



# **A modified method for the determination of chemical oxygen demand in sea water**

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## **ABSTRACT**

A modified method for the determination of the chemical oxygen demand in sea water is presented in this paper. The proposed method differs from the alternate method for low COD samples described in the 17th edition of the Standard Methods for the Examination of Water and Wastewater in that it employs a pretreatment step resulting in complete halides removal from the sea water sample. Complete removal of halides is realised by adding 3 g silver sulphate per 30 ml sea water sample in a 50 ml erlenmeyer flask and mixing for 60- 90 min (when a fade lilac colour appears) followed by settling of the precipitates formed for 5-10 min with the flask in a 40 ° inclined position and finally taking slowly and with care the volume of the cleared sea water required for the COD test with a volumetric pipette.

## **INTRODUCTION**

The chemical oxygen demand of a sample is used as a measure of the oxygen equivalent of the part of the organic matter oxidised by a strong chemical oxidant under defined experimental conditions. Potassium permanganate and potassium dichromate are the oxidizing agents used in chemical oxygen demand determinations. The oxygen equivalent of potassium permanganate consumed in such a chemical oxidation is defined as 'oxidizability' or permanganate value and the oxygen equivalent for the case of potassium dichromate is defined as 'chemical oxygen demand (COD)'. The permanganate value test was developed by Forchamer in 1849 [1] but today the dichromate reflux method [2] is considered as the more appropriate choice for a wide range of samples mainly because of its superior oxidizing ability and also because it is considered as a method of good reproducibility for daily practice carried out by simple laboratory equipment. The prevailing problem in COD determinations is



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that the values obtained may also reflect some of the oxidizable inorganic ions in the sample giving afterward inaccurate impression for the concentration of the the organic matter. The dichromate method is the best choice for waste water and highly polluted surface waters and the permanganate method may be the first choice for unpolluted waters and especially , under alkaline conditions, for the high salinity sea water.

Since the purpose of the determination is to record only the oxidizable organic substances, the influence of the oxidizable inorganic substances has to be excluded. Potassium permanganate has an oxidizing effect on many organic and a number of inorganic substances under acidic, neutral and alkaline conditions. Chloride concentrations over 300 mg/ l affect the analysis under acidic conditions and at higher chloride concentrations the determination must be carried out under alkaline conditions [3]. It must be noted that the potassium permanganate method is suitable for determining the oxidizability of all water samples which have a potassium permanganate consumption of at least 1 mg/ l ( oxygen equivalent 0.25 mg/ l ). The potassium dichromate method is not recommended in the Standard Methods for the examination of Water and Wastewater for samples containing over 2000 mg/ l chlorides.

The low concentration of organic matter and the high salinity of sea water are the two main factors which make any results obtained by using the dichromate reflux method questionable. The alternate procedure for low COD samples given in the 17th edition of Standard Methods [2] is recommended to determine COD values from 5 to 50 mg/l. COD values in clean sea water are expected below 5 mg/ l and as chloride concentrations are about 20000 mg/ l the alternate procedure for low COD samples is not satisfactory. COD Data obtained by the potassium dichromate alternate procedure for low COD would be important in sea water pollution monitoring studies if the interferences from halides could be completely excluded and these data could be considered at least as rough indicative figures for the pollution level of the sea water. Purpose of this paper is to present a modified method for the determination of COD values in sea water after complete removal of halides in an effort to exclude this major source of interfering inorganic ions.

### MATERIALS AND METHODS

Sea water from the Patraikos Gulf was used for the tests carried out in this work. Removal of the halides from the sea water samples prior to COD determinations was performed by using silver sulphate. The halogen ions chloride and bromide form precipitates with low solubility products with silver ions. Silver sulphate was preferred to highly soluble silver nitrate because it is used as a catalyst in the COD test and so its presence in the samples is acceptable. The usual laboratory equipment for COD determinations with the open reflux method as described in the Standard Methods [2] had also been used. In the halides removal step laboratory magnetic stirrers and 50 ml erlenmeyer flasks were employed.

Table 1. COD measurements in the initial studies

No of sample	Type of sample			
	Standard solution (A)	Standard solution (B)	Diluted influent (C)	Diluted effluent (D)
	Measured COD , mg/l			
1	6.4	1.9	4.2	2.7
2	4.9	1.7	3.5	3.0
3	3.8	2.9	3.6	2.1
4	5.6	2.7	2.9	2.6
5	5.9	1.4	3.9	3.0
6	4.3	2.7	4.0	2.1
7	6.0	1.7	2.9	3.5
8	4.3	3.1	3.7	3.1
9	6.7	4.1	2.0	2.5
10	4.0	3.1	3.4	3.7

## EXPERIMENTAL STUDY AND RESULTS

Salinity of the sea water samples was about 38‰ and chlorinity about 21‰ so the chloride equivalent amount in the sea water studied was about 0.021 g/ ml and the stoichiometric quantity of the silver sulphate required for complete halides removal was about 0.093 g/ ml. A slight excess of silver sulphate was used (0.007 g/ ml over the computed stoichiometric requirement). This dose of silver sulphate (1 g/ 10 ml) is enough for salinity levels in sea water up to 40‰.

