



REVIEW OF MARINE PHYSICS ANALYSIS OF THE
DISSOLVED OXYGEN CONTENT OF SEAWATER

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INTERNAL DOCUMENT 288

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1989

The Marine Physics Group have achieved only poor quality dissolved oxygen data for several years. In an attempt to define the cause of this the Winkler titration procedure is reviewed and compared with the method used by the Marine Physics Group. The results from recent cruises are examined and several short comings are identified and recommendations made for both short term and long term improvements, automatic titration being the most important for the latter.

Following this review further work was done (appendix II) incorporating such short term improvements as were possible. Greatly improved measurements were made as demonstrated by the analysis of duplicate samples but this showed the inadequacies of the multisampler system, which has yet to be replaced and as such, limits the accuracy of the dissolved oxygen analysis.

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1. INTRODUCTION

Recent cruises have highlighted problems with the analysis of the dissolved oxygen content of sea water by the Marine Physics Group. The accuracy has generally been poor, no absolute figures have been calculated but one of the features has been the inconsistency of the results. It is estimated that the accuracy has varied up to 4%, culminating on *RRS Discovery* Cruise 174 when the values were 10% low (see Section 5.2). On *RRS Discovery* Cruise 181 the accuracy of the results varied greatly when compared with the CTD oxygen sensor and it appeared that this was related to the person who drew the samples - see Section 5.3.

The analysis has been done using the Winkler titration procedure and this paper summarises the technique; section 2.2-2.8 could be used as a manual. Marine Physics procedure has deviated from the standard in some aspects as discussed in Section 4, and it should be possible to improve the results by correcting these differences. Alternative equipment as described in Section 3 is available which could further improve the precision and flexibility of the analysis.

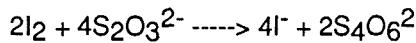
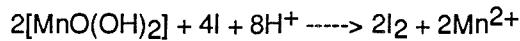
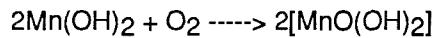
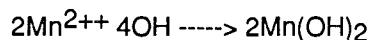
Using the Winkler technique and the existing equipment it should be possible to achieve an accuracy of 0.1% and with upgraded equipment this could be improved to 0.05%. An accuracy of 0.1% would be sufficient to calibrate the CTD oxygen sensor as the manufacturers specification of accuracy is only 0.2ml/l. However for intercomparisons with other data sets 0.05% would be preferable.

2. WINKLER TITRATION PROCEDURE

2.1 Description

The principle of the titration is as follows: manganous sulphate and alkaline sodium iodide ions are added to seawater resulting in a precipitate of manganous hydroxide. The oxygen in the seawater oxidises some of the hydroxide to a tetravalent manganous compound. The quantity of this compound is determined by making the solution acid, when the compound oxidises iodide ions (present in the added alkali) to iodine. The iodine is then determined by titration with sodium thiosulphate. (UCNW notes for BOFS/JGOFS).

The method is approximated by the following chemical reactions:



(thus O_2 is equivalent to $4\text{S}_2\text{O}_3^{2-}$)

The following is a summary of the Winkler titration procedure taken from various sources, most agree on the procedure but where differences occur these have been noted. Some aspects are not discussed here as they have been adopted as standard practise e.g. transfer of the solution, and use of particular reagents. These points were explained by Carpenter (1965) but a full list of references is given in Section 7.

2.2 Reagents

1. $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ 600g/litre (3M)
2. NaOH 320g/litre (8N)
NaI 600g/litre (4M)
3. H_2SO_4 280ml/litre (10N)
4. Starch 1% solution
5. $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ 35g/litre (0.14N)
6. KIO_3 0.3567g/litre (0.01N)

1. Manganous chloride: dissolve 600 g in distilled water by stirring and make up to 1 litre. Manganous sulphate may be substituted but the chloride is recommended because of its solubility and freedom from higher valence manganese compounds.
2. Sodium iodide-sodium hydroxide (Alkaline iodide): dissolve 320 g sodium hydroxide in 400 ml of distilled water, allow to cool, add 600 g of analytical grade sodium iodide and dissolve, allow to cool and make up to 1 litre. Prepare this solution as quickly as possible to avoid take up of carbon dioxide. The sodium iodide - sodium hydroxide solution should be clear when made up. Any cloudiness or crystallisation is due to contamination of the pellets with carbon (sodium carbonate which is very difficult to dissolve). Discard the solution and use a new batch.

3. Sulphuric acid: add 280 ml of concentrated sulphuric acid to about 500 ml distilled water - add slowly with stirring. Allow to cool and make up to 1 litre.
4. Starch: mix 1 g of soluble starch in 5-10 ml of cold water, and pour into 100 ml of boiling water. Stir until dissolved. It may retain its sensitivity for several weeks but is best prepared fresh. Discard if a reddish colour is produced with iodine.
5. Sodium thiosulphate: dissolve 35 g of sodium thiosulphate pentahydrate in distilled water that has been boiled for about 10 mins to expel carbon dioxide (allow to cool before adding the sodium thiosulphate). If carbon dioxide is present the pH of the water will be low and a colloidal haze of sulphur will result. Make up to 1 litre, add a few drops of chloroform (or carbon bisulphide - Parsons, Maita & Lalli) as a preservative, and 0.1 g sodium carbonate Na_2CO_3 . The solution will be stable for several months.
6. Potassium iodate: dry analytical quality potassium iodate at 105°C for 1 hour, weigh out exactly 0.3567 g and dissolve in 2-300 ml distilled water, warming if necessary. Cool and make up to 1 litre. If well stoppered the solution should remain stable.

$$\text{Molarity of iodate standard} = 0.001667 * \frac{\text{weight}}{0.3567}$$

Potassium biiodate ($\text{KH}(\text{IO}_3)_2$) can be used as an alternative but should be dried by vacuum dessication for a week before use. Dissolve 0.3250 g in 1 litre of distilled water to give 0.01N solution.

Commercially prepared chemicals may also be used.

2.3 Equipment

Sample bottles may be Erlenmeyer flasks of nominal 125 ml capacity, or BOD 125 ml bottles, or any suitable glass bottle. The volume displaced by the stopper must be sufficient to allow the entire sample to be titrated without transfer of the solution. The end of the stopper should be rounded or tapered to avoid trapping air bubbles.

The bottles must be calibrated 'to contain' by weighing: wash each stopper and flask, inside and out thoroughly in hot soapy water. Rinse with tap water followed by distilled water. Once the flask has been cleaned do not touch it with your fingers. Weigh the flask and stopper empty (W_e). Slowly fill the bottle with distilled water that has been sitting for at least 2 hours, replace the stopper, check that there are no air bubbles, dry the outside of the flask and weigh (W_f). Read the temperature of the contents of the bottle. The bottle volume is calculated as follows:

$(W_f - W_e) * \text{temp interpolation value}$

see Table 1 for the temperature interpolation value.

Bottles and stoppers must not be chipped or cracked as this may trap air bubbles and make them difficult to keep clean.

Reagent dispensers must be accurate to $\pm 1\mu\text{l}$ to give an uncertainty of ± 1 ppt in water containing 5.5 ml O₂/l and requiring approximately 1.000 ml of sodium thiosulphate for titration.

Reagents should be stored in dark glass bottles.

Titrating apparatus should consist of a burette attached to a 3-way stopcock for delivery of the titre. This is mounted in a container with a white interior, and with a swivel mounted magnetic stirrer to position the sample under the burette with the delivery tip immersed in the sample. Fluorescent lights are fixed on the forward edge of the interior.

2.4 Sampling Procedure

1. Oxygen samples should always be drawn as soon as possible from the water bottle (Nansen/Niskin) and should be drawn first, ie before salinity or nutrient samples. However it may be necessary to draw some tracer samples before oxygen samples depending on the risk of contamination from the atmosphere.
2. Clean bottles should be used and rinsed twice with seawater before sampling. If the bottles have not been pre-rinsed, rinse once with a small amount of sample water and discard (running water through the sampling tube will help get rid of bubbles from the tubing).
3. Fill the bottles by siphoning using tygon tubing. (Bubbles are likely to form inside a new piece of tube, overcome this by soaking it in seawater for 2-3 days before use). The tube should reach to the bottom of the bottle. Overflow at least twice the volume of the bottle to displace any air bubbles, but try not to agitate the sample too much. Replace the stopper as described below before adding the reagents and avoid trapping any air bubbles.
4. The reagent pipettes must deliver 1.0ml $\pm 1\mu\text{l}$. Add 1ml of manganese chloride, followed by 1ml of the sodium iodide-sodium hydroxide reagent. Pipette just below the surface because the dense reagents sink. (The Marine Technicians Handbook suggests introducing the reagents about one inch above the bottom of the flask but

this is not common practise and increases the risks of contamination). Stopper immediately, it is essential to avoid trapping air bubbles: tilt the bottle slightly and insert the stopper with a twisting motion.

N.B. Pipetting Technique: separate pipettes must be used for each reagent. Insert the tip of the pipette just below the surface of the reagent and wipe off any excess fluid against the lip of the reagent bottle before inserting the tip just below the sample surface - this prevents the introduction if any excess reagent into the sample. Wipe the pipette after dispensing the reagent to avoid contaminating the reagent bottle with the sea water. When dispensing the reagents with a fixed air displacement type pipette one small air bubble should be blown from the pipette to ensure that all the reagent has been dispensed. Care must be taken to avoid any contamination between the two reagents.

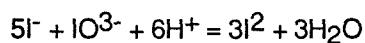
5. Shake the sample vigorously for about 10 seconds holding the top in place. There is occasionally some expansion at this stage and the stopper must be tightened.
6. Allow the precipitate to settle halfway down the flask (about half an hour) then shake again. Allow the precipitate to settle 2/3rd way down the flask before titrating (about 1 hour).
7. Samples may be stored but it is preferable to titrate them as soon as possible after they have reached ambient temperature (ie, within 6 hours - Parsons, Maita & Lalli). To prevent thermal contraction drawing air into the bottles keep them underwater. Also store in a dark box at the same temperature (these samples can then be kept for up to a week - Marine Technicians Handbook).

If either the manganeseous chloride or the alkaline iodide reagent forms a precipitate discard it.

Do not allow reagents to contaminate each other.

