

## The Dichromate Method *versus* the Photoelectrochemical Method: the Synergistic Influence of Turbidity and Chlorides on Chemical Oxygen Demand Analysis

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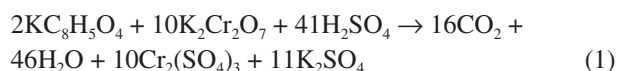
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This paper compares the dichromate method with the photoelectrochemical method (PeCOD), with regards to the influence of chloride and turbidity with chemical oxygen demand (COD) determination. Whereas the upper limits of chloride concentration are well established for both techniques, the influence of turbidity and the combined interference of underdosing chlorides and turbidity together have never been reported. When only potassium hydrogen phthalate or sorbitol were analyzed, the results show no significant difference in either method when 607 mg Cl<sup>-</sup> L<sup>-1</sup> or 230 NTU of turbidity were added to the samples within the range of 100-900 mg L<sup>-1</sup> COD. However, a combined effect of these two interferents leads to significantly different results, mainly for low COD range, as evidenced by the Student's *t*-test for paired samples (*p* = 0.05).

**Keywords:** advanced oxidation process, interference study, organic matter determination, wastewater characterization

### Introduction

Chemical oxygen demand (COD) is a very common analysis used in the sanitary and environmental areas to infer the organic matter content of natural waters and wastewaters. There are different ways to determine COD, but the worldwide reference method for effluent analysis is based on closed-reflux digestion followed by colorimetric analysis.<sup>1</sup> In detail, the standard COD method consists of the reaction between a liquid sample and a mixture of sulfuric and chromic acids (oxidant), in the presence of silver sulfate (straight-chain hydrocarbons oxidation catalyst) and mercuric sulfate (halide complexing agent), under 2 h of digestion block heating (150 °C). For instance, mineralization of potassium hydrogen phthalate (KHP) is presented in equation 1.



In spite of COD being an easy-to-run and low-cost

analysis system, some drawbacks are noteworthy: a hazardous waste containing residual Cr<sup>VI</sup>, Ag<sup>I</sup>, and Hg<sup>II</sup> in strongly acidic media is produced; Ag<sup>I</sup> salts are expensive; digestion time is relatively long; chlorides are normally present in wastewaters and constitute the most serious interferents; nitrogenous organic compounds (NOCs) are not quantitatively degraded through this technique, even under the triple catalyst effect (H<sub>2</sub>SO<sub>4</sub>, Ag<sub>2</sub>SO<sub>4</sub>, and heat).<sup>1,2</sup>

For this reason, it is desirable to search for environmentally friendly analytical methods that are able to yield accurate results, as recognized by the Green Chemistry philosophy.<sup>3</sup> Throughout recent decades, modifications from the dichromate method have been proposed, such as the replacement of dichromate salt with cerium salt<sup>4</sup> or with permanganate salt,<sup>5,6</sup> attempts at automation,<sup>7</sup> the use of bismuth-based adsorbents<sup>8</sup> or correction curves<sup>9</sup> to alleviate chloride interference, modifications of the digestion technique<sup>6,10</sup> or the quantification technique.<sup>11</sup> However, no modification shows any factual advantage in environmental or analytical terms that are sufficient enough to overcome the dichromate method protocol.

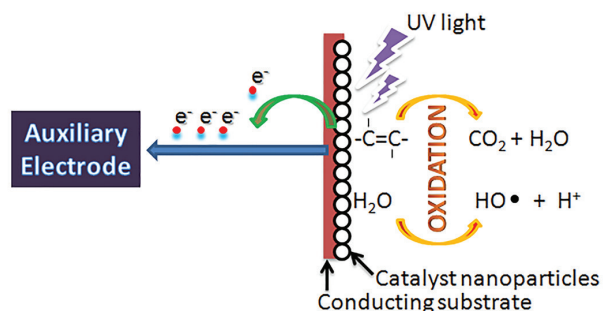
The total replacement of the dichromate method with others that have less impact, normally electrochemical

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techniques ones,<sup>12,13</sup> was also intended; but the proposals for the COD determination using other methodologies do not have the coverage and acceptance of the dichromate method.

The use of advanced oxidation processes (AOPs) for the degradation of recalcitrant organic compounds is not innovative, but the approach of these methodologies for the determination of COD is relatively recent.<sup>14-18</sup> Research projects carried out in Australia<sup>14,15</sup> resulted in a patented<sup>19</sup> photoelectrochemical oxidative degradation method, which is promising for the determination of COD in place of the dichromate method. The acronym PeCOD was chosen to represent this technique.

