.7	27.7	1.89	1.67	
712	63.9		27	24.8	1.93	1.71	27.8
712		70.6	26.9	24.7	1.93	1.73	
712	70.7	78					28
712							
713	67.9	73.9	26.7	24.4	1.89	1.69	28.1
713			26.5	24.3	1.85	1.63	
714	67.8	74.3	26.4	24.4	1.92	1.67	
714	68.4	74.5	26.7	24.6	1.9	1.69	
715	68.9	74.3	26.8	24.7	1.89	1.67	
715	67.4	73.5	26.7		1.91		
716	69.1	75	27.1	24.4	1.75	1.51	
716	60.1	74.9	22.4		1.75	1.48	
718	69	75.2	26.9	24.5	1.95	1.65	28.5
718	68.6	74.7	26.8	24.5	1.91	1.66	
717	69.1	75.5	26.8	24.4	1.88	1.64	28.44
717	68.6	74.7	26.8	24.5	1.84	1.59	
719	69.1	76.2	26.8	24.5	1.93	1.64	30.06
719	68.8	76.3	26.4	24.6	1.94	1.63	
720	69.7	76	29.9	27.2	1.77	1.5	29.6
720	69.8	76	27.5	29.6	1.83	1.65	
721	69.1	75.1	29.4	27.3	1.74	1.55	31.91
721	69.2	75.7	29.8	27.8	1.91	1.73	
722	68.4	75.1	29	26.7	1.9	1.65	32.24
722	69	76.8	29.9	27.4	1.94	1.7	
723	66.4	74.5	27.1	25.4	1.86	1.66	26.94
723	68.1	74.8	27.7	26	1.92	1.72	
725	66.3	74.5	26.7	25.2	1.92	1.74	28.8
725	66.2	74.8	26.8	25.4	1.89	1.72	
726	62.5	68.8	25.5	23.4	1.99	1.74	23.6
726	64.6	71.2	22.3	20.6	1.81	1.54	
727	69.6	77	26.6	24.5	1.81	1.56	
727	67.8	75.6	26.5	24.4	1.79	1.56	
728	68.7	75.5	33.5	30.8	1.8	1.56	37.61
728	66.7	74	39.4	36.5	1.85	1.62	
730	68.6	75.5	27.3	31.8	1.88	1.63	43.16
730	68.1	75	25	37	1.87	1.64	
731	69.3	76.1	27.3	25	1.76	1.55	28.23
731	69.1	76.3			1.71	1.52	
732	69.5	76.1	26.4	24.4	1.81	1.55	28.45

Station	Si - QC1	Si - QC2	NO3 - QC1	NO3 - QC2	PO4 - QC1	PO4 - QC2	NO2
732	69.2	76.3	26.7	24.5	1.67	1.51	
733	68.2	74.6	26.2	24.2	1.67	1.48	25.52
733	52.1	63.6	21.4	20.5	1.33	1.21	
734	69.2	76.1	26.5	24.5	1.46	1.27	27.35
734	68.9	75.8	24.5	22.5	1.5	1.28	
735	69.5	76	26.6	24.6			28.61
735	69.4	76.2	26.6	24.6			
736	68.9	75.6	26.7	24.7	1.31	1.57	28.84
736	69	75.8	26.7	24.9	1.02	1.34	
737	65.1	73.2	28.4	28.5	1.54	1.33	
737	71.3	75.8	25.2	24.9	1.41	1.28	
738	67.8	74.2	26.3	24.1	1.35	1.15	27.17
738	67.6		25.9				
739	68.1	74.6	26	24.1	1.75	1.62	27.64
739	71.1	77.8	27	25	1.76	1.64	
741	67	73.3	25.3	23.6	1.72	1.52	27.81
741	66.8	73.5	25.3	24	1.65	1.5	
742	72.6	73.8	23	24	1.47	1.58	27.66
742	64.5	73.1	24.3	23.7	1.62	1.53	
743	65.6	72.9	24.7	23.8	1.7	1.51	27.28
743	65	72.6	24.6	23.5	1.59	1.46	
744	68.2	74.5	27.1	25	1.78	1.72	
745	67.6	73.8	26.9	24.7	1.84	1.5	28.15
745	68.2	74.3	27.1	24.8	1.92	1.52	
746	69.2	75.2	27.4	25.2	1.94	1.55	28.69
746	68.1	73.9	27.3	24.8	1.61	1.48	
747	67.8	74.2	26	24.4			28.36
747	67.5	73.8	26.3	24.2			
748	66.9	73	25.7	23.9	1.76	1.58	28.53
748	66	72.6	25.4	23.9	1.7	1.54	
749	70.3	76.5	25.8	23.8			27.57
749	70.6	77.1	26	24			
750	69.6	75.6	25.6	23.5			28.08
750	69	75.8	25.5	23.6			
751	67.2	72.3	24.6	22.5	1.32	1.17	27.95
751	68.5	72.8	25	22.7			
752	68.3	74.8	29.8	27.2	1.96	1.78	33.22
752	68.5	74.4	30.8	28.4	1.99	1.81	
753	68.9	75.8	29.7	28.1	1.95	1.83	33.32
753	67.7	75	29.9	28.5	1.92	1.83	
754	70.7	76.1	30.3	28	2.41	2.27	34.84
754	70.2	75.6	30.6	28.4			
755			29.1	27.4			32.93
755			30.2	29			
756	68.7	73.6	26.1	24	1.7	1.59	
756	68.7	73.7	26.5	24.4	1.75	1.62	
757	68.3	72.3	26	26.5	1	1.51	
757	68	71.8			1.64		
758	67.7	71.5	21.6		1.66	1.47	
758	61.5	70.5			2.01	1.48	
759	61.8	67.5					
759	73.2	47.7					
760	67.4	73	26.1	23.9	1.96	1.73	31.26
760	64.1	67.1	25.6	24.1	1.87	1.75	
761	67.3	72.4	25.6	23.5			
761	67.1	72.2	25.6	23.6			
759	68.2	73.1	26	23.9	1.96	1.73	
763	68.7	74	25.9	24	1.69	1.55	28.64
763	68.8	74.5	26.5	24.2	1.76	1.67	
764	68.9	74.6	26.9	24.8	1.73	1.6	
765	68.4	74.6	26.2	24.2	1.72		

Station	Si - QC1	Si - QC2	NO3 - QC1	NO3 - QC2	PO4 - QC1	PO4 - QC2	NO2
765	67.8		25.7				
766	68	72.9	26.6	24.2	1.74	1.56	
766	66.7		26.2		1.73		
767	68.7	74.4	26.7	24.4	1.5	1.59	
767	68.3		26.6		1.5		
768	68.5	74.8	26.7	24.8	1.47	1.61	
768	68.2		26.1		1.78		
769	67.4	73.2	26.2	24.7	1.76	1.61	
769	69		27.1		1.77		
770	67.5	69.9	26	22.8	1.7	1.44	
770	67.1		26.2		1.71		
771	65.3	68.4	25.2	22.6	1.64	1.41	
771	64.9		24.9		1.61		
772	68.8	70.7	25.1	22.3			
772	68.5		25.2				
773	68.4	71.2	26	22.8			
773	69.6		25.7				
774	69.1	71.3	25.5	22.6			
774	67		25.6				
775	67	68.7	27.2	23.7			
775	67.2		27.3				
776	67.6	74.8	30	26.7			
776	68						

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