

Rapid Determination of Chemical Oxygen Demand (COD) Using Focused Microwave Digestion Followed by a Titrimetric Method

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Chemical oxygen demand (COD) is an important parameter in water-pollution control analysis. It is closely related to the organic contamination level of a water or wastewater sample. The Cr-COD method is used as the standard in USA and Taiwan. Compared to Japanese Mn-COD method, it has a higher detection limit and severe chloride ion interference because of the stronger oxidant and the longer digestion time. In order to reduce the chloride-ion interference, the mercury salt (*e.g.* HgSO₄) is usually added to mask the chloride ion. On the other hand, the closed reflux-titrimetric method is recommended by the Standard Method to reduce the large amount of hazardous waste.¹ However, it still requires a long time (2 h) for the digestion step to be completed in this COD analysis, and the tolerance of the chloride ion interference is only up to 2000 mg Cl⁻/L.

The objective of this research was to investigate the availability of a rapid procedure to determine the COD in water and wastewater by digesting samples in open vessels located in a focused microwave system followed by ferrous ammonium sulfate titration. The results obtained using this microwave system were also compared with those obtained by a closed reflux method described in the Standard Method.

Experimental

Apparatus

A focused microwave system (Microdigest 3.6, Prolabo Corp.,

France) with a nominal maximum power of 250 W was used for sample digestion. The system has six individual magnetrons which can directly focus the microwave radiation to each sample added in a glass digestion tube (250 mL) placed in the system's waveguide. Each digestion tube was also connected to a condenser circulating with cooling water so as to avoid the loss of any volatile substances existing in the sample.

Reagents

All reagents were of analytical grade. Active carbon absorbed and deionized water were used throughout. The reagents were prepared as described in the Standard Method for the open and closed reflux titrimetric methods.

Samples

A solution of KHP (potassium hydrogenphthalate) with a theoretical COD of 500 mg O₂/L was used as a stock standard. Appropriate dilutions gave standard solutions of different COD values. Real water samples were supplied by a local environmental monitoring company. Samples were filtered through a 0.45 μm membrane and preserved with sulfuric acid (pH <2).

Closed reflux method

A semi-micro COD determination was carried out according to the Standard Method using a 5 mL sample volume.

Table 1 COD determination of various KHP standard solutions by the microwave and closed reflux methods

ThOD/ mg L ⁻¹	Microwave method			Closed reflux method		
	COD ^a / mg L ⁻¹	CV ^b , %	Recovery, %	COD ^a / mg L ⁻¹	CV ^b , %	Recovery, %
0	6 ± 3	50	—	6 ± 3	50	—
50	44 ± 5	11	88	52 ± 4	8	104
100	98 ± 2	2	98	99 ± 1	1	99
150	150 ± 3	2	100	151 ± 2	1	101
200	192 ± 3	2	96	192 ± 2	1	96

a. Mean ± s.d., *n* = 10.

b. Coefficient of variance.

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Table 2 Effect of the chloride concentration on COD determination by the microwave method

Chloride/ mg L ⁻¹	ThOD = 0 mg L ⁻¹		ThOD = 150 mg L ⁻¹	
	COD ^a / mg L ⁻¹	COD ^b / mg L ⁻¹	COD ^a / mg L ⁻¹	COD ^b / mg L ⁻¹
0	6	6	144 ± 6 (10) ^c	145 ± 2(5) ^c
2500	—	—	146 ± 1(10)	138 ± 0(5)
5000	18	3	146 ± 5(10)	147 ± 3(5)
7500	—	—	152 ± 7(10)	145 ± 1(5)
10000	52	4	154 ± 3(3)	147 ± 3(3)
15000	64	16	165 ± 4(3)	149 ± 4(3)
20000	331	127	187 ± 10(3)	151 ± 2(3)

a. No HgSO₄ added.

b. 0.5 g HgSO₄ added.

c. Mean ± s.d. (*n*).

Table 3 COD values and spike recoveries for real water and wastewater samples

Sample type	Microwave digestion				Closed reflux digestion			
	COD (mg O ₂ /L)			Recovery, %	COD (mg O ₂ /L)			Recovery, %
	Initial ^a	Added	Found		Initial ^a	Added	Found	
River water	19 ± 3	25	41	88	14 ± 3	25	37	92
Seawater ^b	30 ± 3	30	58	92	31 ± 3	30	59	93
Metal wastewater	40 ± 6	25	62	88	37 ± 5	25	62	100
Chemical wastewater ^c	231 ± 6	250	491	104	240 ± 7	250	483	97
Food wastewater	48 ± 5	25	68	80	42 ± 2	25	63	84
Hospital wastewater	168 ± 2	150	307	93	171 ± 2	150	309	92
Animal wastewater ^c	255 ± 8	150	389	89	247 ± 5	150	390	95

a. Mean ± s.d., $n = 5$. b. Chloride ion has been precipitated as silver chloride and removed before analysis. c. Sample diluted 5 times before analysis.