The PeCOD operation is based on heterogeneous photoelectrocatalysis, which uses titanium dioxide and ultraviolet radiation to generate highly oxidant radicals such as HO• in thin layer cells. Electrons involved in the photoelectrocatalytic process yield an electrical charge that is converted into mg O<sub>2</sub> L<sup>-1</sup>, proportionally to the mineralized organic matter content.<sup>15,16,20</sup> Figure 1 shows a scheme for this process.



**Figure 1.** Schematic design diagram for PeCOD™ analytical signal generation.

Commercial flow injection instruments based on the photoelectrochemical mechanism are already available, and

the PeCOD® L100 Assay Plus™ analyzer from Mantech Inc. (hereinafter, referred just as PeCOD™) was used in the present study.

Concerning precision and bias, relative standard deviation (RSD) is typically 8.8% for the dichromate method (KHP, 193 mg O<sub>2</sub> L<sup>-1</sup>), but it can increase up to 9.4% in the presence of chlorides (100 mg Cl<sup>-</sup> L<sup>-1</sup>).<sup>1</sup> For the photoelectrochemical method, the quality control criteria is an RSD up to 10%, but values of 2.97% are commonly achieved with COD calibrant solutions (sorbitol, 120 mg O<sub>2</sub> L<sup>-1</sup>). In addition, Table 1 summarizes the principal advantages and limitations for both the dichromate and PeCOD™ methods.<sup>1,20</sup>

PeCOD™ adopts the combination of the synergistic PeCOD effect<sup>21</sup> and the organic addition effect<sup>22</sup> by using a patented auxiliary solution that contains the supporting electrolyte (LiNO<sub>3</sub>) and oxidizable hydroxyl organic compounds (natural sugars).

Theoretically, the auxiliary solution should be responsible for surpassing the three principal drawbacks that the dichromate method is not capable of: promoting the complete oxidation of NOCs, causing the estimation of pollution charge to be more accurate; not generating hazardous waste at the end of the analysis; and overcoming chloride ion interference.<sup>22-25</sup> Indeed, the two former disadvantages are satisfactorily surmounted, but the chloride still remains as a critical source of errors for that analysis. In a quantitative basis, the maximum acceptable amount of chlorides for PeCOD operation is proportional to the COD range; this information is provided by the instrument manufacturer (Table 2).

However, the effects for underdosing chlorides as well as the combined interference of this ion with any other factor have never been reported.<sup>24</sup> Because the PeCOD™ uses a flow injection (FI) process and depends on the efficiency of the photoactivation effect, the sample turbidity

**Table 1.** General comparison between the two studied methods

Criteria	Dichromate COD method	PeCOD method
Waste generation	potentially toxic metals in strongly acidic media	aqueous solutions with low toxic potential
Operation cost, maintenance and consumables	low-cost reagents, simple instrumentation	patented instrumentation, high-cost replacement parts and consumables
Type of process	batch	continuous flow
Average time analysis for each sample / h	3	0.35
Efficiency to degrade nitrogenous analytes	unable to completely degrade NOCs	able to completely degrade NOCs
Labor qualification	less	more
Risk to operator	medium	low
Portability	difficult	easy
Interference	chloride and other reduced inorganic species, suspended solids	chloride, pH < 4.0, suspended solids

**Table 2.** Maximum acceptable amount of chlorides for the PeCOD™, according to the operation's range<sup>a</sup>

Code (color)	COD range / (mg L <sup>-1</sup> )	Ratio sample:electrolyte	Max Cl <sup>-</sup> allowed <sup>b</sup> / (mg L <sup>-1</sup> )
Blue	up to 25	4:3	350
Green	up to 150	1:1	400
Yellow	up to 1,500	1:9	2,000
Red	up to 15,000	1:49	10,000

<sup>a</sup>Adapted from reference 20; <sup>b</sup>after dilution with electrolytes the chloride concentration remains below 200 mg L<sup>-1</sup>.

can cause an adverse outcome, varying the intensity according to the assay conditions; nevertheless, the limits for the presence of suspended solids are not published.