2.5 Standardising Procedure

Thiosulphate is not a primary analytical standard, therefore it is necessary to standardise it. Potassium iodate is used for this and under acid conditions the iodate reacts with the iodide ions to liberate iodine, which is then titrated with the thiosulphate.



Run standards before every set of samples. Run them until two agree within $\pm 0.0020 \mu\text{l}$ of titre.

1. Clean two flasks by scrubbing with soapy water, rinse with tap water and distilled water. (Keep these flasks for standards and blanks only).
2. Pipette 10 ml iodate into each flask.
3. Fill flask with distilled water (If seawater is used instead add the three reagents to the 10 ml iodate before adding the seawater).
4. Add 1 ml sulphuric acid and stir.
5. Add 1 ml sodium iodide-sodium hydroxide solution and stir. If a precipitate is formed by the addition of sodium iodide - sodium hydroxide to the standard (or blank), it must be stirred and dissolved before addition of the manganous chloride or the result could be up to 10% higher.
6. Add 1 ml manganous chloride solution, do not insert the pipette tip into the solution when adding any of these reagents.
7. Begin stirring and titrate immediately because the iodine is lost quickly through volatilisation. Add thiosulphate quickly at first to consume most of the iodine. Titrate to a pale yellow straw colour and add 0.3 ml starch solution, continue the titration to the end point.

Avoid a large vortex when stirring to minimise iodine loss, but after the starch is added more rapid stirring is suggested.

Repeat the above procedure until standards agree within $\pm 0.0020 \mu\text{l}$ of titre.

Ensure the flasks are thoroughly cleaned to remove all manganous ions.

$$\text{Molarity of thiosulphate (M)} = (6 \cdot M_1 \cdot V_2) / V_1$$

where: V_1 = volume of thiosulphate added (ml),

V_2 = volume of iodate added (ml),

M_1 = molarity of iodate standard.

2.6 Blank Determination

It is important to establish the presence of any impurities that liberate or react with iodine in acid solution and this is done by blank determination.

1. Pipette 1 ml of potassium iodate into a clean flask (those used for the standard determination may be used here. It is important that no manganous ions are present in the bottle), and nearly fill with distilled water.
2. Add 1 ml of sulphuric acid, and mix.
3. Add 1 ml sodium iodide-sodium hydroxide reagent. Mix thoroughly, and if a precipitate is formed ensure that this is dissolved before adding the manganous chloride or the result could be up to 10% higher.
4. Add 1 ml of manganous chloride reagent.
5. Titrate to the end point.
6. Pipette 1 ml of potassium iodate into the solution and titrate the liberated iodine to a second end point. About 80% of the first titration of sodium thiosulphate can be added before adding the second 1 ml of potassium iodate to reduce the amount of blue and prevent precipitation.

The reagent and indicator blank is the difference of the second less the first titration subtracted from the first titration value. (or the initial value doubled, less the second value). The procedure can be repeated with seawater instead of distilled water to determine the impurities in seawater that may affect the titration. The method is unsuitable for badly polluted samples.

Blanks should be run regularly throughout a cruise and whenever a reagent is changed. Run at least four, or more, until a reasonable agreement is reached between at least three.

2.7 Titration Procedure

Before titration shake the sodium thiosulphate bottle to ensure the solution is homogenous. Discard sufficient volume to flush any pipework/tubing/burette.

1. Add 1 ml of sulphuric acid just below the surface, it displaces about 1 cm^3 of solution but this contains no oxygen if the precipitate has settled. Mix thoroughly until the precipitate dissolves.

Carbon dioxide may be liberated during acidification but this should not affect the analysis.

If the oxygen concentration is excessive (ie nearing saturation) a dark brown/black precipitate may persist in the bottle after acidification. It should dissolve if mixed for longer, or given a few more drops of acid. Light precipitate can be ignored if well dispersed throughout the aliquot.

Once the bottle has been opened the solution must be titrated immediately.

The oxidised iodine solution (ie after acidification the compound oxidises iodide ions to iodine) is stable for many hours or days. But if the water sample contains much organic matter this may be slowly oxidised by the iodine, therefore it is advisable not to delay the titration.

2. Add the sodium thiosulphate mixing all the time, until the solution reaches a pale yellow straw colour. Add 0.5 ml of the starch solution and continue the titration to the complete disappearance of the blue complex.

Or measure the extinction of the iodide ions using a photometric cell (in which case do not add the starch indicator solution)

The solution should remain colourless for 20 seconds once the end point is reached. A creeping end point is due to atmospheric oxidation of iodide to iodine which becomes increasingly rapid as the pH is lowered. But this should not affect the titration for many minutes.

If the samples were initially much colder than laboratory temperature they should be titrated at once, or allowed to warm up before acidification. If the iodine solution is allowed to expand through warming small errors may be introduced, although these are probably negligible.

The old solution may be left in the bottle until it is needed for another sample as the acid solution inhibits bacterial activity. However they should be rinsed thoroughly with seawater before reuse (section 2.4).

Overtitrated samples can sometimes be retrieved by back titration. Note the over titrated value, add 1 ml of iodate standard and titrate to a new end point. (10 ml of iodate can be added if there is room in the flask for it). The final titration value should have one tenth of the standard determination (the full value of 10 ml is used) subtracted from it to give the actual end point (which should be less than the over titrated value).

2.8 Calculations

Dissolved oxygen content in millilitres per litre:

$$\frac{(R_{\text{sam}} - R_{\text{blk}}) * V_{\text{IO}_3} * N_{\text{IO}_3} * 5598.0 \text{ ml/O}_2\text{equiv.}}{(R_{\text{std}} - R_{\text{blk}}) * (V_{\text{bot}} - V_{\text{reag}})} - D_{\text{Oreag}}$$

where:
 R_{sam} - burette reading for sample titration
 R_{blk} - burette reading for blank titration
 R_{std} - burette reading for standard titration
 V_{IO_3} - volume of potassium iodate standard (ml)
 V_{bot} - volume of sample bottle (ml)
 V_{reag} - volume of sample displaced by manganous and hydroxide-iodide reagents (ml)
 N_{IO_3} - normality of potassium iodate standard
 D_{Oreag} - dissolved oxygen added with the reagents

for 140 ml sample	$D_{\text{Oreag}} = 0.018$
130	0.020
120	0.022
110	0.023
100	0.025

2.9 OXYGEN EQUIVALENTS

$$\begin{aligned} 43.57 \mu\text{m/kg} &= 1 \text{ ml/l} \\ 11.196 \text{ ml/l} &= 1 \text{ mg - at /l} \\ 0.6998 \text{ mg/l} &= 1 \text{ ml/l} \\ 16 \text{ mg/l} &= 1 \text{ mg - at /l} \end{aligned}$$

3. AUTOMATIC TITRATION

Various papers (Carpenter (1965), Carritt and Carpenter (1966), Bryan, Riley and Williams (1976), Oudot, Gerard and Morin (1988), Aminot (1988)) describe equipment and techniques for increasing the accuracy, precision and speed of the Winkler procedure. The equipment can be divided into three components: determination of the end-point, automation of titre addition and microprocessor control of the titration.

3.1 Photometric End-point Determination

The different techniques of detecting the end point of the titration are summarised by Carpenter (1965). The options include visual starch, colorimetric starch, amperometric

technique and ultraviolet absorption. Of these the ultraviolet absorption is the most sensitive being over twenty times more accurate than visual starch.

The most abundant type of iodide ion during titration is the tri-iodide ion and this ion absorbs ultraviolet light. It is therefore possible to measure the presence, or absence, of iodide by the amount of ultraviolet light passing through the solution. Bryan, Riley and Williams (1976) describe a simple photometric arrangement whereby the extinction of iodide ions can be measured. Output from a photometric cell drives a chart recorder and the end-point is indicated by a distinct change in the trace. The authors claim that with practise the end-point can be determined within $\pm 0.05\%$ and by including the modifications described by Williams and Jenkinson(1982) this can be reduced to 0.01% (see Section 3.3).

3.2 Automatic Burette

Williams and Jenkinson (1982) and Oudot, Gerard and Morin (1988) describe automatic burettes which can start, stop, refill, zero and have a variable rate of delivery. The Metrohm Dosimat E535 gives a high accuracy at 1 cc total addition, and the Metrohm Multidosimat burette delivers quantities of $1\mu\text{l}$. Both these can increase the speed with which each titration is done and the accuracy of them.

3.3 Microprocessor Control

The addition of some small microprocessor to control the titration is the next obvious step to increase the speed, accuracy and consistency of the titration results. Two systems are described in the literature; that by Oudot *et al* (1988) uses potentiometric end-point detection (amperometric) and that by Williams and Jenkinson (1982) uses photometric determination of the end-point. Both employ similar logic to use the potential or photocell output to control the addition of the titre. Initially a quantity of titre is added, the volume depending on the amount of iodide in the solution. After this Oudot *et al* add the titre in pulses of decreasing volume as the end-point is reached. Williams and Jenkinson deliver the titre in a series of fixed volume additions until a preset output signal is reached, then in smaller volume additions until the transmission of ultraviolet light is at about the 50% level and 1% of the titre remains to be added. Then small additions of $0.2\mu\text{l}$ or $0.3\mu\text{l}$ are made and after each the photocell output is compared with the previous value. When the difference between the two is less than 0.1% of the final signal the end-point has been reached. Further additions are made to see if there is any further increase in the photocell output. Throughout the titration the burette reading and

photocell values are stored in memory. When the titration is complete the program searches backwards through the photocell data until a consistent downward trend is found. The associated burette reading at the inflection point is recorded and displayed - if the operator accepts the value the program continues with the calculation of oxygen content.

The software described by Williams and Jenkinson is more sophisticated than that of Oudot *et al* and should provide a very reliable and consistent method of titration. The authors claim an accuracy of 0.01%.

4. COMMENTS ON MARINE PHYSICS PROCEDURE

Positive displacement type syringe pipettes have been used for the reagents as recommended by Carritt and Carpenter (1966), but fixed displacement pipettes are now available which would provide greater accuracy.

The reagents have always been introduced into the bottom of the sample rather than just beneath the surface.

