

# Chemical Oxygen Demand Using Closed Microwave Digestion System

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A new approach to determine the chemical oxygen demand (COD) using a closed microwave digestion (CMD) system to replace the conventional, time-consuming open reflux (OR) method is proposed. The procedure uses a laboratory-grade closed microwave digestion system (one magnetron) for the digestion of small volume of samples (3.0 mL) in a completely closed (90 mL) Teflon vessel, digesting 10 samples at a time in the range of COD values of 5–1000 mg L<sup>-1</sup>. The digestion time required is 15 min as compared to the 2 h required for the conventional OR method. Chloride ion interference can be removed up to 6000 mg of Cl<sup>-</sup> ions L<sup>-1</sup> as compared to the 2000 mg of Cl<sup>-</sup> ions L<sup>-1</sup> removed by conventional OR method. The present work reveals that the filtration of effluent samples by membrane filter or homogenization is not essential to obtain reproducible results. The proposed method is cost-effective; saves time, energy, and reagents with providing precise results for both the pure organic compounds and wastewater samples; and is ecofriendly.

## Introduction

Chemical oxygen demand (COD) is widely used as an important parameter for understanding the pollutional strength of water and wastewater. The conventional method envisages the oxidation of organic matter present in water and wastewater by using one of the strong oxidizing agents such as potassium dichromate, ceric sulfate, potassium iodate, potassium permanganate, etc. (1–5). The method measures the organic contamination of aquatic samples, and sensitivity depends on the type of oxidant used and the method of digestion carried out for oxidation of the carbonous matter. However, potassium dichromate has been found to be the most suitable oxidizing agent since it is capable of oxidizing the carbonous matter completely to carbon dioxide and water. In this method, the oxidation of the sample is carried out by the open reflux (OR) procedure, which is suitable for a wide range of samples wherein a large sample volume is required and is also time-consuming (approximately 2–2.5 h). This procedure has a few limitations, namely: (i) the method error is 10–20% with high precision; (ii) reduction in oxidation potential; (iii) volatilization of organics; (iv) high consumption of pure reagents and therefore high blank values; and (v) contamination from external sources to some extent.

The closed reflux (CR) COD method is considered as the standard method in the United States and Taiwan. As

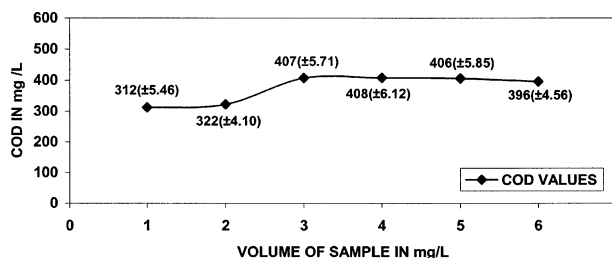


FIGURE 1. Optimization of sample volume using KHP having COD of 400 mg L<sup>-1</sup> as a standard solution for the CMD method.

TABLE 1. Minimum and Maximum COD Determination by CMD Method

no.	vol of standard KHP (mg L <sup>-1</sup> )	COD (mg L <sup>-1</sup> ) <sup>a</sup>	recovery (%)	CV (%) <sup>b</sup>
1	005	004 ± 1(5)	80	25.0
2	010	012 ± 3(5)	120	25.0
3	025	024 ± 2(4)	96	8.33
4	050	051 ± 4(5)	102	7.84
5	100	098 ± 5(5)	98	5.10
6	150	157 ± 6(4)	104	3.82
7	200	200 ± 4(3)	100	2.00
8	250	252 ± 4(5)	100	1.58
9	300	307 ± 4(6)	102	1.30
10	350	976 ± 6(5)	100	1.98
11	400	409 ± 5(5)	102	1.22
12	450	467 ± 15(5)	103	1.07
13	500	518 ± 7(5)	103	1.35
14	550	558 ± 2(4)	101	0.35
15	600	612 ± 4(4)	102	0.65
16	650	652 ± 4(5)	100	0.61
17	700	714 ± 9(7)	102	1.26
18	750	760 ± 4(5)	101	0.52
19	800	816 ± 4(3)	102	0.49
20	850	862 ± 3(5)	101	0.34
21	900	906 ± 5(5)	100	0.55
22	950	946 ± 9(5)	99	0.95
23	1000	976 ± 6(5)	97	0.61