The present work aims to highlight that even at acceptable concentrations of chloride and turbidity when regarding each one individually, the combined influence of both interferences can produce a synergistic effect that upsets the PeCOD™ performance. This kind of interference has not been taken into account, and constitutes a critical issue for COD analysis as the wastewater samples normally possess these above and beyond the described features. Assuming that the avoidance of hazardous chemical waste generation overcomes any other disadvantage from the PeCOD method, the replacement of the dichromate method with the PeCOD method must be attempted.

## Experimental

The chloride and turbidity effects were assessed via PeCOD and dichromate methods, using their respective standard substances, KHP and sorbitol (Synth, Brazil). PeCOD™ (Mantech Inc.) was used in the instrumental determination of COD. The dichromate method used 16 × 100 mm borosilicate culture tubes, a COD digestion block (TE-021, Tecnal) and a spectrophotometer (DR4000, Hach). Additional physicochemical parameters such as electrical conductivity (conductivity meter B330, Micronal), apparent color (spectrophotometer DR4000, Hach), pH (pHmeter 410A+, Thermo Orion), turbidity (turbidimeter 2100N, Hach), and total organic carbon (TOC, TOC analyzer 5000A, Shimadzu) were also measured. For weighing, an analytical balance (Explorer, Ohaus) was used. All solutions were prepared with ultrapure water (Academic, Millipore).

### Analytical curves and physicochemical analysis

Aiming for the comparison between the two studied methods, two kinds of analytical curves were made: control curves and test curves. Control curves were constructed from standard solutions containing 100, 200, 500, 700, and 900 mg L<sup>-1</sup> COD. Test curves were control curves

that contained proper additions of 360 g NaCl L<sup>-1</sup> stock solution and/or solid kaolin, for the chloride and turbidity influence assessments, respectively. In total, 12 curves for each analyte were made in duplicate, as shown in Table 3.

**Table 3.** Control and test curves setup, varying the concentration of chlorides and turbidity

Curve	Added NaCl/Cl <sup>-</sup> / (mg L <sup>-1</sup> )	Final turbidity / NTU
1		0
2		35
3	0/0	230
4		2,300
5		0
6		35
7	100/60.7	230
8		2,300
9		0
10		35
11	1,000/607	230
12		2,300

According to the PeCOD™ manufacturer's recommendation,<sup>20</sup> the pH of all solutions was within the operational limit of 4.0-10.0. TOC was measured only for the control curves (no chloride/turbidity additions), to avoid damages to the instrument.

### PeCOD™ determinations

For the PeCOD™ determinations, a commercial electrolyte solution was added to the blank, calibrant and standard solutions, according to the operation range of COD. The KHP and sorbitol standards were analyzed within the yellow range (COD < 1,500 mg L<sup>-1</sup>) according to the manufacturer's guidelines (Table 4).

### Student's *t*-test for paired samples

The paired *t*-test was used to compare the two datasets from the different analytical methods, sample-by-sample (paired), when the comparison between two means was not

**Table 4.** Preparation of blank, calibrant, and standard solutions for KHP and sorbitol, within the yellow range of PeCOD™ (COD < 1,500 mg L<sup>-1</sup>)

Substance	Aliquot in the final solution / mL		
	Blank	Calibrant	Standard (1:9)
Deionized water	50	–	–
Commercial calibrant	–	25	–
KHP/sorbitol	–	–	2
Commercial electrolyte <sup>a</sup>	450	225	18

<sup>a</sup>Commercial formulation containing water, natural sugars and lithium nitrate (up to 20%). KHP: potassium hydrogen phthalate; COD: chemical oxygen demand.

appropriate. In that case, the null hypothesis ( $H_0$ ) says there is no significant difference between the methods.

In this study, COD values from different analytes were compared by paired  $t$ -test, in order to evaluate whether or not the two methods were statistically different.

The difference ( $d$ ) between each pair of results obtained from different methods was determined. If the mean of  $d$  (i.e.,  $\bar{d}$ ) is close enough to zero, the calculated  $t$ -value ( $t_{\text{calc}}$ ) should be less than the tabulated critical  $t$ -value ( $t_{\text{crit}}$ ), within the defined confidence interval. Therefore,  $H_0$  is retained when  $t_{\text{calc}} < t_{\text{crit}}$  (i.e., the tested methods do not present significant statistical differences) or rejected when  $t_{\text{calc}} > t_{\text{crit}}$ .<sup>26</sup> The statistical  $t$ -value is calculated from equation 2:

$$t = \frac{\bar{d} \sqrt{n}}{s_d} \quad (2)$$

where  $\bar{d}$  is the mean of the differences between the pairs of results ( $d$ );  $s_d$ , the standard deviation of  $d$ ;  $n$ , the number of pairs.

