Chemical oxygen demand using microwave digestion: A tentative new method

NP Slatter* and H Alborough
Umgeni Water, Pietermaritzburg 3200, South Africa

Abstract

The standard dichromate chemical oxygen demand (COD) method is a time-consuming analysis requiring a large instrumentation area. The microwave digestion COD method, a tentative new method, was evaluated using potassium hydrogen phthalate standard (KHP) and domestic and industrial effluent. It was found to be comparable to the standard dichromate reflux COD method for accuracy in the range 20 to 1 800 mg O_2/ℓ. The microwave digestion COD method considerably improved the efficiency of Umgeni Water's Head Office Laboratory COD analysis.

Introduction

COD is used as a measure of the oxygen equivalent of the oxidisable matter of a sample that is susceptible to oxidation by a strong chemical oxidant. The COD is measured in terms of the amount of potassium dichromate reduced by the sample during two hours of refluxing in a medium of sulphuric acid and silver sulphate catalyst. Complete oxidation of all organic compounds, except for straight chain carboxylic acids, is achieved. Chloride interferences are removed by the addition of mercuric sulphate which complexes as mercuric chloride (*Standard Methods* (1980), method 508A). After digestion the residual dichromate is determined by titration with ferrous ammonium sulphate to the ferroin indicator end point.

The microwave digestion COD method was developed as a result of the Kingston and Jassie (1986), Mahan et al. (1987) and Nadkarni (1984) microwave metal digestion studies. Alternative COD digestion methods were investigated because of the long refluxing time and the large instrumentation area required by the conventional dichromate COD method. Extensive preliminary microwave COD digestion studies were undertaken to develop an alternative method.

The aim of this investigation was to assess COD microwave digestion critically.

Experimental

The experimental work was carried out in parallel using the standard dichromate COD method (*Standard Methods* (1980)) and the 30-min microwave digestion COD method, using the CEM microwave digestion oven model MDS-81 D. All the samples were homogenised in a high speed blender for one minute immediately prior to analysis. Twenty aliquots of each sample analysed were taken. Ten aliquots were analysed simultaneously using the standard dichromate COD method and the remaining aliquots were analysed using the microwave digestion COD method.

Standard potassium hydrogen phthalate solution (KHP) with a theoretical COD of 400 mg O_2/ℓ was prepared according to *Standard Methods* (1980) and analysed using the standard dichromate method and the 30-min microwave digestion COD method.

The limit of detection of the microwave digestion COD method was determined statistically by analysing ten aliquots of ultra-pure deionised water.

Results and discussion

A summary of the COD results for the standard using the 30-min microwave digestion method is given in Table 1 and the results are illustrated graphically in Fig. 1.

The KHP COD analyses using the standard dichromate and the microwave methods meet the 95,5% confidence limits required to produce statistically acceptable results. The mean KHP COD for both methods is marginally lower than the theoretical value of 400 mg O_2/ℓ. The coefficient of variation and the standard deviation for the microwave analyses are significantly lower than those for the dichromate COD analyses indicating the higher precision of the microwave COD method.

The summary of the COD analyses using the standard dichromate and the microwave methods for a variety of domestic and industrial samples is given in Table 2 and Fig. 2. The data summarised in Table 2 are mean COD values for ten replicates.

The correlation coefficient of the dichromate and microwave COD analyses is 0,997 and the slope of the plot is 0,979. The pairs test indicates that there is no significant difference between the standard dichromate method and the microwave method. In addition, the non-parametric Wilcoxon sign test for paired samples shows no significant difference between the COD methods.

The detection limit as calculated from the standard deviation of ten ultra-pure microwave COD analyses is 5,4 mg O_2/ℓ.

Conclusions

The standard dichromate and microwave COD analyses of the KHP standard meet the 95,5% confidence limits, thus the analytical results are within two standard deviations of the theoretical COD value. Thus it can be concluded that for accuracy the microwave COD and the standard dichromate COD methods are comparable. The microwave COD method has a significantly lower standard deviation and coefficient of variation, from which it can be concluded that the microwave method has a higher precision than the dichromate COD method.

The correlation coefficient of the dichromate and microwave COD analyses on industrial and domestic effluent samples is 0,997 and the slope of the plot is 0,979. The pairs test confirms that no significant difference was found between the dichromate

* To whom all correspondence should be addressed.
Received 7 June 1990; accepted in revised form 8 April 1992.

TABLE 1
COMPARISON OF KHP COD ANALYSES USING THE STANDARD DICHROMATE AND MICROWAVE METHODS

Results	COD microwave digestion (mg O_2/ℓ)	COD dichromate digesion (mg O_2/ℓ)
Mean	393,1	394,5
Standard deviation	5,9	14,3
Coefficient of variation	1,5	3,6
Mean error	6,9	5,5
Per cent relative mean error	1,7	1,4