<sup>a</sup> Mean ± SD (*n*), where *n* is the number of observations. <sup>b</sup> Coefficient of variance.

compared to the Japanese (Mn COD) method, the method used in the United States has a higher detection limit but has severe interferences due to chloride ions. By reducing the quantity of reagents, the CR spectrophotometric method has been prescribed (Standard Method 5220 C) (6), which is more economical in the use of metallic salt reagents and generates smaller quantities of hazardous waste with lesser requirement of reagents. However, these methods also require more time (approximately 2 h) and homogenization of samples containing suspended solids to obtain reproducible results.

In view of these drawbacks in the COD determination discussed above, attempts were made to evaluate other suitable methods. The closed microwave-assisted wet digestion procedure is one of the powerful technique known for the rapid digestion (oxidation and reduction) of various compounds (7). Microwave-assisted pretreatment of environmental samples offered a considerable advantage of both speed and consumption of reagents (8). The focused microwave technology can be used to accelerate the oxidation of the organic products, and some inorganic salts in water by potassium dichromate are reported in the literature (9–13). The long refluxing period of the classical method could be decreased, up to 60 times, using the microwave digestion procedure (14). Chen et al. (15) have attempted to use a

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TABLE 2. COD Determination of Various KHP as a Standard Solution by the OR and CMD Method

no.	theoretical COD using KHP (mg L <sup>-1</sup> ) (a)	determination of COD (mg L <sup>-1</sup> ) by		ratio		CV (%)	
		OR method (b) <sup>a</sup>	CMD method (m) <sup>a</sup>	b/a	m/a	OR method <sup>b</sup>	CMD method <sup>b</sup>
1	0	nd <sup>c</sup>	3 ± 1.09(6)	nd	d		36.00
2	5	nd	5 ± 1.48(8)	nd	1.0		28.19
3	25	16 ± 3.16(5)	24 ± 2(4)	0.64	0.96	19.75	8.33
4	50	36 ± 3.26(4)	51 ± 4(5)	0.72	1.02	9.05	7.84
5	100	82 ± 2.82(6)	98 ± 5(5)	0.82	0.98	3.43	5.10
6	500	420 ± 9.05(5)	518 ± 7(5)	0.84	1.03	2.15	1.35
7	800	680 ± 9.36(6)	816 ± 4(5)	0.83	1.02	1.41	0.49
8	900	756 ± 8.48(6)	906 ± 5(5)	0.84	1.00	1.12	0.55
9	1000	840 ± 13.62(6)	976 ± 6(5)	0.84	0.97	1.62	0.61

<sup>a</sup> Mean ± SD(n), where n is the no. of observations. <sup>b</sup> Coefficient of variance. <sup>c</sup> nd, not detectable. <sup>d</sup> Infinite.

TABLE 3. COD Determination of Pure Organic Compounds by OR and CMD Method<sup>a</sup>

no.	compound	theoretical COD (mg L <sup>-1</sup> )	COD by		% deviation from theoretical value by	
			OR method	CMD method	OR method	CMD method
1	glucose	1066*	1061*	1065*	0.46	0.00
2	KHP	1136	1132	1136	0.35	0.00
3	oxalic acid	126	120	126	4.76	0.00
4	cane sugar	1128	1120	1128	0.70	0.00
5	citric acid	685	688	689	0.43	0.58
6	starch**	1185	446	768	62.36	35.18
7	maltose	1066	1056	1058	0.94	0.75
8	glycerol	1216	1200	1207	1.315	0.74

<sup>a</sup> Key: \*, mean of 6 values; \*\*, soluble part.

microwave-assisted digestion system (Microdigest 3.6 Pro-labo Corp, France having six magnetron power) to quantify the COD load in aquatic samples. The system used by them had six individual magnetrons focusing microwave radiation to six individual samples. Wilson and Jarbus (16) have used an industrial microwave system (700 W, turnable, commercial microwave oven) for the digestion of aquatic samples for quantification of COD load. However, the digestion procedure suggested by these workers is costly and energy-consuming.