The number of degrees of freedom was  $n - 1$ , and the confidence interval adopted was 95% ( $p = 0.05$ ).

## Results and Discussion

### Physicochemical parameters

All solutions were measured for pH, turbidity, apparent color, and electrical conductivity (EC); the results can be seen in Table 5.

**Table 6.** Average turbidity of the COD test for all analytes

Kaolin / (g L <sup>-1</sup> )	Expected turbidity / NTU	Final turbidity ± standard deviation / NTU (RSD / %)	
		KHP	Sorbitol
0.060	30	35 ± 12 (35)	34 ± 15 (44)
0.390	200	230 ± 40 (16)	230 ± 50 (22)
2.180	2,000	2,300 ± 600 (25)	1,900 ± 400 (22)

COD: chemical oxygen demand; RSD: relative standard deviation; KHP: potassium hydrogen phthalate.

**Table 5.** Physicochemical featuring of all solutions

Parameter	KHP	Sorbitol
Initial pH	4.3 ± 0.1	5.4 ± 0.3
Initial turbidity / NTU	0.07 ± 0.01	0.75 ± 0.50
Initial apparent color / (mg Pt-Co L <sup>-1</sup> )	2 ± 0	6 ± 0
EC for 607 mg Cl <sup>-</sup> L <sup>-1</sup> adjusted standards / (mS cm <sup>-1</sup> )	2.392 ± 0.072	2.070 ± 0.027

KHP: potassium hydrogen phthalate.

According to Table 5, all the analyte solutions obey the pH limit previously stated by the PeCOD™ manufacturer,<sup>20</sup> ranging from 4.0 to 10.0. For this reason, no adjustments are necessary. Solutions containing the maximum amount of added NaCl (1,000 mg L<sup>-1</sup>) have their EC ruled by this substance, regardless of other compounds in the mixture. Thus, EC can be used as a simple and non-destructive inference for chlorides when combined with a sample history report.

The final turbidity of the test COD solutions was adjusted by adding the correct mass of kaolin, resulting in three turbidity levels: 35, 230, and 2,300 NTU. The average values and standard deviations can be seen in Table 6.

Apparent color was measured and yielded a non-linear relationship with turbidity, but can be used for estimations when there is no available turbidimeter. TOC has a linear relationship with COD and can be used for the quality control of standards, however, instrumental limitations do not allow for the analysis of rich-chloride or rich-turbidity samples. The apparent color and TOC results are not shown.

### Control curves

The mathematical parameters for the control curves obtained through the dichromate COD method are showed in Table 7.

PeCOD™ provides no analytical signal to be processed outside the instrument; only the final COD value is shown. Thus, no control curve can be obtained through this technique.

**Table 7.** Parameters of the control curves obtained through the dichromate COD method

Analyte	Intercept	Slope	R <sup>2</sup>	Standard deviation (S <sub>y/x</sub> )	Limit of detection / (mg L <sup>-1</sup> )	Limit of quantification / (mg L <sup>-1</sup> )
KHP	0.0045	3.89375 × 10 <sup>-4</sup>	0.99978	0.00221	17	57
Sorbitol	-0.00189	3.84777 × 10 <sup>-4</sup>	0.99902	0.00465	36	121

KHP: potassium hydrogen phthalate; COD: chemical oxygen demand.

Effect on COD values from the individual additions of chloride or turbidity

#### Dichromate COD method with KHP

The control COD curve and test COD curves containing KHP provided recovery values that can be seen in Table 8.

In practically all cases, significant differences to the recovery were not obtained between the control COD and COD samples tested for chloride addition. As expected, significant differences due to chlorides can only be noticed above the concentration of 2,000 mg Cl<sup>-</sup> L<sup>-1</sup>,<sup>1</sup> in the

dichromate method, which is much higher than what was assessed in this study (607 mg Cl<sup>-</sup> L<sup>-1</sup>). The paired *t*-test confirmed that there was no significant interference in the COD tested for chlorides (Table 9).

The paired *t*-test showed no significant differences in recovery towards to turbidity increments (H<sub>0</sub> is retained), but the criterious analysis of Table 9 revealed a positive tendency of the COD values when the turbidity increased. This effect is more evident in the aliquot containing both the lowest COD value and the highest added turbidity; a difference of 44% was verified in comparison to the control COD value.

