



## Trivalent manganese as an environmentally friendly oxidizing reagent for microwave- and ultrasound-assisted chemical oxygen demand determination

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### ABSTRACT

In the present work manganese(III) has been used as oxidant and microwave radiation and ultrasound energy have been assessed to speed up and to improve the efficiency of digestion step for the determination of chemical oxygen demand (COD). Microwave (MW) and ultrasound-assisted COD determination methods have been optimized by means of experimental design and the optimum conditions are: 40 psi pressure, 855 W power and 1 min irradiation time; and 90% of maximum nominal power (180 W), 0.9 s ( $s^{-1}$ ) cycles and 1 min irradiation time for microwaves and ultrasound, respectively. Chloride ion interference is removed as hydrochloric acid gas from acidified sample solutions at 150 °C in a closed reaction tube and captured by bismuth-based adsorbent suspended above the heated solution. Under optimum conditions, the evaluated assisted digestion methods have been successfully applied, with the exception of pyridine, to several pure organic compounds and two reference materials. COD recoveries obtained with MW and ultrasound-assisted digestion for five real wastewater samples were ranged between 86–97% and 68–91%, respectively, of the values obtained with the classical method (open reflux) used as reference, with relative standard deviation lower than 4% in most cases. Thus, the Mn(III) microwave-assisted digestion method seems to be an interesting and promising alternative to conventional COD digestion methods since it is faster and more environmentally friendly than the ones used for the same purpose.

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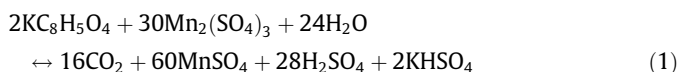
### 1. Introduction

Oxygen demand is an environmentally important parameter which reflects the degree of organic pollution in water. Since the degradation of organic compounds requires oxygen, their concentrations can be estimated by the amount of required oxygen [1,2]. Chemical oxygen demand (COD), biological oxygen demand (BOD) and total organic carbon (TOC) are three main indexes used to assess this organic pollution in aqueous systems. In particular COD, which is defined as the amount of oxygen equivalents consumed in the oxidation of organic compounds by strong oxidants (such as dichromate, permanganate, etc.) [3], represents the total pollutants load of most wastewater discharges [4]. As a pollution monitoring parameter, COD has the advantage of speed and simplicity compared with BOD, and requires less equipment than to TOC determination. Thus, COD is preferred for estimating organic pollution in water [2,5,6].

In the conventional COD evaluation methods, a known excess of oxidant is added to a sample and the mixture is boiled. Whereas the sample is digested, COD material in the sample is oxidized by the oxidant. After the oxidation has proceeded for a finite period

of time, the initial concentration of organic species can be calculated by determining the amount of the remaining oxidizing agent commonly by titration or UV–vis spectrophotometry [7].

The conventional methods, however, require the time-consuming process (about 2 h) of closed refluxing samples to achieve more complete oxidation. Moreover, these methods consume some expensive ( $Ag_2SO_4$ ) and toxic (hexavalent chromium and mercury) chemicals [8–10]. For these reasons, many efforts have been done to develop new COD tests that shorten the digestion time and eliminate metals such as Cr(VI), Hg, and Ag [11]. For the latter purpose, manganese(III) has been recently suggested as a new environmentally friendly oxidizing reagent. The reaction occurring in this COD method is best represented by the following equation, where the Mn(III) oxidant is reacted with potassium hydrogen phthalate (KHP):



However, this new oxidant still needs 1 h to digest organic matter at 150 °C [11].

The acceleration of chemical reactions is a feature shared by microwave (MW) and ultrasound radiation. The advantages of

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microwaves in the analytical laboratories are well known [12]. Microwaves have also been used for COD determination with good recoveries and an important reduction in the time of digestion step [12–18]. Other advantages of microwave digestion over the conventional hot-plate digestion methods include reduced contamination, lower reagent and sample usage and easy to handle. The microwave oven heats the reaction mixture to a high temperature very rapidly and the closed vessel helps to prevent losses due to volatilization of compounds. However, one of its main drawbacks is the high initial cost of the equipment and safety limitations (i.e., high pressure and temperature). On the other hand, power ultrasound is being extensively used in a great variety of applications such as solution degasification, cleaning, aerosol generation, metal extraction and organic synthesis [19–26]. Applying of continuous systems for this step has not been frequently used, even though this approach speeds sample treatment up to considerably [27–30]. Other advantages of continuous ultrasound-assisted leaching are modest consumption of sample and reagents, and the need for few or none of the chemicals required for dissolution in manual methods [31]. However, surprisingly ultrasound-assisted sample preparation is still not commonly used for analytical purposes.

Recently, Domini et al. [18] Canals and Hernández [32] and Canals et al. [33] have used ultrasound energy for the determination of chemical oxygen demand (COD).

Sample preparation depends on a variety of experimental factors controlled by the operator. This set of conditions must be optimized and several optimization approaches could be used. Among them, multivariate statistics (i.e., factorial design) shows the next main advantages: (i) if the effects of the factors are additive, then the factorial design needs fewer measurements than the classical “one-at-a-time” approach in order to give the same precision (i.e., in general, for  $k$  factors, a classical approach involves  $k$  times as many measurements as a factorial one with the same precision); (ii) the factorial experiment detects and estimates any interaction between factors that could affect the result [34].