Focused microwave digestion method

In this method, a microwave system was used to replace the conventional heating apparatus usually used in the standard open reflux method. To 20 mL of a sample present in the glass digestion tube were added 0.5 g of mercuric sulfate, 10 mL of dichromate solution, and 5 mL of sulfuric acid reagent. The tube was placed into the well of the microwave system and connected to a condenser. Cooling water was turned on and a 25-mL volume of sulfuric acid reagent from the top of the condenser was added. The mixture was microwave digested at 150°C for 8 min. After digestion, the digested solution was transferred into a flask using some clean water. Excess dichromate in the digested solution was titrated with an FAS (ferrous ammonium sulfate) standard solution using ferroin as an indicator.

Results and Discussion

Optimum digestion time for microwave digestion

The temperature used for microwave digestion in this study was set at 150°C, as described in the Standard Method. The digestion time was then varied from 6 to 30 min. All of the results indicate that 8 min is suitable for the standard sample digestion (theoretical COD value 150 mg O₂/L). The time required for digestion is almost consistent with the results mentioned by Jardim and Rohwedder.² They proved that 7 min microwave digestion was suitable for samples having up to 1000 mg O₂/L of COD when a closed microwave digestion system was used. This shows that open microwave digestion has the same performance as closed microwave digestion even though the power is less. The possible reason that the open mode is as good as the closed mode is that in an open microwave system the microwave energy is directly focused to a sample placed within the waveguide, whereas in a closed system the microwave is dispersed in a large cavity. Consequently, heating in an open system is more efficient than that in a closed system. Afterwards, 150°C and 8 min were used in this study for focused microwave sample digestion.

COD determination of KHP standard solution

The COD values of various standard solutions prepared with KHP were determined by the proposed microwave method. The results are given in Table 1. For comparison purposes the COD values determined by the closed reflux method are also included in the results. The detection limits calculated by three-times the standard deviation of the blank test are both 9 mg/L. The ratio

of the measured value (COD) and the theoretical value (ThOD) are in the range of 0.88 to 1.00 for the microwave method and 0.96 to 1.04 for the closed reflux method. The precision and accuracy of the proposed microwave digestion procedure are comparable with those of the closed reflux method. Slatter and Alborough reported that the closed microwave COD method has a significant lower standard deviation and coefficient of variation (1.5%) than that of the conventional dichromate COD method (3.6%) for a 400 mg O₂/L standard KHP solution.³ The results reported in our study using the open microwave method also have good precision, except for a lower COD standard solution (<50 mg O₂/L).

COD determination of organic compounds

Eleven organic compounds were used to prepare the standard solutions, and their COD values were determined by the open focused microwave method. The ratios of the measured and theoretical COD values of benzoic acid, salicylic acid, glucose, lactose, phenol, malic acid and citric acid are between 0.86 and 1.00; on the other hand, acetic acid, glutamic acid, glycine and benzene show ratios of between 0.24 and 0.60. The low values of glutamic acid, glycine and benzene may be caused by incomplete decomposition. In order to completely decompose these compounds during digestion, the digestion time was increased up to 30 min. This obviously indicates that the recoveries of these compounds increase with a longer digestion time, because the microwave method can offer more energy to the sample solution. Since good recovery was obtained by the closed reflux method, the low value of acetic acid may have been caused by volatilization during the heating step.

COD determination of a saline standard solution

KHP standard solutions having a theoretical oxygen demand value of 150 mg O₂/L were added to various amounts of the chloride (0 to 20000 mg Cl⁻/L). The COD values were measured by the focused microwave method; the results are listed in Table 2. The COD values of saline water without organic matter (KHP) were also measured. The results show that more chloride ion resulted in larger COD values. It was observed that interference is more serious when the measured sample does not contain any organic substance, since more unreacted dichromate enhances the oxidation of the chloride ion.⁴ The results also indicate that the tolerable concentration of chloride is ~20000 mg/L with mercuric sulfate, compared to ~10000 mg/L without mercuric sulfate when ThOD is 150 mg O₂/L. The tolerable concentration is lower when ThOD is lower. The conventional COD method can only analyze a

sample having a chloride concentration less than 2000 mg/L. The focused microwave method shows a much better tolerance.

COD determination of real water and wastewater samples

Both microwave digestion and closed reflux digestion were used to determine the COD values of a variety of water samples, which included river water, seawater and the wastewater from food, chemical, metal industries *etc.*, to evaluate the applicability of the focused microwave digestion method. The data listed in Table 3 show that the results obtained by both methods are agreeable. Spike tests were also performed. The recoveries of the spike tests were in the range of 80% to 104%. This shows that the proposed method has feasibility.

References

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