The objectives of this study are to develop the rapid and accurate method for higher recoveries of COD load in wastewater samples with higher elimination of chloride ion interferences using a closed microwave digestion (CMD) procedure. The results obtained by the closed microwave digestion procedure have been obtained by an open reflux method (Standard Method 5220 B) (6).

## Experimental Section

**Microwave Digestion System.** A laboratory-grade CMD system (ETHOS-900 Microwave Laboratory Systems, Italy) was used for digestion of samples. The system has a provision to digest 10 samples at a time. The system works with only one magnetron, which can focus the microwave radiation to each sample added in the transparent Teflon (tetrafluoromethylene or TFM) vessels (90 mL capacity) having high mechanical strength to sustain high pressure and temperature (435 psi, 300 °C). All digestion vessels in microwave digestion rotors (MDR) are protected by a patented reclosing (vent and reseal) relief valve mechanism. The digestion system is connected to a high-performance acid base scrubber module to avoid dangerous fumes, which are neutralized before being discharged into the atmosphere.

**Reagents.** All the reagents used were of analytical reagent (AR) grade and prepared as per the standard procedure,

described in the standard method for the OR method using double-distilled water throughout the analysis.

**Standards.** A standard solution of potassium hydrogen phthalate (KHP) with a theoretical COD value of 1000 mg L<sup>-1</sup> was used as a stock solution throughout the work. Wastewater samples were collected from various industries, and samples were preserved below 4 °C.

**OR COD Determination Method.** Standards having different concentrations and wastewater samples collected from various industries were divided in two batches, and the COD load was measured for the first batch by OR method using 20 mL of sample volume as per the standard method. The standards and samples of the second batch were preserved in the laboratory for digestion by the proposed microwave digestion procedure.

**Proposed Microwave Digestion Procedure.** The samples and standards preserved in the second batch were processed by the newly developed procedure. Instead of 20 mL sample volume, only 3 mL of sample was taken in TFM vessels; reagents were added in proportionate amount {0.06 mg of mercuric sulfate, 1.5 mL (0.250 N) of potassium dichromate, 4.5 mL (16 N) of concentrated sulfuric acid, and 0.05 mg of silver sulfate} as suggested for the OR method to determine the COD load (Standard Method 2550 B) (6). The total volume in all the TFM vessels was 9 mL. The samples were exposed to microwaves for a total optimum period of 15 min at various watts in the range of 0–600 W. After digestion, samples were transferred into a volumetric flask. Excess potassium dichromate in digested samples was titrated with standard ferrous ammonium sulfate (FAS) using ferroin (1,10-phenanthroline) as an indicator.

## Results and Discussion

**Optimization of Digestion Time.** To optimize the digestion time for proposed method, samples were digested for various intervals of time, in the range of 3–20 min. The total optimum time required for complete digestion was found to be 15 min. As per Chen et al. (15) and Wilson and Jarbas (16), optimum time for digestion of COD was found to be 8–9 min for samples having 1000 mg L<sup>-1</sup> of COD for a small quantity of samples. The difference in time of digestion may be attributed to the difference between the microwave systems used and the number of samples digested at a time in the present work. According to Kingston and Jassie (9), the microwave power and heating time strictly depends on the number of samples being digested simultaneously; however, the present work reveals that, with the ordinary microwave system usually available in the laboratory, one can digest 8–10 samples at a time in a period of 15 min for variety of industrial effluents.

**Optimization of the Sample Volume.** To develop the procedure for CMD method, the total volume of the reaction mixture in the TFM vessel was a major issue and essentially needed to be investigated. During the digestion, sample

**TABLE 4. Recoveries in COD Values with Spike Test in Different Wastewater Samples**

no.	different wastewater	CMD method				OR method			
		COD (mg L <sup>-1</sup> )			recovery (%)	COD (mg L <sup>-1</sup> )			recovery (%)
		initial <sup>a</sup>	added	found		initial <sup>a</sup>	added	found	
1	domestic sewage	274 ± 5(6)	100	362	97	256 ± 6(6)	100	328	92
2	dairy wastewater	431 ± 6(6)	150	534	92	407 ± 6(5)	150	506	91
3	dyes wastewater	846 ± 8(6)	100	908	96	846 ± 8(5)	100	890	94
4	refinery wastewater	2353 ± 5(6)	400	2396	87	2332 ± 6(6)	400	2378	87
5	tannery wastewater	1566 ± 9(6)	200	1660	94	1544 ± 10(6)	200	1500	86
6	herbal pharmaceutical wastewater	5488 ± 7(6)	400	5064	86	5095 ± 12(7)	400	4396	80
7	seawater	33 ± 3(6)	50	74	89	28	50	62	79