Both MW and ultrasound-assisted digestions have been used to speed up the sample digestion for COD determination using hexavalent chromium as oxidant. One recent trend is that analytical methods decrease their output of hazardous materials. This includes laboratory wastes that contain toxic materials (hexavalent chromium, mercury, and silver metals). Therefore, the goals of this work were: (i) to use manganese(III) as oxidizing reagent for COD determination assisted by microwave radiation (closed) and ultrasound energy and; (ii) to apply a factorial design technique in order to accelerate the optimization process of these digestion steps in order to suggest a fast, safe, easy to handle and environmentally friendly COD method.

## 2. Experimental

### 2.1. Apparatus

A microwave system (MSP 1000, CEM corp., Matthews, N. Carolina, USA) with 950 W effective power output and a pressure control system was used for the microwave digestion. Advanced composite vessels (CEM corp., Matthews, N. Carolina, USA) with maximum pressure of 200 psi were used.

The sonication system used has been previously described [18]. A 200 W, 24 kHz ultrasonic processor (Dr Hielscher, Teltow, Germany) was used as the sonic generator. An all-glass cylindrical sonotrode (12 mm o.d.; 125 mm long, reference SG12, Dr Hielscher, Teltow, Germany) was directly introduced 4.5 cm into the reaction mixture. On this length the higher recoveries were obtained.

A spectrophotometer UV–vis (Unicam Instruments, Helios Gamma & Delta, Great Britain) and a quartz cell (HELLMA), 10 mm length pass, were used to measure the excess of oxidants (chromium(VI) and manganese(III)).

The method used in this study for the reduction of chloride interference in the determination of COD using bismuth-based adsorbents instead of Hg(II) has been previously described [11,35].

### 2.2. Reagents and samples

All reagents were of analytical grade. Distilled and deionized water was used throughout (18 M $\Omega$  cm resistivity).

Classical COD assay solutions were prepared according to the closed reflux reference method [7]. Briefly, the digestion solution was prepared by mixing 10.216 g K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 33.3 g HgSO<sub>4</sub>, and 167 mL H<sub>2</sub>SO<sub>4</sub> (concentrated), and then diluting up to volume of 1000 mL with deionized water. Previously, silver sulphate was added to the sulfuric acid in the proportion 5.5 g Ag<sub>2</sub>SO<sub>4</sub> per kg of H<sub>2</sub>SO<sub>4</sub>.

The manganese(III) digestion solution was prepared by mixing two solutions. One solution was prepared by dissolving approximately 1.0 g of KMnO<sub>4</sub> in deionized water and diluting to 0.5 L. The solution was boiled during 2 h and was settled an overnight. Latter, the solution was filtered. Second solution was prepared dissolving approximately 5.0 g of MnSO<sub>4</sub> in the minimum amount of deionized water and diluting to 0.5 L with concentrated sulfuric acid. Finally, both solutions were mixed and on this way a digestion solution of 1.6 g/L of Mn(III) on 18 N H<sub>2</sub>SO<sub>4</sub> (saturated with MnSO<sub>4</sub>) was prepared. Solution concentration was determined by titration against standardized 0.25 M FeSO<sub>4</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>·6H<sub>2</sub>O (FAS) solution that was prepared by dissolving 98 g of iron(II) ammonium sulphate on 20 mL of concentrated sulfuric acid, and after cooling diluting to 1000 mL. This solution was standardized daily against standard potassium dichromate solution [7]. Manganese(III) has a broad absorption band in the region between approximately of 420 and 620 nm, with a single maximum at 510 nm [11]. Calibration graphs were prepared using dilutions of potassium hydrogen phthalate (KHP) standard solution. The working range of the test is 50–1500 mg/L COD. The calibration slope is negative because manganese(III) color decreases as COD concentration increases, being the slope 0.0005 and 0.0006 absorbance/(mg/L) and the correlation coefficient 0.9977 and 0.9967 for microwave and ultrasound, respectively.

For optimization, calibration graphs and interference studies a standard solution of potassium hydrogen phthalate (KHP), corresponding to 2000 mg/L COD, was prepared by dissolving 1.702 g of dried (120 °C, overnight) KHP in water and diluting up to 1 L with water. Appropriate dilutions gave solutions of different COD values. To compare digestion methods, solutions of seven organic compounds (*D*-glucose, lactic acid, salicylic acid, methyl isobutyl ketone, acetic acid, pyridine and picric acid) other than KHP were prepared, encompassing a wide range of oxidability. The theoretical COD values of each of these solutions would be about 100 mg O<sub>2</sub>/L, assuming that the oxidation was completed. Standard solution of chloride was prepared for interference studies corresponding to 20000 mg/L, and solutions of different concentration were prepared by appropriate dilutions.

Bismuthate-based adsorbent (as S1 on Ref. [35]) and basket were prepared as described by Vaidya et al. [35].

Blank determinations were carried out on distilled and deionized water.

Two reference materials (RMs) (a 200 mg O<sub>2</sub>/L reference material, Reagecon, Ireland, UK, and GBW08624B, National Research Center for Certified Reference Materials, PR of China) were used to evaluate the bias on the proposed methods. Real wastewater samples were supplied by a local private water-analysis laboratory

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