**Table 8.** KHP recoveries obtained through the dichromate method, when chloride or turbidity is added

Theoretical COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Control COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Recovery / %					
		COD tested for Cl <sup>-</sup>		COD tested for turbidity			
		60.7 mg L <sup>-1</sup>	607 mg L <sup>-1</sup>	35 NTU	230 NTU	2,300 NTU	
100	96	94	101	109	109	140	
200	104	101	100	101	104	119	
500	99	103	101	102	103	109	
700	100	100	100	104	103	104	
900	100	100	97	101	102	105	

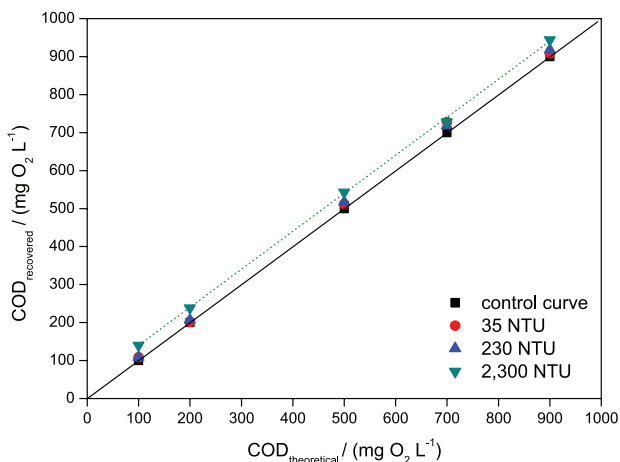
KHP: potassium hydrogen phthalate; COD: chemical oxygen demand.

**Table 9.** Parameters of paired *t*-test for KHP through the dichromate method, when chloride or turbidity is added

Control COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Recovery variation between control and test COD values / %					
	COD tested for Cl <sup>-</sup>		COD tested for turbidity			
	60.7 mg L <sup>-1</sup>	607 mg L <sup>-1</sup>	35 NTU	230 NTU	2,300 NTU	
96	2	-5	-13	-13	-44	
104	3	4	3	0	-15	
99	-4	-2	-3	-4	-10	
100	0	0	-4	-3	-4	
100	0	3	-1	-2	-5	
Paired <i>t</i> -test parameters ( <i>p</i> = 0.05)						
$\bar{d}$	0.2	0	-3.6	-4.4	-15.6	
s <sub>d</sub>	2.7	3.7	5.9	5	16.5	
n	5	5	5	5	5	
n - 1	4	4	4	4	4	
<i>t</i> <sub>calc</sub>	0.17	0	1.36	1.96	2.12	
<i>t</i> <sub>crit</sub>	2.78	2.78	2.78	2.78	2.78	
H <sub>0</sub>	retained	retained	retained	retained	retained	

KHP: potassium hydrogen phthalate; COD: chemical oxygen demand;  $\bar{d}$ : mean of the differences between the pairs of results; s<sub>d</sub>: standard deviation; n: number of pairs; n - 1: number of degrees of freedom; *t*<sub>calc</sub>: calculated *t*-value; *t*<sub>crit</sub>: tabulated critical *t*-value; H<sub>0</sub>: null hypothesis.

When the control curve and the turbidity test curves for KHP are plotted together (Figure 2) it is possible to see that the turbidity displacement of the recovered COD values was the same, independently of the theoretical COD value.



**Figure 2.** Comparison between the control curve and the turbidity test curves for KHP when using the dichromate method.

Complementarily, the slopes of the curves were virtually the same (the control curve was  $3.894 \times 10^{-4}$  while the test curve for 2,300 NTU of turbidity was  $3.892 \times 10^{-4}$ ), resulting in a marked parallelism; at the same time, the intercept of the test curve for 2,300 NTU (0.01961) showed a more than four fold increase, comparatively to the control curve (0.0045). Assuming that the kaolin is chemically unable to convert  $\text{Cr}^{\text{VI}}$  into  $\text{Cr}^{\text{III}}$ , the recovered COD increment only exists owing to the physical interference (light scattering).

#### Dichromate COD method with sorbitol

The control COD curve and test COD curves containing sorbitol provided recovery values that can be seen in Table 10.

According to Table 10, interference by chlorides is not easily noticed, but the increment in the turbidity provides

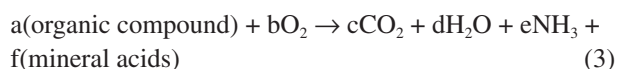
significantly different results from those of the 230 NTU, which can be corroborated by the paired *t*-test.