Attention should be paid to the details of pipetting technique: only the tip of the pipette should be placed beneath the surface of the reagent, or the sample. This prevents any excess liquid on the outside of the pipette contaminating the sample. The pipettes should also be kept clean to prevent any contamination.

The reagents have been stored in plastic bottles whereas glass bottles would be more suitable.

Potassium iodate has been obtained as a 'ConvoL' solution, ie. ready prepared, with a known molarity. It is now possible to get sodium thiosulphate in the same form which may improve the quality of this reagent.

Although sodium thiosulphate was not prepared with boiled distilled water no contamination through uptake of carbon dioxide has been observed.

'a few drops' of starch were used. It would be more accurate to conform to 0.5 ml of starch.

A black/blue precipitate has often been observed in the samples. Possibly more sulphuric acid should be added to see if this will completely dissolve the precipitate, but it is more likely that the solution has not been titrated far enough before addition of the starch causing precipitation.

Two types of bottles have been used. Recently a set of Erlenmeyer type flasks were bought, however the stoppers had to be altered to fit the storage boxes and this left them weakened and susceptible to breakage (Several stoppers have already broken). The original glass bottles are still in use but the stoppers are flat bottomed and so tend to trap air bubbles. They should be tapered or rounded to prevent air bubbles being trapped.

The titration unit contains a 3-way stopcock to deliver the titre positioned above a magnetic stirring unit and illuminated by fluorescent lights, as described for the Winkler titration procedure (Section 2.3).

5. DUPLICATE SAMPLE ANALYSIS

In the following section some specific aspects of dissolved oxygen analysis are considered. Over the last few years duplicate samples have been taken on several cruises, i.e. two separate samples have been drawn from the water bottles, one immediately after the other. On different cruises these have been used to test the repeatability of the analysis (165A), the difference between operators (164) and to compare different sets of equipment (181). On *RRS Discovery* Cruise 174 the oxygen results appeared completely wrong, this is discussed with reference to a later cruise (*RRS Charles Darwin* 34A).

5.1 *RRS Discovery* Cruises 164 and 165A

On *RRS Discovery* cruise 164 (S. W. Indian and Southern Oceans, December 1986 - January 1987) duplicate samples were drawn by two people on one CTD cast in an identical manner and analysed on the same equipment.

Station no	Pres dbar	First sample ml/l	Second sample ml/l	A-B
11428	4050	4.94 B		
	2500	4.82 B	4.92 A	0.10
	1250	3.96 A	3.91 B	0.05
	600	5.38 B		
	400	5.38 B	5.42 A	0.04
	10	6.51 A	6.45 B	0.06

The results obtained by Sampler A were all higher than those of Sampler B, however the number of duplicates drawn (four) do not provide a statistical sample.

On *RRS Discovery* cruise 165A (Aguilhas Retroflection Zone, February 1987) duplicate samples were drawn by the same person on two CTD casts.

Station no	Pres dbar	First sample ml/l	Second sample ml/l	1-2
11462	4101	5.61	5.53	0.08
	1584	3.53	3.50	0.03
	10	5.12	5.06	0.06
11463	3000	5.05	5.06	-0.01
	1412	4.56	4.63	-0.07
	500	5.37	4.84	-0.53

All but one of the results lay within ± 0.1 , however, again the number of duplicates drawn (six) do not provide a statistical sample and no conclusions have been drawn from either of these experiments.

5.2 *RRS Discovery* Cruise 174 and *RRS Charles Darwin* Cruise 34A

Saunders (p.c.) reports that the bottle oxygen results from *RRS Discovery* cruise 174 (Faeroes - Charlie Gibbs Fracture Zone, June 1988) were systematically 10% lower than expected. They were produced by the same operator using the same technique and the same equipment as previous cruises which had given more accurate results. The only other unknown was the chemicals used to make up the reagents. The remainder of that batch of chemicals were used on a later cruise, *RRS Charles Darwin* cruise 34A (Western Equatorial Pacific, Sept 1988). Here problems were encountered with the first standardisation and experimentation suggested that the sulphuric acid was too dilute. The bottle had been marked up as concentrated acid but it was decided that the solution had been made up to the correct concentration for oxygen analysis. Very few oxygen samples were taken on cruise 34A and the deepest was at 600 m so no samples were drawn from the deeper, more stable layers. However some of the values have been compared with data from other cruises in the same area. In fig. 1a the values from station 8 (at 6°N, 142°E) were plotted against Western Equatorial Pacific Ocean Circulation Study (WEPOCS) stations 1, 125, (WEPOCS I) and 97 (WEPOCS II) (at 5°N, 143°E). It can be seen that the oxygen values from station 8 lie within the variability that might be expected from the region. Certainly no systematic error is apparent. Similarly in fig. 1b the values from station 6 (3°N, 132°E) and 7 (3°N, 132.5°E) are compared with Japan Meteorological Agency stations (1986) RY6632 (3°N, 130°E) and RY6643 (3°N, 137°E) (Ryofu-Maru) and again no systematic error is apparent.

One comment from cruise 174 was that the white precipitate present in the oxygen samples did not all dissolve when the sulphuric acid was added. Therefore it seems most likely that the mistake in the concentration of the acid was not noticed. Care must always be taken in preparing all the titration reagents.

5.3 *RRS Discovery* Cruise 181

On *RRS Discovery* cruise 181 (N. E. Atlantic, April 1989) the association with the BOFS program enabled Marine Physics to borrow a semi-automatic titration unit from UCNW, Bangor. This used an automatic burette to deliver the sodium thiosulphate and a photometric cell attached to a chart recorder to indicate the titration end-point.

Dissolved oxygen samples were taken on 57 CTD casts over a period of 4.5 weeks and were drawn by four different people. It appeared that each individual had his own method of drawing samples and the results indicated that these varied in accuracy. Differences were observed in the way the sample bottles were filled, and the technique with which the reagents were added.

Other deviations from the recommended titration procedure were noted:

1. The samples were stored underwater but in daylight for periods up to days long.
2. Sample shaking was not particularly vigorous and in some cases the precipitate was not allowed to settle before titration.
3. The normality of the sodium thiosulphate was measured only once at the beginning of the cruise and no blanks were determined.
4. The sodium thiosulphate bottle in the titration unit was not shaken prior to a batch of titrations.

During the cruise there were problems with the CTD multisampler, rosette and Niskin bottles (see cruise report), so, many of the samples were taken from unknown depths. A combination of salinity, oxygen and temperature data were used to decide what depths the samples were taken from.

A new Beckman Instruments oxygen sensor was installed on the CTD about two weeks into the cruise and the oxygen samples were used to calibrate this. Calibration of individual casts showed that the CTD oxygen sensor was not stable, but also that the samples on some casts were quite inaccurate. The samples had to be rigorously culled before 'averages' for the temperature and pressure constants could be calculated using selected CTD casts. A value for the voltage conversion was chosen to vary monotonically with time. Typical profiles are shown with bottle samples in fig. 2. The samples for each profile were taken by a different person. Part of the data were contoured along a section and this is shown

in fig. 3. The deep water showed a cell-like pattern from which it can be seen that the calibration was still incorrect.

Saunders (1986) demonstrated that the deep waters of the eastern North Atlantic had a remarkably homogenous oxygen content below about 3500 m. Unfortunately this was not appreciated until late in the cruise and the CTD casts went only to 3500 m. However assuming that the water at 3500 m remains homogenous the CTD profiles have been corrected to the average value for the North East Atlantic basin (5.67 ml/l, Saunders, 1986) either by addition or subtraction of the difference from this value. (The average value of the deep oxygen samples was slightly lower than this at 5.58 ml/l + 0.154). The results are contoured in fig. 4 and this shows some improvement in the data below 1200 dbar. Possibly the data above this level could be improved by changing the calibration equation to take into account the rapid changes in temperature.

Cruise 181 was used as an opportunity to compare the Marine Physics titration unit with the alternative UCNW unit. To compare the two units duplicate samples were drawn on eight CTD casts. The initial samples were taken by four different people but the duplicate samples were all drawn by one person using the Marine Physics procedure. A total of 64 samples were analysed on the Marine Physics Unit, using the same chemicals as the UCNW unit. Unfortunately the comparison was complicated by the problems with the UCNW data set which were not appreciated until late in the cruise. They may be summarised as follows:

1. Different sampling techniques achieved very different accuracies, i.e. the UCNW data set was inconsistent.
2. Problems with the CTD equipment meant there was some uncertainty in what the results actually represented.
3. The CTD oxygen sensor was unstable.

Thus there was no consistent data set against which the duplicate samples could be compared. The data from station 11830 were omitted altogether as the UCNW values appeared hopelessly wrong, leaving 54 samples.

Standardisation of sodium thiosulphate proved difficult and only one sensible value was achieved, similarly blank determination caused problems although eventually a reasonable average was obtained. The problem was caused by using a very dilute solution of potassium iodate (provided for BOFS, and of which there was a very limited supply). The rapid volatilisation of the iodine content made it very difficult to titrate by eye. This was not a problem with the UCNW semi-automatic unit. It was appreciated that the absolute value of the oxygen data might be incorrect but it was thought that this would only produce an offset and it was the

scatter between the two data sets that was of interest, as this indicates the randomness introduced by visual determination of the end-point.

A least squares regression between the data derived using the two techniques on the 54 samples gave a line with a gradient a little greater than one, the equation being:

$$y = 1.088x - 0.418$$

the regression coefficient was 0.915, but with the inaccuracies in the UCNW data it is impossible to say how much scatter was from the Marine Physics unit, and how much from the UCNW data.

The standard error of the slope was 0.066 + 0.272, and is shown in fig. 5 as the 95% confidence level. A line of gradient one is within this limit and within the spread of the data. This suggests that the different gradient calculated by the least squares regression is within the scatter of the data.

6. CONCLUSIONS

The preceding discussion reinforces what is repeatedly written ie, that to achieve accurate results it is essential that the greatest care be paid to the details of obtaining good samples. The titration procedure cannot improve the results from poor samples.

Following on from this it is essential to have good CTD sampling equipment. At present Marine Physics needs to renew the CTD multisampler, rosette and sample bottles before good water samples can be obtained. Until this is done there is little point in improving the oxygen titration equipment.