<sup>a</sup> Mean ± SD(*n*), where *n* is the no. of observations.

volume inside the vessel was always kept at 1/10th of its total volume. This has been followed as a safety measure recommended by Geadye et al. in 1988 (14). In the present study, a different volume of standard KHP in the range of 1–6 mL having 400 mg of COD L<sup>-1</sup>, was studied for maximum recovery. Figure 1 shows that a 3 mL sample volume of standard KHP is suitable for achieving 100% recovery with lower standard deviation, having 1.4% coefficient of variance.

**Range for Quantification of COD.** To determine the minimum as well as the maximum COD values, experiments were conducted on optimized digestion conditions using standard solutions of KHP, ranging from 5 to 1000 mg of COD L<sup>-1</sup> (Table 1). The results reveal that the minimum concentration, which can be measured by the proposed procedure, is 5 mg L<sup>-1</sup> with reproducibility and high percent recovery.

**Comparison of OR and CMD Procedure.** OR and the proposed CMD procedure were compared using KHP standards (Table 2). The proposed microwave procedure is found to be more suitable even for samples containing a lower COD load of 5 mg L<sup>-1</sup>. The standard deviation and coefficient of variance of the results reveals that the proposed microwave digestion procedure is efficient with greater repeatability, sensitivity, and selectivity.

**COD Determination of Standard Solution of KHP.** The COD values of KHP standards in different ranges (lower, medium, and higher) of KHP were determined by the proposed CMD method and also by the OR method (Table 2). The CMD method was found to be more suitable even at lower range of (5–50 mg L<sup>-1</sup>) COD as compared to the OR method. The results indicate that the ratio of COD value measured by the proposed procedure and theoretical COD value is in the range of 0.96–1.02; however, the ratio of COD value measured by OR method and theoretical COD value is in the range of 0.64–0.84. The results show that the coefficient of variation of COD values obtained by the proposed procedure is on the lower side as compared to OR method and shows that the proposed procedure is more precise.

**COD Determination of Pure Organic Compounds.** The pure organic compounds, namely, glucose, KHP, oxalic acid, citric acid, cane sugar, starch, (soluble part), maltose, and glycerol, were digested in an appropriate concentration (>1000 mg L<sup>-1</sup>) by the OR method and the CMD procedure. Furthermore, the COD value of these compounds was determined and compared with the theoretical COD value (Table 3). COD by CMD method for standard organic solutions of KHP, glucose, oxalic acid, and cane sugar were found to have 0% deviation, while citric acid, maltose, and glycerol show slightly higher percentage deviation of 0.58, 0.75, and 0.74, respectively. Starch (soluble part) shows a relatively high percentage deviation of 35.18 from the theoretical COD values. Thus, the results show that the developed microwave digestion procedure is highly suitable as compared to the OR procedure.

**TABLE 5. Effect of the Chloride Ion Concentration on COD Determination by CMD Method**

no.	chloride ion concn (mg L <sup>-1</sup> )	100 <sup>a</sup> (mg L <sup>-1</sup> )		
		measd COD (mg L <sup>-1</sup> )	COD (mg L <sup>-1</sup> ) <sup>b</sup>	CV (%) <sup>c</sup>
1	500	100	100 ± 1(6)	1.0
2	1000	100	100 ± 1(6)	1.0
3	2000	100	100 ± 1(6)	1.0
4	4000	104	104 ± 4(5)	3.84
5	6000	100	100 ± 1(6)	1.0
6	8000	166	166 ± 5(5)	3.0
7	10000	300	300 ± 10(5)	3.33
8	12000	686	686 ± 5(5)	0.12

<sup>a</sup> Theoretical COD. <sup>b</sup> Mean ± SD(*n*), where *n* is the no. of observations.

<sup>c</sup> Coefficient of variance.