30 ml of sea water were placed in a 50 ml erlenmeyer flask and after that 3.0 g of silver sulphate were added. The flask was positioned on the plate of a magnetic stirrer and a small magnetic rod was put inside the flask. Mixing was performed at room temperature and after a period of mixing ranging for 60 to 90 min in the different samples studied the initially white precipitate was turned to a fade lilac mixed coloured precipitate. At this point mixing was stopped and the flask was taken from the magnetic stirrer and put in a 40 ° inclined position on a suitable inclined supporting frame. Sedimentation of the coloured precipitate was very quick and 20 ml of the cleared sea water were taken carefully from the upper end of the flask bottom after a rest period of 5-10 min. After that the 20 ml of the cleared sea water were used for the COD determination with the alternate low COD method as it is described in the 17th edition of the Standard Methods [2] with the difference that the sample volume was 20 ml, the added reagent quantities were for 20 ml sample volume and 0.0125 M (instead of 0.025 M) ferrous ammonium sulphate titrant was used.



Table 2. COD measurements in the final studies

No of sample	Type of sample				
	Sea water	50% sea water+50% stand. A	50% sea water+50% stand. B	50% sea water+50% waste C	50% sea water+50% waste D
	Measured COD, mg/ l				
1	1.9	2.7	1.9	2.0	1.8
2	2.0	3.3	2.9	3.1	3.5
3	2.3	3.6	1.1	2.7	1.9
4	0.9	4.1	3.0	4.1	3.6
5	1.0	3.8	2.1	1.9	1.7
6	1.2	1.9	4.2	5.2	1.8
7	1.9	2.4	1.3	2.1	4.6
8	3.2	2.9	3.7	2.6	1.4
9	2.6	3.6	1.9	1.9	1.5
10	0.0	1.9	2.1	1.6	2.7
11	0.4				
12	2.8				
13	2.0				
14	1.9				
15	2.3				
16	2.5				
17	2.1				
18	3.9				
19	1.2				
20	1.9				

Two series of COD studies with standard COD solutions, raw and treated wastewater and sea water were performed for the purposes of this investigation. The initial studies with standard COD solutions and normal waste water were the following : (a) The first study was to determine the COD of a standard potassium hydrogen phthalate solution with a theoretical COD value of 5 mg/ l (Standard A). (b) In the second study the COD of a standard potassium hydrogen phthalate solution with theoretical COD value 2 mg/ l (Standard B) was determined . (c) In the third study the influent and effluent from the Patras University Campus Wastewater Treatment Plant were used in the COD determinations. An influent volume with a mean COD value of 375 mg/ l (determined with the open reflux method for high COD in 5 samples taken from this waste volume) was diluted 100 times with distilled water and this diluted waste (Waste C) was used for COD determinations with the alternate method for low COD. Also an effluent volume from the Patras University Campus Wastewater



treatment Plant with a mean COD value of 32 mg/l (determined with the alternate method for low COD in 10 samples) was diluted 10 times with distilled water and this diluted effluent (Waste D) was also used for COD determinations with the alternate method for low COD. The results of the above initial COD studies are given in Table 1.

The final studies with sea water were the following: (a) In the first of the final studies a volume of sea water was taken from the Patraikos Gulf and COD values were determined in 20 samples taken from this volume with the proposed modified method for the determination of COD in sea water. (b) In the second study 10 ml of sea water after complete halides removal were mixed with 10 ml of standard potassium hydrogen phthalate solution with the theoretical COD value of 5 mg/l (Standard A) and the COD of the combined volume of 20 ml was determined. Ten parallel samples were prepared and measured in this study. (c) In the third study the COD of ten parallel samples each consisting of 10 ml of sea water after complete halides removal and 10 ml of a potassium hydrogen phthalate solution having a theoretical COD value of 2 mg/l (Standard B) was measured. (d) In the fourth study ten parallel samples of 50% by volume sea water after complete halides removal and 50% of the diluted influent used in the initial studies (Waste C) as well as 10 parallel samples of 50% by volume sea water after complete halides and 50% of the diluted effluent used in the initial studies (Waste D) were used in the COD determinations with the alternate method for low COD. The sea water as well as the influent and effluent waste from the Patras University Campus Wastewater Treatment Plant were preserved in a deep freeze room (- 20 °C ). The results of these final studies are also given in Table 2.