It is also important that the reagents are made up with great care, the Marine Technicians Handbook recommends that all the reagents should be prepared before a cruise. This might cause problems if the cruise were to start from a foreign port, but it might be worth adopting this policy for U. K. cruises.

With a few improvements to sampling technique it should be possible for Marine Physics to achieve 0.1% accuracy with the equipment it already has. The improvements necessary (in order of importance) are:

1. New, more accurate pipettes (these cost £52 each, four are needed, plus disposable tips: £20 for 1000).
2. Improved pipetting technique.

Introduction of the manganous chloride, sodium hydroxide-sodium iodide and sulphuric acid reagents just beneath the surface of the sample.

4. Glass bottles for storage of reagents (these are about £5 each, and six are needed).

When the Marine Physics CTD equipment is improved this should be followed by upgrading the oxygen titration equipment. It was unfortunate that the accuracy of the semi-automatic unit was not demonstrated on Cruise 181 because of poor sampling technique. Nevertheless this system would improve the accuracy and speed of oxygen titration and reduce variability between operators. A microprocessor controlled system would further increase the turn over of dissolved oxygen samples and minimise the possibility of operator error.

The WOCE Implementation period commences in 1990 and the WOCE Hydrographic Program will require large numbers of high precision sample analyses to be made. As IOSDL has a strong commitment to this project, it is important that the Marine Physics oxygen titration equipment and technique is upgraded as far as possible before the start of the Program.

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TABLE 1
Oxygen Bottle Calibration Interpolated W_{18° Values
from Chemical Rubber Handbook Ed. 44 page 1678

	18°	19°	20°	21°	22°
0	1.0024410	1.0026080	1.0027850	1.0029720	1.0031700
.1	1.0024577	1.0026257	1.0028037	1.0029918	1.0031909
.2	1.0024744	1.026434	1.0028224	1.0030116	1.0032118
.3	1.0024911	1.0026611	1.0028411	1.0030314	1.0032327
.4	1.0025078	1.0026788	1.0028598	1.0030512	1.0032536
.5	1.0025245	1.0026965	1.0028785	1.0030710	1.0032745
.6	1.0025412	1.0027142	1.0028972	1.0030908	1.0032954
.7	1.0025579	1.0027319	1.0029159	1.0031106	1.0033163
.8	1.0025746	1.0027496	1.0029346	1.0031304	1.0033372
.9	1.0025913	1.0027673	1.0029533	1.0031502	1.0033581
	23°	24°	25°	26°	27°
0	1.0033790	1.0035970	1.0038250	1.0040630	1.004310
.1	1.0034008	1.0036198	1.0038488	1.0040877	
.2	1.0034226	1.0036426	1.0038726	1.0041124	
.3	1.0034444	1.0036654	1.0038964	1.0041371	
.4	1.0034662	1.0036882	1.0039202	1.0041618	
.5	1.0034880	1.0037110	1.0039440	1.0041865	
.6	1.0035098	1.0037338	1.0039678	1.0042112	
.7	1.0035316	1.0037566	1.0039916	1.0042359	
.8	1.0035534	1.0037794	1.0040154	1.0042606	
.9	1.0035752	1.0038022	1.0040392	1.0042853	

8. APPENDIX I

Beckman Instruments Oxygen Sensor

IOS have incorporated a Beckman Instruments dissolved oxygen sensor into their CTD for many years. The sensor is designed to operate in depths greater than 3000 m, it contains a gold cathode and silver anode with a gelled KC1 electrolyte. It is impermeable to liquids, ions and dissolved solids, but molecular oxygen and water vapour pass through a thin plastic membrane to the gold cathode where an electro-magnetic field of 0.75 volts applied across the electrodes electrochemically reduces oxygen to hydroxyl ions. Simultaneous oxidation of the silver anode to silver chloride establishes a chemical cell where the internal resistance is inversely proportional to the partial pressure of molecular oxygen in the sample water. Current induced in the external circuit is thus proportional to the partial pressure of dissolved oxygen at the external membrane interface. The permeability of the plastic membrane varies exponentially with changes in temperature and hydrostatic pressure and so affects the output current. Although the saturation partial pressure of oxygen in water is independent of salinity a second order effect results from changes in the partial pressure of water vapour which is affected by salinity. A 1% plus correction for salinity effect is required for the most accurate results. When corrected for the effects of temperature, pressure and salinity the polarographic oxygen sensor provides an output which is a function of the samples partial pressure of molecular oxygen. This output is then converted to the concentration of dissolved molecular oxygen by multiplication with the known function of temperature relating solubility of oxygen to temperature for any given partial pressure of molecular oxygen.

The major source of error is depletion of oxygen from the water immediately outside the membrane therefore it is necessary to balance the sensor time constant and the sample flow rate ie, a sensor with a rapid response will consume a relatively large amount of oxygen and therefore require a correspondingly high rate of exchange of sample water. For example a membrane with a 2 second time constant gave a 98% reading at 15 min flow rate. For field use 40 m/s provides essentially full response. Note that velocity dependence is greater at high temperatures because of the large coefficient of the sensor membrane, which results in about 3% per °C increase in oxygen consumption.

Taken from 'An In Situ Molecular Oxygen Profiler - a quantitative evaluation of performance' J. W. VanLandingham & M. W. Greene Mar. Technology Soc. J., Jul-Aug 1971, vol. 5, no. 4

APPENDIX II

RRS Charles Darwin Cruise 42

Dissolved oxygen samples were taken on 16 of 24 CTD casts. Two samples were drawn from each 1.7l Niskin bottle giving a total of 350 samples for analysis by the Winkler titration procedure.

Following a study of the Winkler titration procedure made since *RRS Discovery* cruise 181 various modifications had been made to the Marine Physics procedure for drawing and analysing dissolved oxygen samples. In detail these were:

1. The first batch of chemical reagents were made up at the laboratory before the beginning of the cruise. This was a useful exercise as it was found that the sodium hydroxide pellets were contaminated with carbon (sodium carbonate) making them very difficult to dissolve. A new batch was bought and used, and the old discarded.
2. The bottles were filled with seawater drawn from the ships non-toxic seawater supply at the beginning of the cruise and were always kept full to help reduce the formation of air bubbles on the inside of the bottle while drawing samples. Due to a problem with the ships seawater supply the bottle were only filled about 12 hours before the first set of samples were drawn. The samples from the first station contained a lot of air bubbles when they were titrated. It is not clear whether this was the result of poor sampling technique or oxidisation of particles of rust from the CTD wire strop - which was replaced immediately after the first cast. After this the bottles were kept full of fresh water when the seawater supply was unavailable. The problem with air bubbles did not reoccur.
3. The tygon tubing was soaked in Decon solution several days before the beginning of the cruise, after which it was thoroughly washed and kept soaking in fresh water throughout the cruise. There were no problems with air bubbles.
4. It was difficult to control the flow of water from the Niskin bottles as the inflow of air at the top tap sucked the 'O' ring seal against the air holes. This is presumably a problem with all Niskin bottles of this design. The 'square' taps gave much better flow control because they had no 'O' ring but both bottles with this type of tap tended to leak.
5. The drawing of samples from the Niskin bottles and the addition of reagents were separated into two operations, i.e. first all the samples were drawn, then all the reagents added. This was a simpler operation then drawing one sample then adding the reagents and reduced the risk of contaminating the reagents or the samples.

6. New, positive displacement Labindustries Micropipettor pipettes worked well except that the viscous sodium iodide - sodium hydroxide reagent tended to clog the pipette making the plunger action sticky. Thorough cleaning (of all pipettes) after every batch of sampling or analysis reduced this problem to a minimum. An air displacement type pipette (Gilson Pipetman) had been borrowed and was used for one set of samples for the sodium iodide - sodium hydroxide reagent but it was felt that this was less accurate as not all the 1 ml aliquot of reagent was forced out of the tip. (It was also harder to pick up because the handle was moulded to fit the hand so could only be picked up one way). However, the air displacement pipette had a much better shaped tip - the end being much smaller than that of the positive displacement pipettes. It would be worthwhile investigating the possibility of positive displacement type pipettes with better shaped tips.
7. The bottles used for analysing standards and blanks were stored in Decon solution to keep them clean.

Some bottles were easier to titrate than others because of the colour of the glass. This may be important if photometric end-point determination is to be used.

8. For many of the sample bottles the volume displaced by the bottle top was insufficient to titrate the samples taken on this cruise. It was necessary to add 1 ml of sulphuric acid, between 1.1 - 1.4 ml of sodium thiosulphate plus 0.5 ml of starch. As this would have overfilled the bottle a 1 ml aliquot was carefully removed from the surface without disturbing the precipitate settled in the bottom of the bottle. Thus this water contained no oxygen and while poor practise it was better than losing the redissolved and mixed solution by overflowing, which would reduce the amount of oxygen in the sample.

Many of the bottle tops are chipped or jagged and should be ground down. However this would reduce the volume displaced even more. Buying new sample bottles would have more to recommend it.

The amount of starch added was reduced to 0.3 ml to prevent overflowing the bottle. But this should not have had any effect on the end-point determination.

9. The potassium iodate solution used for standardisation and blank determination was ten times stronger than specified so only one tenth of the recommended volume was used.
10. The importance of stirring the standard or blank solution well enough to dissolve any precipitate before addition of the manganous chloride reagent was demonstrated

during one session. Three sets of blanks had to be analysed before a reasonable figure was produced. After this more care was taken over this procedure to produce more precise results.

11. The three way stopcock caused problems when it failed to produce a seal strong enough to draw the sodium thiosulphate through the pipework. An old spare glass piece still worked and was used. Presumably wear on the teflon key or the glass means that this piece is no longer serviceable. A replacement should be bought if this system is to be used again.

The gas washing bottle head used on the flask of sodium thiosulphate was broken during packing. There is no spare for this, so if the unit is to be used again a replacement must be bought.

12. Excel spreadsheets on an Apple Macintosh SE30 personal computer were used to calculate the dissolved oxygen content. This method proved to be very easy to use and very much quicker than hand calculation.

All of the modifications described above proved quite successful. The difference between duplicates was generally better than 0.01 ml/l, although the average over the cruise was 0.012 ml/l with standard deviation of 0.014 (for 338 samples, the remainder had very much greater differences suggesting errors in the sampling or analysis procedure). This indicated that the accuracy of the measurements was better than 0.2% compared to a possible accuracy of 0.1% for the Winkler titration procedure (Carpenter, 1965).