**COD Determination of Wastewater Samples.** Wastewater samples were collected from various industries and sites (viz., dairy, dyes, petroleum refinery, tannery, herbal pharmaceutical, domestic sewage, and seawater). The COD value was determined by both procedures for these samples. The recoveries in COD values for the spiked samples show 90–100% recovery (Table 4), which shows that the procedure is more accurate. The present work reveals that the filtration of samples by membrane filter or homogenization is not essential to obtain reproducible results for these samples.

**Chloride Ion Interference in COD Determination.** The interference due to chloride ion was studied by adding chloride ions in various amounts in the range of 500–12 000 mg of Cl<sup>-</sup> ions L<sup>-1</sup> in the standard solution of KHP having a theoretical COD value of 100 mg L<sup>-1</sup>. The samples were subjected to COD determination by the proposed CMD procedure. The results are shown in Table 5 and indicate that the chloride ion is not interfering up to 6000 mg of Cl<sup>-</sup> ions L<sup>-1</sup> (17, 18) in the estimation of COD load; however, by the OR procedure, it is reported that chloride ions are interfering above 2000 mg of Cl<sup>-</sup> ions L<sup>-1</sup>. Thus, the potential of the proposed microwave digestion method is higher for the oxidation process, and the procedure is amenable for wastewater samples containing chloride ions up to 6000 mg of Cl<sup>-</sup> ions L<sup>-1</sup>.

In summary, the experimental results demonstrate that the CMD method is the modified method for estimation of COD, which reduces the time, reagent volume, hazardous emission, external contamination, and chloride ion interference with increasing reproducibility and accuracy. The method will be a promising one for use in the laboratory.

## Literature Cited

- Selvapathy, P.; Starlet Jogabeth, J. *Indian J. Environ. Health* **1991**, 33 (1), 96–102.
- Moore, W. A.; Kroner, R. C.; Ruchhoft, C. C. *Anal. Chem.* **1951**, 21, 953–957.

- (3) Simal, J.; Lage, M. A.; Iglesias, I. *An. Bromatol.* **1986**, 37, 125–142.
- (4) Inhimaru, A.; Tanaka, K. *Bunseki Kagaku* **1983**, 32, 493–497.
- (5) Korenaga, T. *Anal. Lett.* **1980**, 13, 1001–1011.
- (6) Clesceri, L. S.; Greenberg, A. E.; Eaton, A. D. *Standard Method for the Examination of Water and Wastewater*, 20th ed.; American Public Health Association: Washington, DC, 1998.
- (7) Kingston, H. M.; Haswell, S. J. *Microwave Enhanced Chemistry—Fundamentals, Sample Preparation, and Applications*; American Chemical Society: Washington, DC, 1997; 772 pp.
- (8) Nakashima, S.; Sturgeon, R. E.; Willie, S. N.; Berman, S. S. *Analyst* **1988**, 113, 159–163.
- (9) Kingston, H. M.; Jassie, L. B. *Anal. Chem.* **1986**, 58, 2534–2541.
- (10) Jassie, L. B.; Kingston, H. M. *Introduction to Microwave Sample Preparation: Theory and Practice*; American Chemical Society: Washington, DC, 1988.
- (11) Matusiewicz, H.; Sturgeon, R. E. *Prog. Anal. Spectrosc.* **1989**, 12, 21–28.
- (12) Dunemann, L.; Meinerling, M. *Fresenius J. Anal. Chem.* **1992**, 342, 714–718.
- (13) Knapp, G. *Mikrochim. Acta II* **1991**, 445–455.
- (14) Gedy, R.; Smith, F.; Wastaway, K. *Educ. Chem.* **1988**, 28, 55–56.
- (15) Chen, S.-C.; Tzeng, J.-H.; Tien, Y.; Wu, L.-F. *Anal. Sci.* **2001**, 17, 551–553.
- (16) Wilson, F. J.; Jarbas, J. R. R. *Water Res.* **1989**, 23 (8), 1069–1071.
- (17) Burns, E. R.; Marshall, C. J. *Water Pollut. Control Fed.* **1965**, 37, 1716.
- (18) Baumann, F. I. *Anal. Chem.* **1974**, 46, 1336.

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