#### PeCOD method with KHP

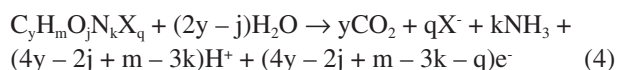
Table 11 shows the obtained recoveries for KHP through the PeCOD method.

The PeCOD method shows significant differences between the control COD and theoretical COD for KHP, resulting in high recoveries for the control (114 to 159%). KHP usually results in higher COD than that obtained for sorbitol, which is the recommended standard for PeCOD™ calibration.<sup>20</sup>

The theoretical oxygen demand (ThOD) of the organic compounds directly influences the sensitivity of PeCOD analysis. ThOD is estimated through the mineralization equation (equation 3), by the coefficient *b*.



For photoelectrocatalytic oxidation processes as PeCOD, it is also possible to use the stoichiometric oxidation presented by Zhao *et al.*<sup>15</sup> (equation 4) that provides the number of electrons transferred during the analyte degradation (net charge), which is also related to ThOD.



When two different compounds are tested as primary standard for analytical curves, the obtained slopes will be respectively proportional to ThOD and the net charge. For instance, 1 mol of sorbitol consumes 6.5 mol  $\text{O}_2$  (net charge = 26), while 1 mol of KHP consumes 7.5 mol  $\text{O}_2$  (net charge = 29), and for this reason the recovering obtained for KHP is higher than sorbitol. Thus, the accuracy obtained by PeCOD™ for a sample is likely to be dependent on the standard selected for the calibration.

**Table 10.** Sorbitol recoveries through the dichromate method, when chloride or turbidity is added

Theoretical COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Control COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Recovery / %					
		COD tested for Cl <sup>-</sup>		COD tested for turbidity			
		60.7 mg L <sup>-1</sup>	607 mg L <sup>-1</sup>	35 NTU	230 NTU	2,300 NTU	
100	100	93	88	95	102	117	
200	84	84	84	95	100	112	
500	93	93	100	98	100	105	
700	94	87	96	87	99	101	
900	92	96	92	96	96	99	

COD: chemical oxygen demand.



**Table 11.** KHP recoveries through the PeCOD method, when chloride or turbidity is added

Theoretical COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Control COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Recovery / %					
		COD tested for Cl <sup>-</sup>		COD tested for turbidity			
		60.7 mg L <sup>-1</sup>	607 mg L <sup>-1</sup>	35 NTU	230 NTU	2,300 NTU	
100	114	76	137	106	170	128	
200	159	142	153	120	130	149	
500	142	139	142	126	141	122	
700	134	125	139	127	120	106	
900	135	127	135	127	129	115	

KHP: potassium hydrogen phthalate; COD: chemical oxygen demand.

Interference of chlorides in PeCOD method is known (Table 2) and as expected, the data for KHP are unable to demonstrate any chloride interference, because the chloride concentration is less than 2,000 mg L<sup>-1</sup>. Test curves for chloride have a recovery variation comparable to that obtained for the control curve according to the paired *t*-test ( $H_0$  is retained).

Similarly to chloride, the paired *t*-test points out that there is no significant difference between the control and test COD recovery for turbidity ( $H_0$  is retained). However, in spite of the possible masking effect caused by the high difference between the theoretical and control COD recoveries, Table 11 shows that the test COD recoveries were systematically lower than the control COD recoveries. In such a case two possible effects should be regarded: the partial occlusion of the tubing and pump from PeCOD<sup>TM</sup>, and the physical interference in the heterogeneous photocatalysis process, due to the scattering UV radiation, which consequently offers less efficiency.

#### PeCOD method with sorbitol

The control COD recoveries for sorbitol through the PeCOD method were quite different from the theoretical COD ( $H_0$  is rejected), which is unexpected. Moreover, all test COD recoveries were significantly different and systematically lower than the control COD. The lowest recoveries are obtained for the turbidity level of 2,300 NTU.

Because of this inaccuracy, the maintenance of the piece of equipment was intensified, according to the manufacturer's recommendation.<sup>20</sup> Exhaustive washes of the tubing were made and the TiO<sub>2</sub> sensor was replaced whenever it was necessary. The sensor's life was shorter than the manufacturer had suggested (300 samples), probably due to the working conditions. As a result, new recoveries for sorbitol via the PeCOD method were obtained, however, the same behavior was verified. The results can be seen in Table 12.