One major problem of the technique was the amount of time necessary for the sampling and analysis:

Drawing & pickling about 24 samples	1 hour
Standard & blank determination	1.5 hours
Titration of 24 samples	2 hours
Bottle washing, calculations & etc	1 hour

i.e. one CTD cast would generate about 5½ hours work. For two sets of samples to be analysed together (when it was not necessary to do additional standards and blanks) it would take about 9 hours. In other words, two full CTD casts were about all one operator could easily cope with in one day. It was very useful to take duplicate samples from all bottles and is a practise to be recommended continuing with. As, in deep water, four or more CTD casts may be completed in one day it is important to find a faster means of analysis i.e. automation of the procedure.

On all stations on *RRS Charles Darwin* cruise 42 at least two Niskin bottles were fired at each sampling depth but the difference between the two sets of samples was much greater, and varied more, than the duplicates drawn from one bottle. At station 001 all the bottles were fired at the same depth and the results varied by 0.5 ml/l between bottles, see Fig. 6. On the second cast the first ten bottles were fired at the same depth and the differences between the bottles showed the same pattern as on station 001. After this various improvements were made to the bottles (new 'O' rings, lanyards, taps & etc) and measurements after this improved. However the difference between the bottles over the cruise averaged to 0.04 ml/l with a standard deviation of 0.07 (for 83 pairs of bottles). Further improvements could still be made to the bottles and it seems clear that the Niskin bottles have been a major cause of 'poor' oxygen samples in the past.

Other possible causes of error include the sampling technique, the calibration of the volume of the sample bottles and the burette used for the sodium thiosulphate.

As the samples taken from the same Niskin bottles were generally within 0.012 ml/l it would appear that there was no great error in the sampling technique. But there were some 'odd' values where the duplicates differed by up to 0.5 ml/l for no obvious reason. It is possible that this was the result of poor sampling.

The burette used for dispensing the sodium thiosulphate titre measured to 1 μ l, equivalent to approximately 0.005 ml/l of dissolved oxygen. The sample bottles were calibrated to 0.1 ml volume also equivalent to approximately 0.005 ml/l of dissolved oxygen. Both burette and bottles are old and while the burette would produce a consistent error for all the samples, any error in the calibration of the bottles would cause differences between duplicate samples.

CTD stations 002 - 006 were all in the Charlie Gibbs Fracture Zone between 51.8 - 52.8°N, 35°W. Both deep and shallow samples had consistent and reasonable values and for comparison they were plotted against TTO data (stations 123 & 124 at 51.7°N, 33.7°W, and 53.25°N, 36.7°W respectively) see fig. 7. This showed a difference between the deep values of approximately 0.1 ml/l (5 μ m/kg) and there are several possible reasons for this:

1. If the calibration of the burette was in error, as discussed above, it would produce a consistent offset in the titration values. However, for as much as 0.1 ml/l it would need to be inaccurate by as much as 20 μ l.
2. If the titre is added quickly to the solution it is possible to obtain a lower value than if it were added slowly because the end point sometimes appears to 'creep' with time (e.g. about 30-60 seconds). Again, it would require the addition of 20 μ l of titre which

is a relatively large amount (about 8% of the total volume). Automatic titration and end-point detection would overcome this problem.

3. The cold, deep overflow water is only about 1-2 years old and may still carry the signature of the year of origin i.e. some years the water may be more oxygenated than others. Hence the difference between the TTO data and that from cruise 42 is quite valid.

Data from the CTD stations in the Faeroe Bank Channel were compared with TTO stations 142 and 141 (61.3°N, 8°W and 58.6°N, 11.5°W respectively), see fig. 8. The deep values, between -1° - 0°C had the same difference of 0.1 ml/l (5µm/kg) as the Charlie Gibbs Fracture Zone. (The TTO values were lower). The surface values were more scattered and no consistent difference is discernible.

In summary, the Marine Physics equipment provided precise and consistent results on *RRS Charles Darwin* cruise 42. But further modifications could yet be made to improve these results:

1. New tips for positive displacement pipettes.
2. New sample bottles.
3. Calibration/replacement of burette and glassware.
4. New Niskin bottles.
5. Automation of the titration procedure.

While item 3 is essential if this unit is to be used again the last two are the most important for improving the sample data and reducing the load on the operator.