## DISCUSSION

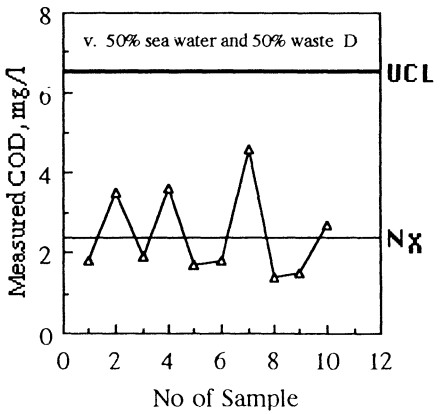
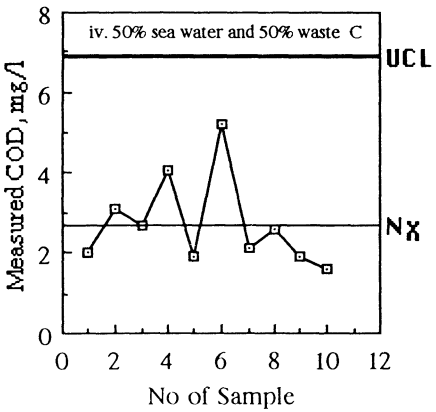
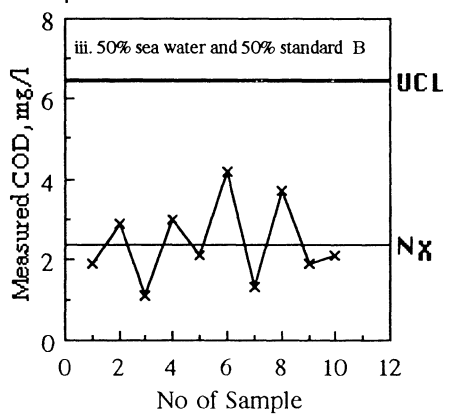
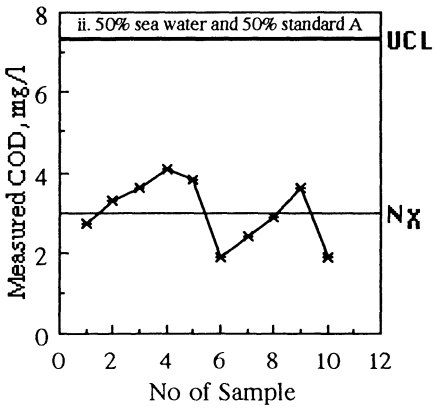
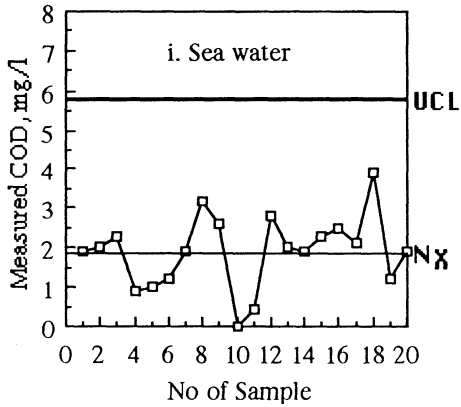
Extreme care was exercised in the determinations of COD with the alternate procedure for low COD samples in order to avoid errors imposed by trace impurities in the glassware used and in the laboratory environment. The results given in Table 1 show that determinations with this procedure are nearly reliable (for the samples studied) even in the range of COD values 2 to 5 mg/l which are below the lower limit of 5 mg/l recommended in the 17th edition of the Standard Methods [2]. It must be noted here that the concentration of chlorides in all the samples measured in the initial studies was well below 10 mg/l.

The proposed (in the present work) modified method for COD determination in sea water differs from the alternate procedure for low COD samples (given in the 17th edition of the Standard Methods) only in that a sample pretreatment step for complete removal of halides from the sea water is included in the proposed method.

Average concentrations of halides in sea water are 19353 mg/kg for chlorides, 67.3 mg/kg for bromides, 1.3 mg/kg for fluoride and 0.6 mg/kg for iodine [4]. The halogen ions chloride and bromide, which are the more



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abundant in sea water, form precipitates with low solubility products with silver ions. The negative logarithms of the solubility products are [5] :  $pK(\text{AgCl})=9.81$  and  $pK(\text{AgBr})=12.11$ . The concentration of chlorides in sea water is much higher (about 288 times) than the concentration of bromides and so bromides precipitation follows that of chlorides. After the addition of the silver sulphate to the sea water sample mixing for 60-90 min was found to be required for complete precipitation of chlorides and bromides. The end of mixing was set to the point of the appearance of a fade lilac colouration and after sedimentation for 5-10 min the concentrations of both chlorides and bromides in the cleared sea water were measured and were found well below 10 mg/l.

The results given in Table 2 as well as in the in the control charts in Figure 1 show that interferences from halides in the COD determination of sea water were complete avoided with the pretreatment step employed. It must be noted that the pretreatment step removes some suspended matter as well as some colloids from sea water and so the organic content of the sample appears lower in the cleared sea water. The proposed modified method could be considered as more accurate for the determination of soluble COD in sea water but in any case it also may be considered as a method that gives reliable figures for the level of COD in sea water as in most of the cases suspended and colloidal organic matter represents the smaller portion of total organics.

## REFERENCES

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