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## Precision and accuracy of dissolved oxygen measurements. A comment on the paper by Oudot et al. 1988: Precise shipboard determination of dissolved oxygen (Winkler procedure) for productivity studies with a commercial system

In the last decades, the determination of dissolved oxygen in seawater has been improved on the one hand by minimizing all sources of physical and chemical errors in the procedure (Carpenter 1965; Green and Carritt 1966; Carritt and Carpenter 1966) and on the other hand by replacing visual detection of end points by optical or electrochemical means (*see* bibliography of Oudot et al. 1988). Fully automated titra-

tion procedures of the acidified samples were developed (Oudot et al. 1988), further reducing the human factor. Dissolved oxygen measurements must be made not only with precision, however, but also with accuracy. Oudot et al. (1988) take into account only the precision of the determination.

Through their proposed titration procedure, transfer of the iodine solution is not avoided. Any transfer either by pipetting or pouring is recognized as a main source of inaccuracy for dissolved oxygen determinations (Carpenter 1965; Green and Carritt 1966; Carritt and Carpenter 1966). Errors

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Table 1. Comparison of dissolved oxygen measurements with a no-transfer or a transfer procedure. Reagents used: A—Strickland and Parsons 1972; B—as in A but saturated with KI; C—Carritt and Carpenter 1966.

1—Comparison of no-transfer and transfer procedures with the same sampling bottle. For each water, two titrations are carried out on the same sample contained in a 280-ml, calibrated oxygen bottle: one on a 100-ml aliquot pipetted with a high-precision glass pipette, the other on the remaining solution. The second titration began not more than 3 min after pipetting the 100-ml aliquot. The thiosulfate solution was 0.01 N and the end point was visually detected with starch indicator.

2—Repeatability of measurements with the whole-bottle procedure. Paired samples in two kinds of bottles: 280 ml (bottle 1) and 115 ml (bottle 2).

Method	Paired samples (No.)	Mean O <sub>2</sub> (ml liter <sup>-1</sup> ± s)		Relative mean difference (D %)	SD on D	Computed paired- <i>t</i>	Critical <i>t</i> at 0.005 level
1—Same bottle		No transfer	Transfer				
A	17	6.407±0.155	6.305±0.154	1.58	0.50	13	2.92
B	9	5.711±0.037	5.688±0.043	0.40	0.26	4.5	3.36
C	7	6.017±0.022	5.986±0.028	0.53	0.26	5.3	3.71
2—No transfer		Bottle 1	Bottle 2				
C	13	6.515±0.064	6.517±0.069	-0.03	0.13	—	—

come from iodine volatilization, as illustrated by the results of comparative determinations on different waters, each with and without transfer (Table 1).

First, these results show that, in all cases, the procedure with transfer induces figures lower than the no-transfer procedure by an average of 0.4–1.5% depending on the reagents used. Second, they show that the magnitude of the discrepancy is lowered when reagents are saturated with iodide, i.e. when iodine is in the I<sub>3</sub><sup>-</sup> complex form to a greater extent. The paired-sample *t*-test indicates that the differences between the two procedures are highly significant, even with the optimized reagents of Carritt and Carpenter (1966). Third, in addition to the decrease of accuracy, the procedure with transfer lowers the precision. This is corroborated by the repeatability experiment of the whole-bottle procedure applied to analyses of paired samples in two kinds of bottles. The variability of the paired-samples differences in this case was compared with the variability of the paired-samples differences with and without transfer (all analyzed by the method of Carritt and Carpenter 1966). The *F*-test shows a significant difference between the variances at a level of 0.05 (*F* = 3.9, although critical *F* = 3.0). This variability originates from the difficulty of repeating, from sample to sample, exactly the same pipetting conditions.

The repeatability experiment also shows the high degree of precision of dissolved

oxygen determination, even with a fully manual method and the old, visual, starch end-point detection. These results, which are derived from strict application of the procedure described by Carritt and Carpenter (1966), give a standard deviation of 0.006 ml liter<sup>-1</sup>, i.e. a relative SD of 0.1%. This is in very good agreement with the precision of the no-transfer procedure found by previous workers. The slight loss of precision between iodine standards and natural samples found by Oudot et al. is also explained by sample transfer. Their rather good precision probably arises from a reproducible pipetting operation. Nevertheless, they could expect an increase of precision with a no-transfer procedure, which will undoubtedly also increase accuracy. As the no-transfer procedure is now widely used (Bryan et al. 1976; Levy et al. 1977; Nimura 1983; Aminot 1983), it is surprising that Oudot et al. (1988) have proposed a procedure that does not take this improvement into account.

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