Fig. 1a Cruise 34A vs W.E.P.O.C.S. Oxygen data

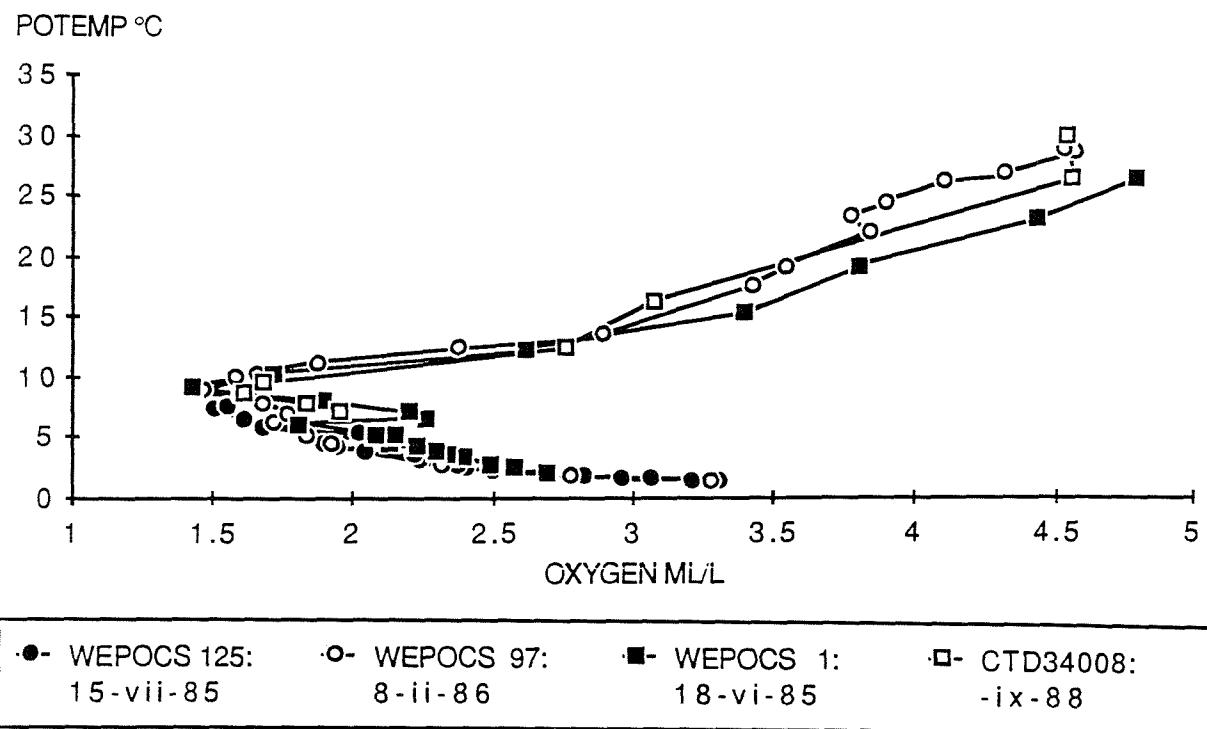


Fig. 1b Cruise 34A vs J.M.A. Oxygen data

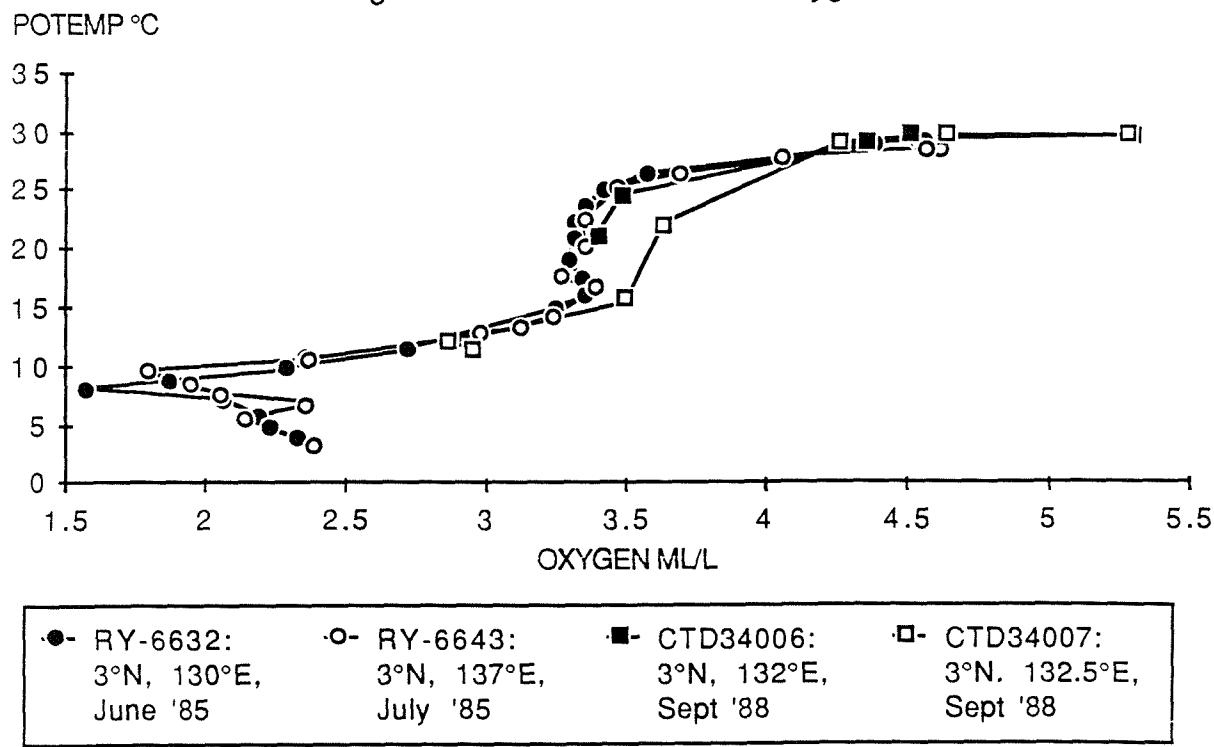
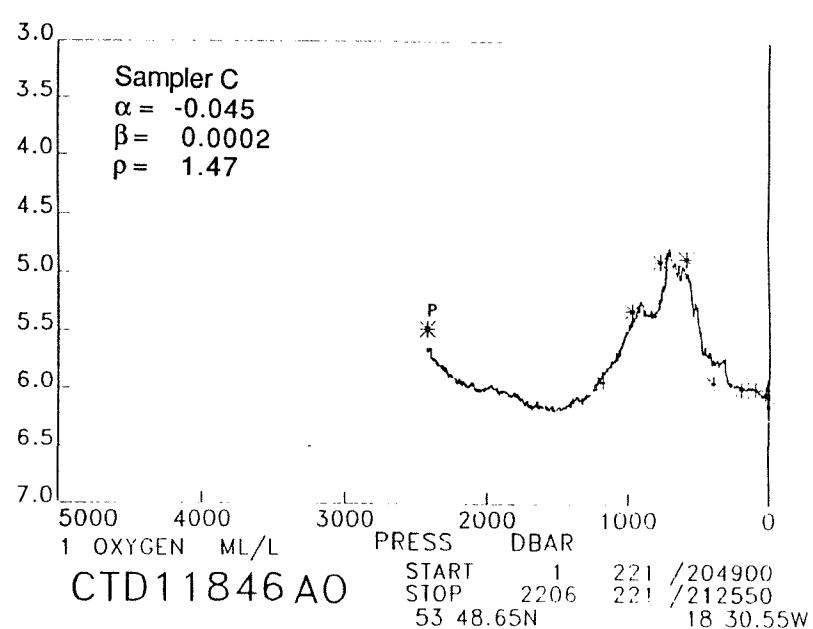
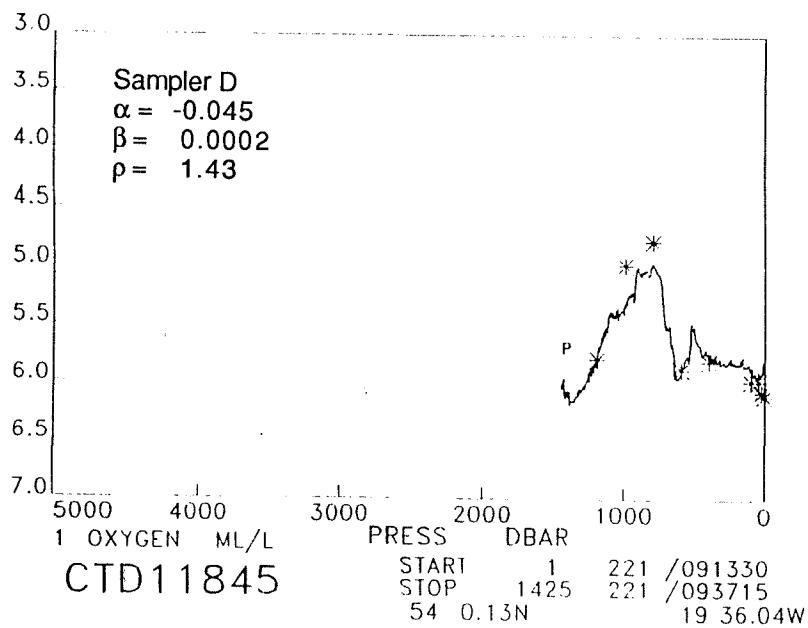
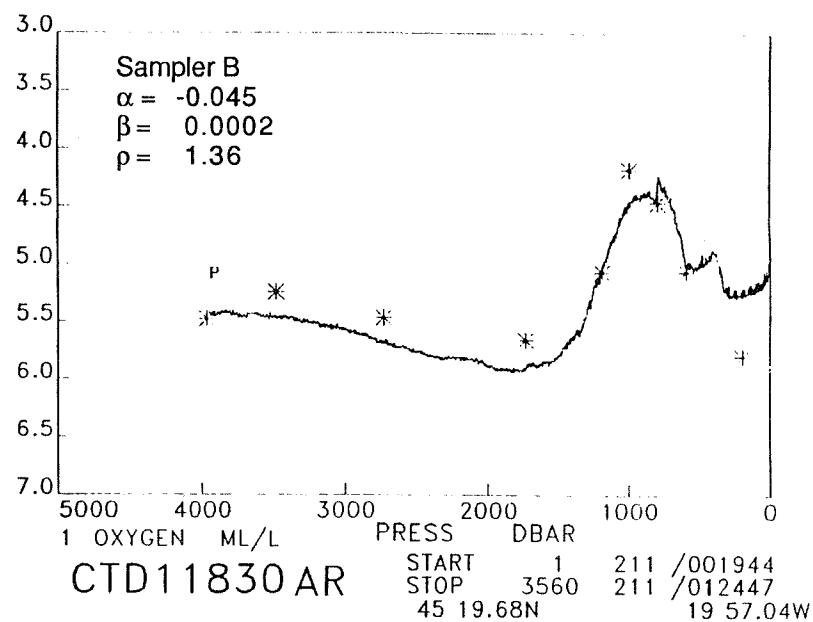
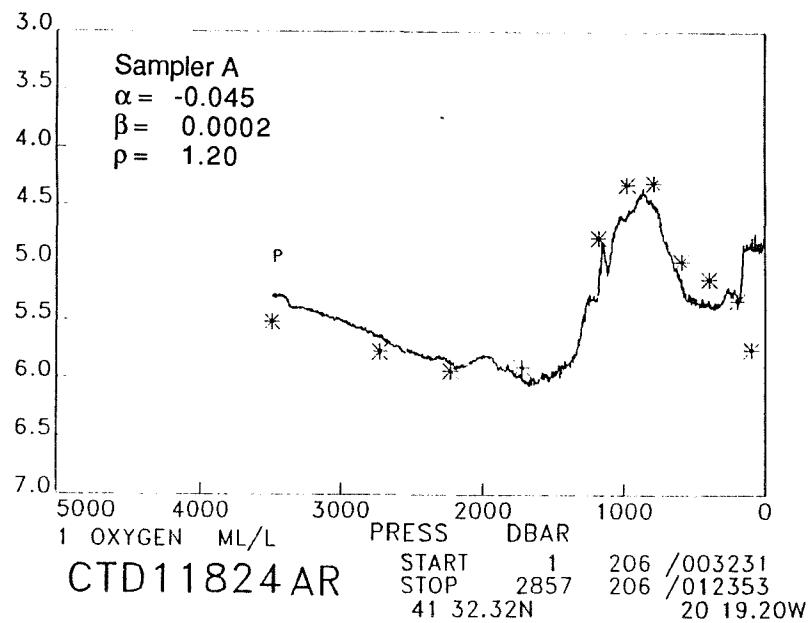


