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Evaluation of COD Determination by ISO, 6060 Method, Comparing with Standard Method (5220, B)

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Abstract: Chemical Oxygen Demand (COD) is an important parameter in water-pollution control analysis. COD often is used as a measurement of pollutants in wastewater and natural waters. The objective of this research was to compare the standard method (open reflux method) and ISO, 6060 method in COD measurement of standard solutions and water and wastewater samples. Solutions of KHP (Potassium hydrogen phthalate) with a theoretical COD of 500 and 1000 mg O_2L^{-1} were used as stock standards. The COD values of standard solutions were determined by the standard method and ISO 6060 (1989) method. After comparison between two method results showed that there is significant difference ($p < 0.05$) only for two concentration (ThOD= 100,400 mg L^{-1}). Both ISO 6060 method and standard method (open reflux method, 5220B) were used to determine the COD values of a variety of water and wastewater samples. Based on average of data from twice measurement, they showed agreeable results which obtained from both methods.

Key words: COD, ISO 6060 method, standard method, water, waste water

INTRODUCTION

Chemical Oxygen Demand (COD) is an important parameter in defining water, domestic and industrial wastewater pollution by organic compounds[1,2]. COD is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions[3]. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence[3]. Because of its unique chemical properties, the dichromate ion ($Cr_2O_7^{-2}$) is the specified oxidant in Methods 5220, C and D[3].

Values obtained depend severely on the experimental conditions especially with the use of permanganate. Because Cr (VI) oxidizes almost all organic compounds in 50% sulfuric acid medium and give reproducible COD values, method with dichromate is widely used today[1]. In most of the water and wastewater chemical laboratories the COD analysis is done by the Standard Methods which consumes more chemical agents. The objective of this research was to compare the Standard Method (open reflux method) and ISO 6060 Method in COD measurements of different concentrations of standard solutions for water and wastewater samples.

MATERIALS AND METHODS

This research has been conducted in late 2004. The wastewater examinations were done by synthetic solutions and then followed by raw wastewater from different industries. This research was done in the environmental chemistry of School of Public Health. Standard solutions have been chosen as to cover different concentrations in water and wastewater (river water, domestic wastewater with COD the range of weak, medium and strength and industrial wastewater). Also, used raw water and wastewater samples in different concentrations for evaluation of two methods. It should be noted that high concentration samples (COD>700 mg L^{-1}) have been diluted.

Experimental (Open Reflux Method, 5220 B): COD determination was carried out according to the Standard Method[3].

Experimental (ISO 6060 Method):
Apparatus: Usual laboratory equipment and Reflux apparatus, heating mantle, hotplate or other heating devices, precision burette and boiling aids.

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Reagents and material:

a) Sulfuric acid C $(H_2SO_4) = 4\ \mu\ L^{-1}$. Add to about 500 mL of water, 220 mL of sulfuric acid, $(\rho = 1.84\ g\ mL^{-1})$ in portions and with caution. Allow to cool and dilute to 1000 mL.

b) Silver sulfate_ sulfuric acid. Add 10 g of silver sulfate (Ag_2SO_4) to 35 mL of water. Add in portions 965 mL of sulfuric acid $(\rho = 1.84\ g\ mL^{-1})$. Allow 1 or 2 days for dissolution. The dissolution is enhanced by stirring.

c) Potassium dichromate, standard reference solution, $c\ (K_2Cr_2O_7) = 0.040\ \mu\ L^{-1}$, containing mercury salt. Dissolve 80 g of mercury (II) sulfate $(HgSO_4)$ in 800 mL of water. Add, with caution, 100 mL of sulfuric acid $(\rho = 1.84\ g\ mL^{-1})$. Allow to cool and dissolve 11.768 g of Potassium dichromate, dried at 105°C for 2 h, in the solution. Transfer the solution quantitatively to a volumetric flask and dilute to 1000 mL. The solution is stable for at least 1 month. Note: If so desired, the dichromate solution may be prepared without the mercury (II) sulfate to the test portion before the addition of the dichromate solution (c solution) in 8.1 and mix thoroughly.

d) Ammonium iron (II) sulfate, standard volumetric solutions, $c\ [(NH_3)_2\ Fe\ (SO_4)_2.\ 6H_2O] \sim 0.12\ \mu\ L^{-1}$. Dissolve 47.0 g ammonium iron (II) sulfate hexahydrate in water. Add 20 mL of sulfuric acid $(\rho = 1.84\ g\ mL^{-1})$. Cool and dilute with water to 1,000 mL.

This solution shall be standardized daily as follow:
Dilute 10,0 mL of potassium dichromate solution (c solution) to about 100 mL with sulfuric acid (a. solution). Titrate this solution with the ammonium iron (II) sulfate to be standardized, using 2 or 3 drops of ferroin (f. solution) as indicator.

The concentration, c, expressed in moles per liter, of the ammonium iron (II) is given by the expression.

$$\frac{10.0 \times 0.040 \times 6}{V} = \frac{2.4}{V}$$

Where, V is the volume, in milliliters, of ammonium iron (II) sulfate consumed.

e) Potassium hydrogen phthalate, standard reference solution, $c\ (KC_8H_5O_4) = 2,0824\ \mu\ L^{-1}$.
Dissolve 0, 4251 g of potassium hydrogen phthalate, dried at 105°C, in water and dilute to 1000 mL.
The solution has a theoretical COD value of 500 mg L^{-1}. This solution is stable for at least 1 week if stored at approximately 4°C.

f) Ferroin, indicator solution. Dissolve 0,7 g of iron (II) sulfate heptahydrate $(FeSO_4.7H_2O)$ or 1 g of ammonium iron (II) sulfate hexahydrate, $[(NH_4)_2\ Fe\ (SO_4)_2.\ 6H_2O]$ in water. Add 1, 50 g of 1,10-phenanthroline monohydrate $C_{12}H_6N_2.H_2O$ and shake until dissolved. Dilute to 100 mL. This solution is stable for several months if stored in the dark. It is commercially available.

