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COMPARATIVE STUDY OF COD PARAMETER MEASURED USING TWO DIFFERENT STANDARD METHODS

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Introduction

The most relevant pollution impact of wastewater is organic matter. The pollution level of organic matter in water bodies is roughly predicted by analysing chemical oxygen demand (COD). The organic matter, present in the water sample is oxidized by potassium dichromate in the presence of sulphuric acid, silver sulphate and mercury sulphate to produce carbon dioxide (CO_2) and water (H_2O). The quantity of potassium dichromate used in the reaction is equivalent to the oxygen (O_2) used to oxidize the organic matter of wastewater.
Monitoring COD helps ensure compliance with the regulations, which are designed to protect water quality and prevent excessive pollution. If the high COD wastewater is directly discharged into the environment, it will threaten aquatic organisms, directly or indirectly affecting human life and health. Therefore, the detection of COD in water has great significance in the prevention and control of environmental and ecological pollution. Many countries and regulatory bodies have established COD limits and guidelines for discharges into water bodies.
This study mainly focuses on the determination of COD parameter measured from different samples of waste waters and surface waters using two Romanian standard methods. The deviations between the values measured with the 2 standard methods were analysed and the advantages and disadvantages of each method were identified.

Materials and methods

Determining COD using $K_2Cr_2O_7$ (called COD_{Cr}) is mainly used for assessing the water quality in moderately or heavily contaminated water bodies (e.g., sewage, wastewater and surface-water). There are two main standard methods to measure COD, described in the Romanian Standards SR ISO 6060:1996 (Open Reflux method, also, called the Macro-digestion method) and SR ISO 15705:2022–Sealed Tube method (ST-COD method, also called the Micro-digestion method).
Different types of water (grab samples) were collected, as follows: *i*) 4 samples of influent and, respectively, effluent of municipal wastewater treatment plants located in Bucharest (Glina WWTP); *ii*) 6 surface waters from several lakes located along the Colentina river. The COD parameter was analysed in all samples by the dichromate oxidation methods: conventional method (open reflux COD method) and small-scale sealed-tube method (ST-COD method).

Table 1. Comparison of the methods used to measure COD

Step of the method	Conventional COD	ST-COD
Digestion	Same reagents: sulphuric acid; silver sulphate (oxidation catalyst); potassium dichromate; mercury(II) sulphate (elimination of chlorine)	
	Sampling amount:10 mL	Sampling amount: 2 mL
	Digestion: open reflux –2 h at 150°C	Digestion: closed reflux procedure – 2 h at 150°C
Detection	Titrimetric, using colour indicator: - the excess $K_2Cr_2O_7$ is titrated against ferrous ammonium sulphate using ferroin as an indicator	Photometric: the amount of $K_2Cr_2O_7$ used in the oxidized sample is determined by measuring the absorbance of the formed Cr^{3+} at an appropriate wavelength. *Low range* COD – measures decrease in oxidant (dichromate ion) or orange/yellow colour at 420 nm; *High range* COD – measures increase in Cr^{3+} or green colour at 620 nm. According with standard method ISO 15705-2002, if COD ≤150 mg/L, the residual Cr^{6+}content is detected at 440 nm; if COD ≦50 mg/L, the remaining Cr^{6+}content is detected at 348 nm.

Results and conclusions

4 determinations of the COD_{Cr} parameter were performed for each wastewater and 3 determinations for surface water sample. Results are presented in Table 2 as the average value for each type of water analyzed. Deviation between the values obtained by COD conventional method and ST-COD were calculated.

The difference between COD and ST-COD is negative for matrix – wastewater with values > 100 mg O_2/L; the relative deviation of the mean of the consensus values for COD and ST-COD varies between -2% and -3.8%. In waters with concentration level of COD content < 100 mg O_2/L (effluent of WWTP and surface water), the values obtained for ST-COD are lower than the ones obtained for COD measures with classical method and the relative deviation varies between 5.7 and 15.3.

ST-COD method presents results that are systematically lower than COD conventional method for waters with COD content <100 mg/L (about 4-5 mg/L).

Method in closed tubes is often used in specialized laboratories, having the undeniable advantage of reducing the use of toxic substances (hexavalent chromium and mercury salts). Also, this method allows the determination of COD at different range of concentration, while the classical method is applicable only to water with COD values between 30 and 700 mg/L.

Table 2. Comparison between COD and ST-COD results obtained in wastewater and surface water

Sample Type	**COD_{Cr} values** (mg O_2/L)		**Deviation** (mg O_2/L)	**Relative Deviation** (%)
	Conventional COD method	**ST-COD method**		
Waste Water				
Influent WWTP-Glina	456	469.8	-13.8	-2.98
	468	486	-18	-3.77
	470	481	-11	-2.31
	452	461	-9	-1.97

Efluent WWTP-Glina	79.6 75 72 74.8	74 70 68 69	5.6 5.0 4.0 5.8	7.29 6.90 5.71 8.07
Surface Water (Colentina River)				
Lake 1	38.5	33.4	5.1	14.2
Lake 2	36.2	31.8	4.4	12.9
Lake 3	35.6	32	3.6	10.65
Lake 4	35.2	31	4.2	12.7
Lake 5	36.8	32.2	4.6	13.33
Lake 6	38	32.6	5.4	15.3

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