Fig. 2 CTD Oxygen profiles showing bottle sample values



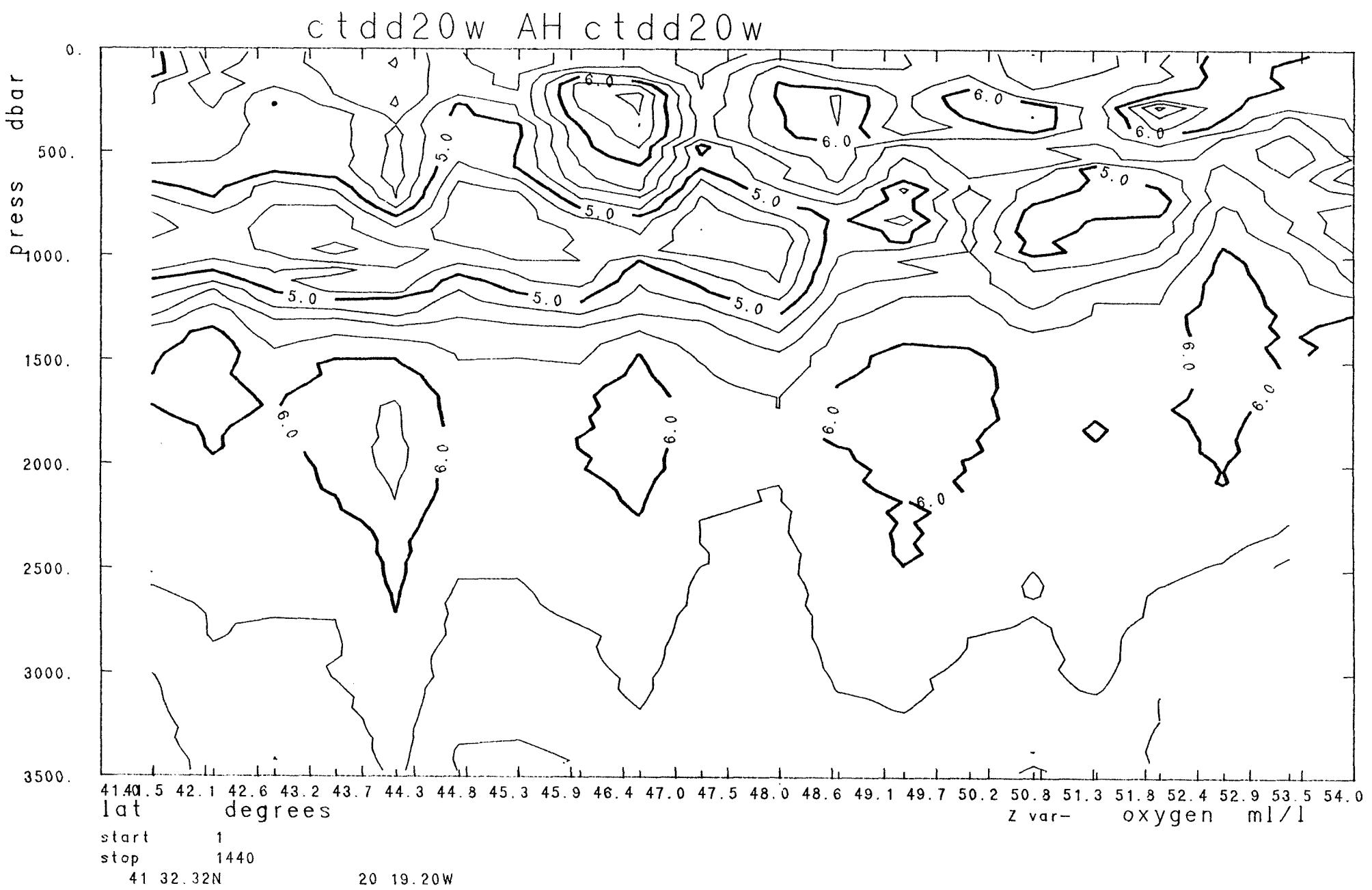


Fig. 3 CTD Oxygen Section along 20°W from Discovery cruise 181

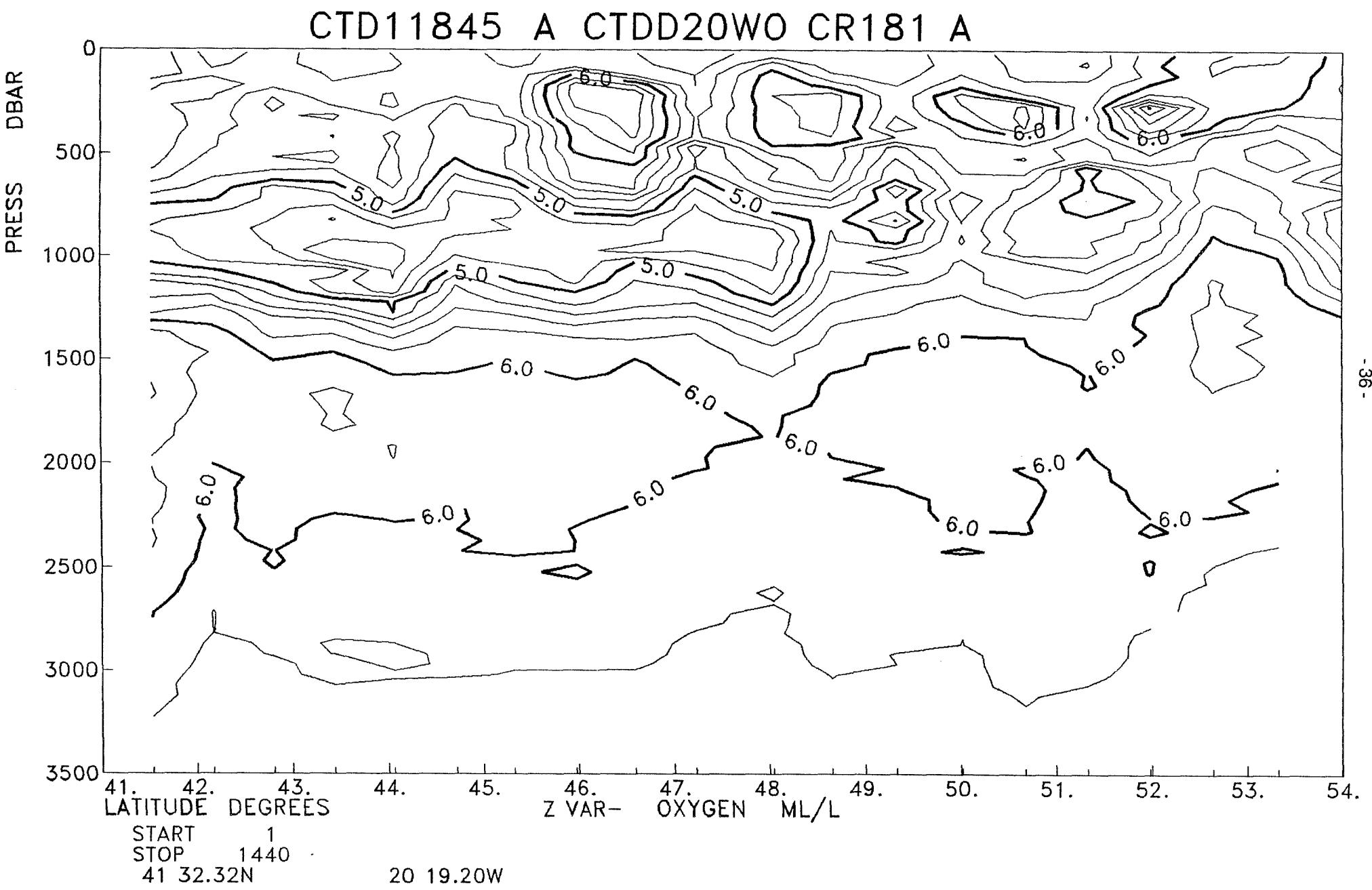


Fig. 4 CTD Oxygen Section along 20°W after correction of deep values

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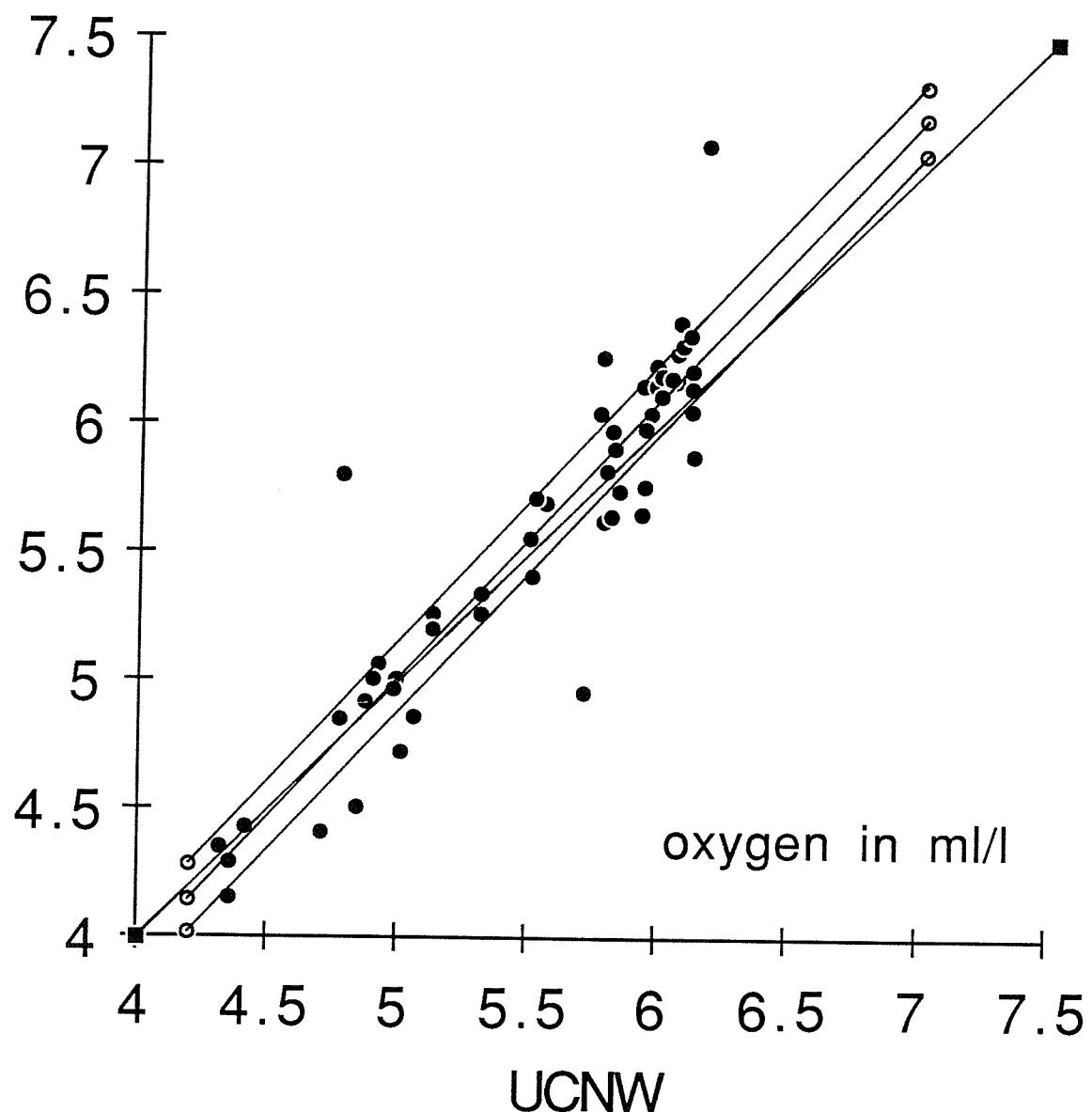


Fig 5. Comparison of titration units

Fig. 6 Comparison of Niskin Bottles fired at the same depth.