Procedure: Transfer 10.0 mL of the sample (diluted if required) to the reaction flask and add 5.00 mL±0.01 mL of the potassium dichromate solution. Add a few boiling aids to the test portion (always 10 mL) and mix well.

Slowly add 15 mL of silver sulfate- sulfuric acid and immediately attach the flask to the condenser. Bring the reaction mixture to boiling within 10 min and continue boiling for another 110 min. The temperature of the reaction mixture should be 148°C±3°C. Cool the flask immediately in cold water to about 60°C and rinse the condenser with a small volume of water. Remove the condenser and dilute the reaction mixture to about 75 mL and cool it to room temperature. Titrate the excess dichromate with ammonium iron (II) sulfate using 1 or 2 drops of ferroin as indicator.

Calculation: The chemical oxygen demand, COD, expressed in milligrams of oxygen per liter, is given by the expression:

$$\frac{8000\ C(V_1 - V_2)}{V_0}$$

Where:

C : The concentration, in moles per liter, of the ammonium iron (II) sulfate

V_0 : The volume, in milliliters, of the test portion before dilution (if any)

V_1 : The volume, in milliliters, of ammonium iron (II) sulfate used in the titration against the blank

V_2 : The volume, in milliliters, of ammonium iron (II) sulfate used in the titration against the test portion

8000 : The molar mass, in milligrams per liter, of ½ O_2

Give the result to the nearest milligram per liter. Values below 30 mg L^{-1} shall be reported as < 30 mg L^{-1}[4].

Sample preparation: A solution of KHP (potassium hydrogen phthalate) with a theoretical of 500 mg $O_2\ L^{-1}$ as stock standards. Appropriate dilutions gave standard solutions of different COD values. The concentration of which were 10, 25, 45, 50, 100, 100, 150, 200, 400, 500, 600, 700 and 900 mg O_2L^{-1}.

RESULTS AND DISCUSSION

The COD values of various standard solutions prepared with KHP were determined by the ISO 6060 method and standard method (open reflux method, 5220 B). Average of data from twice measurement on the various standard solutions is given in Table 1.

Compare of results between two method showed that there is significant difference ($p<0.05$) only for two concentration (ThOD = 100,400 mg L^{-1}).Therefore ISO 6060 method can be a proper alternative in measurement of COD considering relative simplicity, lower laboratory cost and applicability in measuring lower COD concentration, down to 10 mg L^{-1}.

Both ISO 6060 method and the Standard Method (open reflux method, 5220B) were used to determine the

COD values of a variety of water samples, which included river water, domestic wastewater, hospital wastewater and the wastewater from food industry. Average of data from twice measurement listed in Table 2 that show the results obtained by both methods are agreeable. About 40 different laboratories analyzed some samples at the level of COD = 500 mg L^{-1} by ISO method. The standard deviation was 20 mg L^{-1} for a potassium hydrogenphthalate solution and 25 mg L^{-1} for an industrial effluent from a pulp and paper mill. At the level of 50 mg L^{-1} the standard deviation was about 10 mg L^{-1} for a similar effluent[4]. In another study two samples of industrial effluent were analyzed by 32 laboratories. The COD levels were at 140 and 160 mg L^{-1}, respectively and the standard deviation between laboratories was near 14 mg L^{-1} for both samples[4]. The results of this research confirmed results of last researches.

Table 1: COD determination of various KHP standard solutions by the ISO 6060 method and standard method

ISO 6060 method			Standard method (open reflux method)	
ThOD (mg L^{-1})	COD (mg L^{-1})[a]	CV (%)[b]	COD (mg L^{-1})[a]	CV (%)[b]
10	9.12±00.77	8.44	-	-
25	23.45±00.49	2.09	23.80±0.28	1.18
45	42.98±00.70	1.63	44.60±0.85	1.90
50	47.90±00.42	0.88	51.00±1.41	2.78
100	97.79±00.97	0.99	101.60±0.57	0.56
150	144.60±02.55	1.76	150.00±0.00	0.00
200	196.49±01.87	0.95	201.80±0.28	0.14
400	397.99±00.83	0.20	403.20±1.13	0.28
500	505.30±01.56	0.31	510.60±4.52	0.89
600	593.72±19.62	3.30	605.35±2.48	0.41
700	720.99±16.00	2.22	704.95±0.92	0.13
900	-	-	904.60±1.41	0.16

Table 2: COD values for real water and wastewater samples

ISO 6060 method			Standard method (open reflux method)	
Sample type	COD (mg L^{-1})[a]	CV (%)[b]	COD (mg L^{-1})[a]	CV (%)[b]
River water	17±0.7	4.12	19±0.2	1.05
Food wastewater	57±0.3	0.53	64±0.7	1.09
Hospital wastewater	242±0.6	0.25	236±0.3	0.13
Domestic wastewater	412±0.4	0.09	419±0.6	0.14
Landfill leachate	12468±0.8	0.006	12511±0.3	0.002

[a]=Mean±SD,   [b]=Coefficient of Variance (CV=σ/x × 100)

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