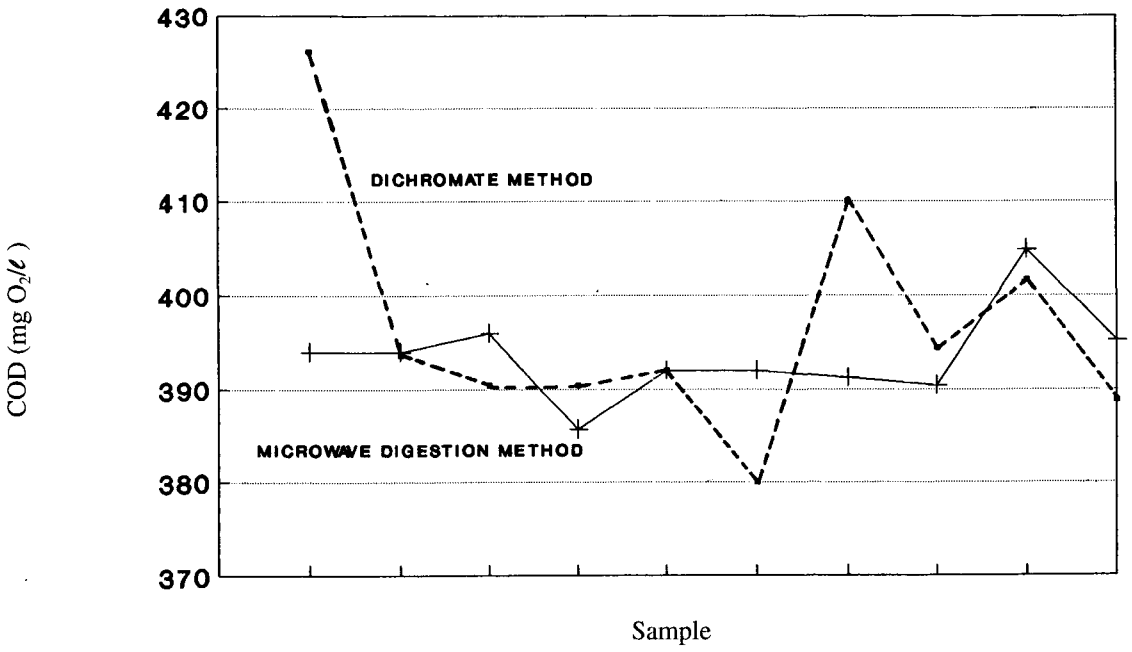

Figure 1
Comparison of COD analyses using the standard dichromate method and the microwave digestion method for KHP standards

and microwave COD methods. In addition, the non-parametric Wilcoxon sign test for paired samples showed no significant difference between the COD methods. Thus it can be concluded that both methods are comparable.

Use of the microwave COD method implies significant cost savings for a water analysis laboratory as a result of the reduction in analysis time per sample. Umgeni Water Central Laboratory has increased its daily COD analyses using the microwave COD digestion method.

The microwave COD method should improve safety as the acid digestion is carried out within the microwave oven.

Acknowledgements

The authors wish to thank Mr G Mockler, Development Technician at Umgeni Water and Mrs M Pillay, Scientist at Umgeni Water, for their assistance. The authors also wish to thank Mr WN Richards, Director of Scientific Services at Umgeni Water for permission to publish this paper.

TABLE 2
COMPARISON OF DOMESTIC AND INDUSTRIAL COD ANALYSES USING THE DICHROMATE AND THE MICROWAVE METHODS

Sample	Microwave COD (mg O_2/ℓ)	% relative standard deviation	Standard dichromate COD (mg O_2/ℓ)	% relative standard deviation	% mean difference
Industrial	1637	1,66	1616	2,13	-1
Industrial	77,8	20,2	84,3	15,3	-12
Industrial	1335	1,58	1413	2,9	8
Domestic	776,5	3,25	692,3	3,2	6
Domestic	405,3	5,92	383,7	5,95	-6
Domestic	167,2	11,7	134,7	16,85	-24
Domestic	358,7	3,69	391,4	7,13	8,0

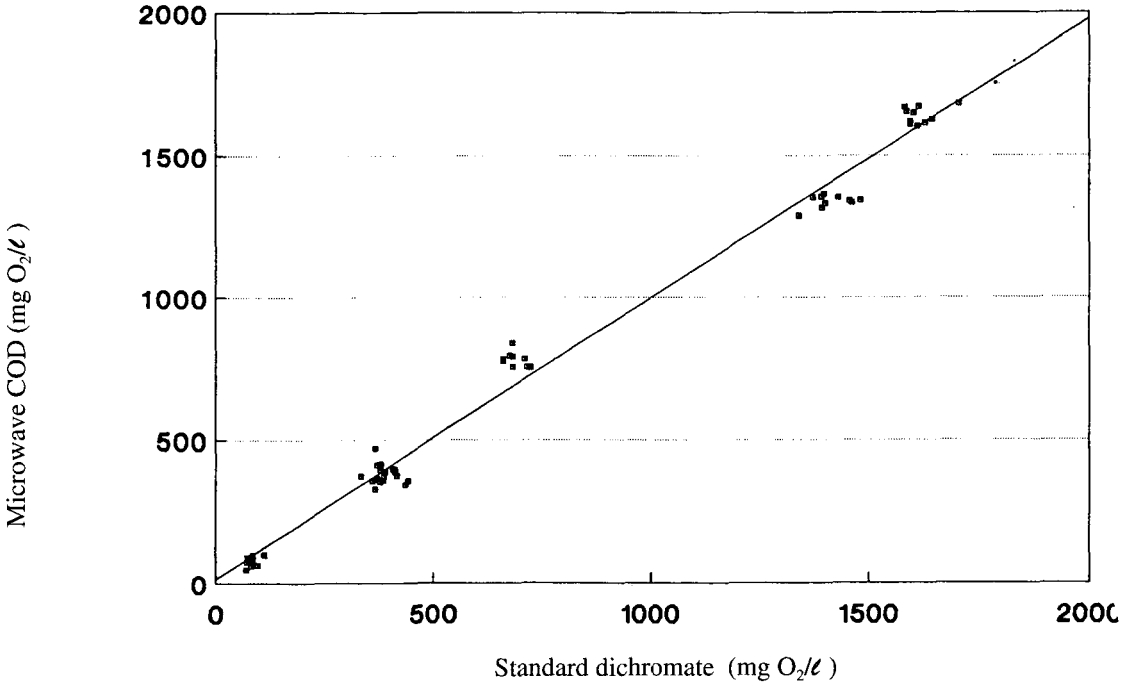

Figure 2
Comparison of standard dichromate and microwave COD methods

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