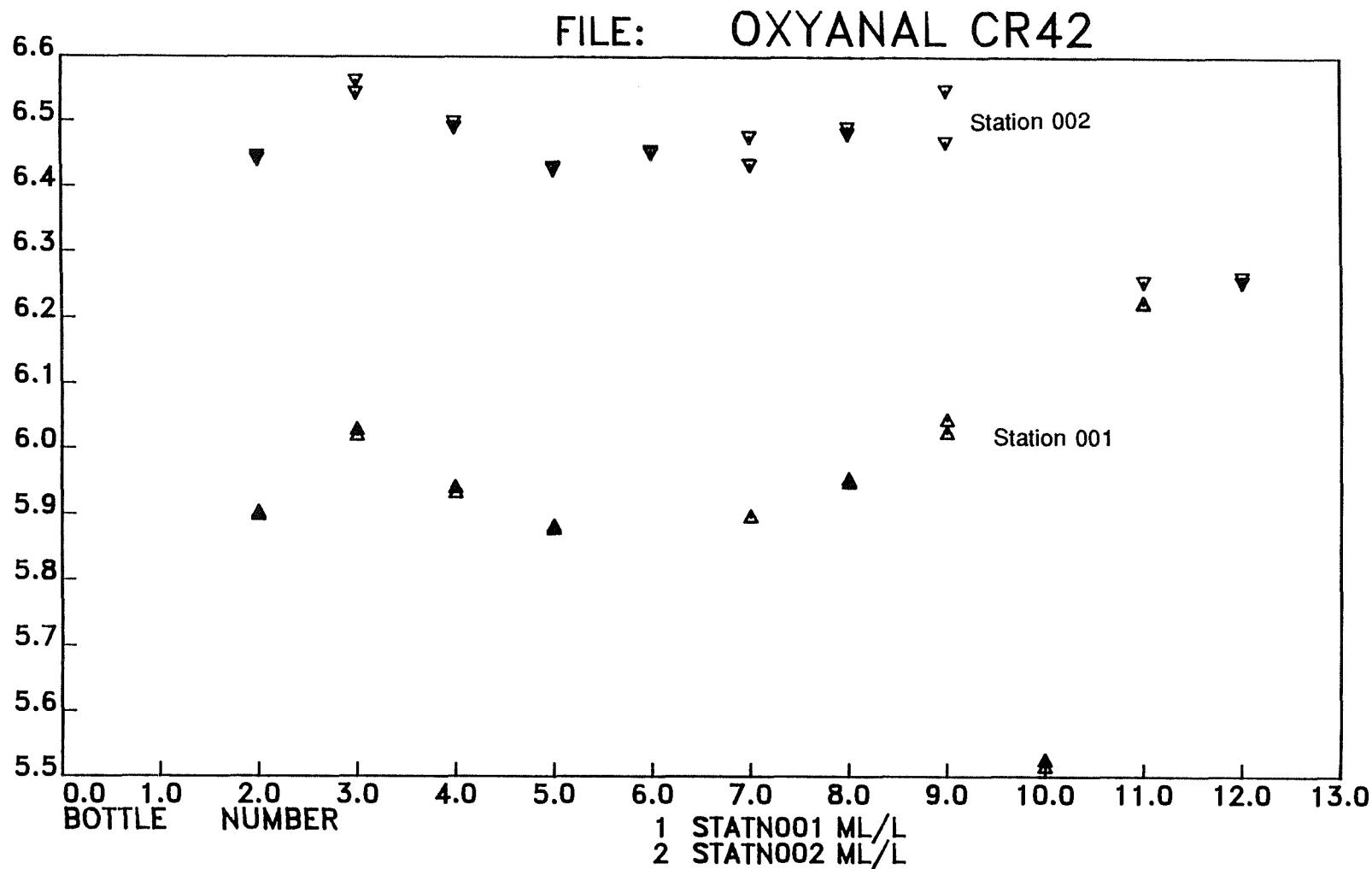
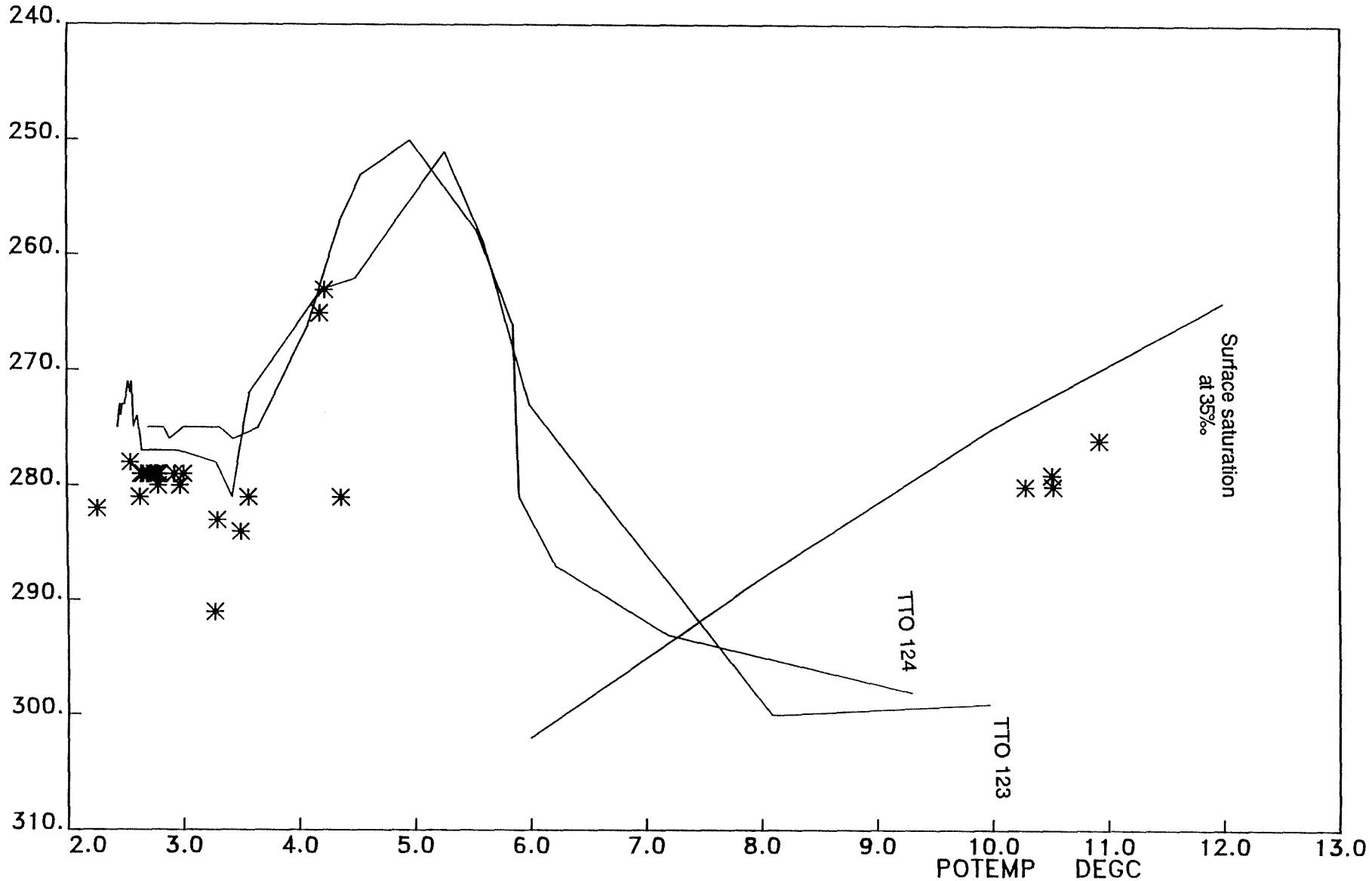


Fig. 7 Comparison of TTO stations 123 & 124 with cruise 42 Charlie-Gibbs Fracture Zone oxygen samples.



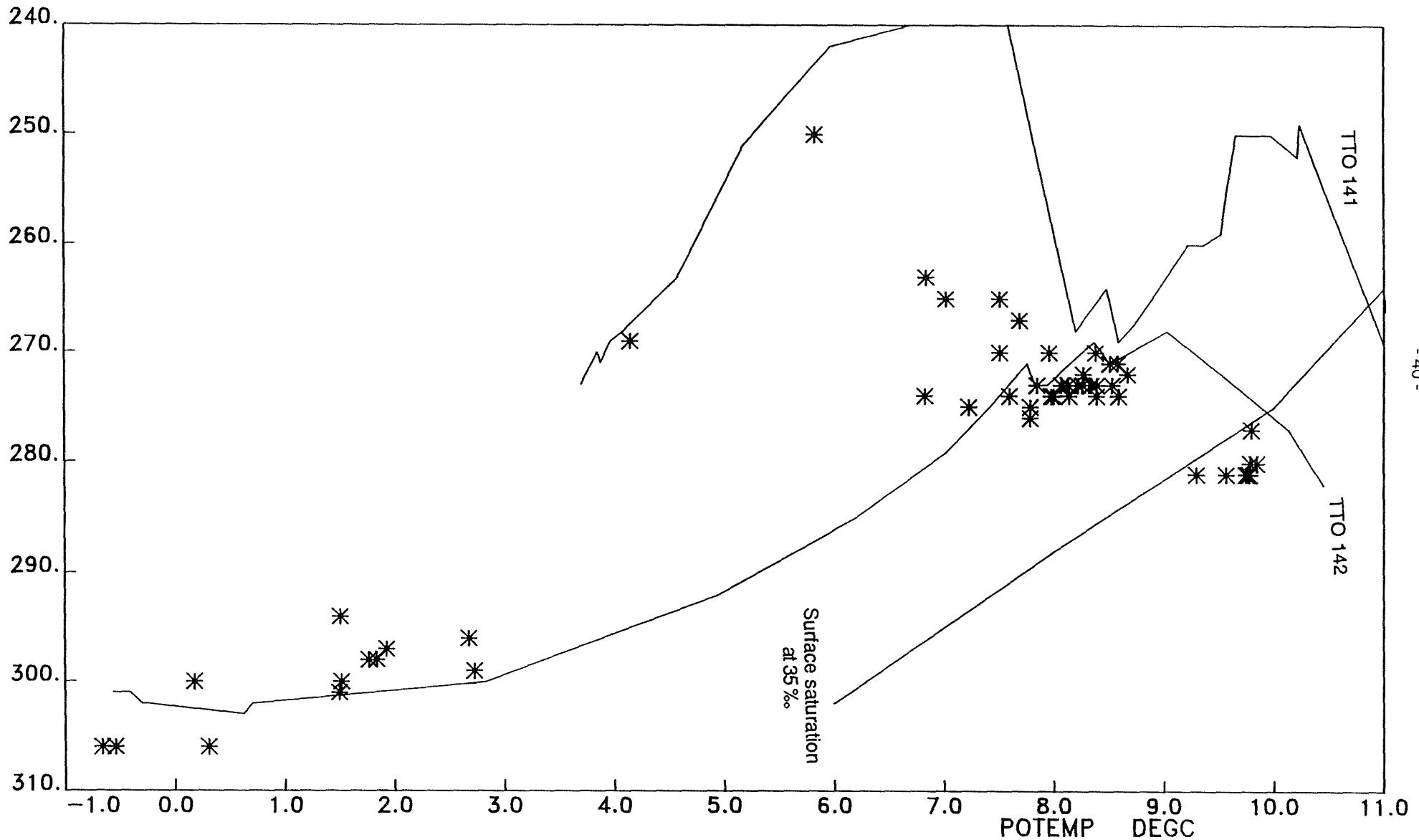


Fig. 8
Comparison of TTO stations 141 & 142 with cruise 42
Faeroe Bank Channel oxygen samples.

