

There are five things that I would like to address from the Technical Note (hereafter simply TN) of Lankhorst et.al. In addressing these points there are 3 important references that are conspicuous by their absence in this TN: Strickland & Parsons "Manual of Seawater Analysis (hereafter S&P), an article by Lou Codispotti (hereafter LC), and an Oxygen Manual published in 1971 (hereafter OM1971). In the course of my comments these references will be cited as they have considerable bearing on the contents of this TN.

1.. How soon after collection should a pickled oxygen sample be titrated using sodium thiosulfate?

After the addition of the pickling reagents to a sample: manganous and alkaline iodide solutions, and the resulting precipitate has been disbursed through the solution twice, S&P make the following comment: (Note b), page 22. " (b) The sample can be allowed to stand indefinitely at this stage provided thermal contraction does not draw air into the bottle."

So it is very clear, 40 + years before the submission of this TN, that once pickled, samples could sit indefinitely before titration without deleterious effects. However, as was pointed out in the TN, to prevent the introduction of air into a bottle after shaking, DI water was added to the top of the flask or bottle. This has been the practice at Scripps Institution of Oceanography (SIO) for some years.

2.. Can the acid reagent ( $H_2SO_4$ ) be added to a flask after the precipitate has settled the second time in the oxygen flask, the stopper be returned to the flask, and the flasks properly stored and analyzed with thiosulfate at some future date.

This technique was addressed directly by LC and indirectly by S&P. Lou indicates that this procedure can be used without deleterious effects provided certain conditions are met. Both LC and S&P list a number of potential problems with this procedure including: a) after the addition of the sulfuric acid and re-stoppering the bottle or flask, no air should be trapped in the bottle; b) iodine solutions in the bottles or flasks are subject to photo-degradation so titration flasks must be kept out of direct sunlight; c) as was pointed out above and in this TN, the area above and around the stopper must be kept full of DI water to prevent air being drawn into the flask; d) and quoting from Lou, "Occasionally after the addition of sulfuric acid, a gas bubble will appear. This bubble is composed largely of carbon dioxide and a little nitrogen which may have been liberated from the solution. The former results from the chemical reaction of the acid and carbonates. The presence of the nitrogen is accounted for by the reduced solubility of this gas upon the addition in electrolytes of the reagents and the possible increased temperature of the sample." If acid is added to the flask and re-stoppered and careful notes aren't provided by the collector to the analyst, the presence of a bubble at the time of analysis may or may not indicate air contamination, perhaps from an air bubble trapped during the re-stoppering of the flask. Lastly e) if the water sample contains much organic matter this may be slowly oxidized by the iodine. And S&P add, It is therefore advisable, not to delay the titration once the acid has been added. So it is clear 25 and more years ago that although this technique could be used without serious consequences, it was best not to do this. Based on the years I have carried out this analysis with many many technicians, I would not recommend this technique for general use. In short, there was no reason to have conducted this test on this cruise.

3.. As to the feasibility of collecting oxygen samples at sea and analyzing them ashore, most of the sampling and subsequent analyses were designed to address this point. Since this was the main thrust of this TN, the experimental design could have been so much better. In the case of the few samples drawn on the New Horizon cruise, the immediate titration of the samples was not performed either at

sea or within the time frame that could be inferred from the manual by Langdon (2010) cited in this TN. Langdon suggested that the first set of titrations be done no sooner than a few hours, and Dickson (1996) and many of the sea-going oxygen manuals not cited indicate that titrations be done soon thereafter. Contrary to the TN, it is not "...standard practice..." to wait "...a few days..." before commencing the analyses. In general this is not practical; much more will be said about this later.

The samples drawn and subsequently analyzed from the Melville cruise came close to satisfying the requirements of a "best" experiment. However, since different equipment and personnel were used to analyze the samples at sea and ashore, it may be fortuitous that the values agree as well as they do. However, the excellent agreement between the two sets of data may say something about the accuracy of the Winkler technique as it is used today. Neither of these questions can be addressed adequately by this data set.

There are other things not mentioned in this TN which would have been helpful in thinking about the data from the two cruises e.g., what size Niskin bottle was used for the sample collection. A number of oxygen samples can be taken from a 10 liter Niskin, regardless of the oxygen concentration, without sacrificing sample quality. This assumes that 5 or more liters isn't removed from the Niskin before oxygen samples are drawn. Unless 5 or more liters were removed initially, there was no reason all samples taken at a particular depth couldn't have been drawn from the same Niskin, thus eliminating one variable. On the NH, up to 3 samples were taken, but it wasn't clear if two of the three came from one Niskin while the first sample came from a different Niskin or what. Since sample collection and standardization are probably the two factors that contribute most to imprecision and inaccuracy the experience of the sample drawer is very relevant.

The biggest problem I have with the premise that oxygen samples can be drawn and pickled at sea and transported to shore for subsequent analysis, is that this is just not reasonable or practical for major expeditions such as a CLIVAR cruise during which 4000 plus samples might be taken and analyzed. At \$35 per flask, we are talking about ~\$150,000 just to purchase flasks. Then there would be the costs of shipping containers and the shipping to and from a vessel. Would there be room to store all of these flasks on the ship? Keeping the area around the flask stopper filled with solution would also have to be addressed not just during the cruise but the return shipment.

Collection, storage and analysis ashore could be done if sample bottles were loaded and offloaded in one's home port at the beginning and end of a short cruise. Also sampling would be limited to the flasks available. Since this generally isn't a reasonable option, those who were asked how long a sample could be stored may have replied as they did because storing samples, as suggested by the TN, was never considered as either a "best" or viable technique.

4.. How do the results from the oxygen analyses compare with the specifications provided by manufacturers for various sensors?

The specifications for most oxygen sensors are less exacting than what most principal investigators would tolerate for discrete bottle measurements, so one must be careful suggesting that what is appropriate for sensor calibration would be acceptable for all data users. Also, I would hate to think that an inexperienced investigator would decide from this TN that a single calibration of an instrument, only available after a cruise, would be acceptable without some other method of monitoring sensor data quality during the cruise.

5.. How do the oxygen data differences compare with the quality indicators attributed to Dickson (1996)

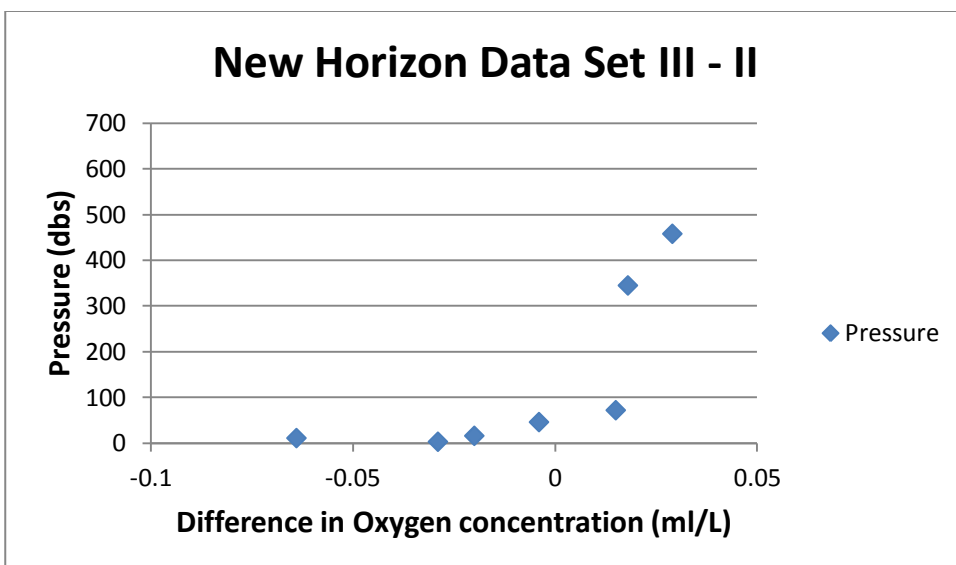
In the technician's manual of 1971 one can find the following data:

Operator	data	stddev
1	6.423	0.056
2	6.423	0.005
3	6.419	0.005
4	6.419	0.008
5	6.427	0.005

A series of oxygen flasks were filled from a 20 liter pail of surface seawater. The flasks were filled by siphoning. The samples were pickled with the pickling reagents. Each operator was given a random assortment of the 20 flasks and titrated 4 samples. The stoppers were removed, acid added, and the titrations completed. The averages above are for 4 samples. Operator 1 had never titrated oxygen samples before and did not titrate samples on this cruise. This operator was provided minimal instruction and the manual (OM1971).

These analyses were done by titration using the visual starch end point which although still used by some today has been replaced by alternate methods of end point detection including the amperometric technique of Langdon (2010)- cited in this paper, and the photometric end point used eg., by the chemists of the Oceanographic Data Facility at SIO. With the exception of one operator that had never done titrations before, the standard deviations were better than the precision specified by Dickson (1996) of 0.011 ml/L and mentioned in this paper. This clearly shows that bottle calibration and operator error do not have to contribute significantly to the imprecision of these analyses. I also believe overall accuracy is significantly better than the 0.046ml/L specified by Dickson (1996) largely because of improvements in sampling technique, standards used, standard preparation, and end point detection.

There was one question raised in this paper that has adequately been addressed by both LC and S&P. It has to do with the comments on page 2453, line 12, regarding a negative bias of some of the comparisons. Clearly this could be the result of degradation of the iodine by organic matter which would be more apparent in near surface than deep water samples. The plot that follows of the New Horizon Data, runs III minus II, excluding two points, shows this trend clearly. This plot of depth (pressure) versus oxygen concentration differences shows the trend, a trend that would be impossible to see in Figure 1 of the TN. Plots similar to this would have made the presentation of the existing data, as limited as it is, much clearer.



Two other very minor things:

- 1.. page 2451, line 19, "...none were treated..." should be corrected to none was treated.
- 2.. In this TN (page 2449, line 26) and many other papers and manuals on seawater oxygen analysis, the flask recommended for use by Carpenter (1965b) for the whole bottle titration is simply referred to as an Erlenmeyer flask. However, it is more elaborate than this. In most of the scientific supply catalogs these modified nominal 125 ml flasks have a listing that would include:

PYREX™ Iodine Determination Flasks with # 22 Barrelhead Stopper. The stopper projects above the liquid seal trough to facilitate removal of the stopper (Fisher Scientific on-line web site).

#### References cited in these comments:

**Anderson, G. C., compiler, 1971. "Oxygen Analysis," Marine Technician's Handbook, SIO Ref. No. 71-8, Sea Grant Pub. No. 9. There have been many updates and improvements to this manual since it was published more than 40 years ago. It was one of the earliest manuals with the details of the whole bottle titration as detailed by Carpenter in 1965b. Carpenter's 1965 paper is cited in this TN.**

**Codispoti, Louis (Lou) April 1988, "One Man's Advice on the Determination of Dissolved Oxygen in Seawater, an on-line document**

**Strickland, John D., and T.R. Parsons, 1972, "A practical handbook of seawater analysis", Second Edition, Bulletin. 167. Fisheries Research Board of Canada, 310 pages.**

**In 1960, John D. Strickland, of Scripps Institution of Oceanography, published "A Manual of Sea Water analysis." This was updated and revised several times and in 1972 was published as "A practical handbook of Seawater Analysis with Strickland and T.R. Parsons as authors.**

**There are many other seagoing oxygen manuals available, that could have been cited, that could have added to the background information found in this TN.**