Regardless of the high values of control COD recoveries in comparison with the theoretical COD, it can be assumed that the errors of control COD and the test COD recoveries are similar; therefore, the comparisons between them are valid.

#### Effect on COD values from the simultaneous addition of chlorides and turbidity

In order to evaluate the combined effect of chloride and turbidity on the recoveries at the same time, three conditions are tested: (i) the highest turbidity with no chloride addition; (ii) the highest chloride concentration with no turbidity addition; and (iii) both the highest turbidity and chloride concentration. Table 13 shows the recoveries obtained for KHP and sorbitol through both the dichromate and PeCOD methods, working at the limit condition concerning chloride (607 mg Cl<sup>-</sup> L<sup>-1</sup>) and turbidity (2,300 NTU), hereinafter named as the combined interference test COD.

**Table 12.** Sorbitol recoveries through the PeCOD method, when chloride or turbidity is added

Theoretical COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Control COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Recovery / %					
		COD tested for Cl <sup>-</sup>		COD tested for turbidity			
		60.7 mg L <sup>-1</sup>	607 mg L <sup>-1</sup>	35 NTU	230 NTU	2,300 NTU	
100	133	60	108	84	76	4	
200	135	71	110	90	92	54	
500	148	88	117	94	106	83	
700	142	93	116	106	106	87	
900	111	91	108	106	108	91	

COD: chemical oxygen demand.

**Table 13.** Combined interference test COD (chemical oxygen demand)

Theoretical COD / (mg O <sub>2</sub> L <sup>-1</sup> )	Recovery / %			
	Dichromate method		PeCOD method	
	KHP	Sorbitol	KHP	Sorbitol
100	112	124	0	0
200	122	106	41	27
500	110	104	86	83
700	111	101	65	81
900	105	100	102	89

KHP: potassium hydrogen phthalate.

The combined interference of chloride and turbidity through the dichromate method is observed when Tables 8, 10 and 13 are analyzed. As previously stated for KHP, turbidity or chloride additions result in recoveries that are not significantly different between the control COD and test COD recoveries, even at their highest individual concentrations (Table 8). However, when both interferents are added together under their highest concentrations at the same time, a synergistic effect is likely to take place, as can be seen in Table 13. In such a case the paired *t*-test shows significantly different recoveries between the test and control COD ( $H_0$  is rejected). Using sorbitol, the test COD with 2,300 NTU of turbidity (Table 10) presents similar recoveries when compared with the combined interference test COD (Table 13); therefore, the synergistic effect cannot be proven in such a case.

Concerning the PeCOD method, the test COD with KHP does not give significant differences after individual additions of turbidity or chloride (Table 11), according to the paired *t*-test. However, the combined interference test COD (Table 13) shows significant differences, as a result of the synergistic effect. Regarding sorbitol, all test CODs are significantly different according to the paired *t*-test. In addition, a careful examination of Table 12 shows that the test COD recovery at a turbidity of 2,300 NTU is lower than that observed for 607 mg Cl<sup>-</sup> L<sup>-1</sup> alone. Finally, the combined interference test COD recovery is the lowest, attesting to the synergistic effect once more. A null recovery (0%) is obtained for the corresponding solution with a 100 mg L<sup>-1</sup> theoretical COD (Table 13).

In summary, the synergistic effect noticed for the PeCOD method is very clear. The interference of chloride ions is partially diminished through a special ‘doping’ effect in the sensor, but there are limitations. At the same time, suspended particles can hinder light passage by scattering effect and adherence on the sensor, besides changing the flow of the fluids by clogging. Combination of these two interferences generates a negative synergistic influence on

the results, compromising the analysis.

#### Critical comparison between both methods

Adoption of the PeCOD<sup>TM</sup> as a complete replacement of the dichromate method could be interesting in several situations, but in many cases the dichromate method remains the most appropriate. Endorsing the PeCOD<sup>TM</sup>, NOC-containing samples must not be analyzed by the dichromate method because of the very low recoveries; the limit of quantification (LOQ) for the PeCOD<sup>TM</sup> is lower than the dichromate method, allowing for the analysis of the low level COD samples such as groundwater and drinking water; the non-generation of hazardous waste is one of the most important advantages of PeCOD<sup>TM</sup>. Concerning disapproving aspects of PeCOD<sup>TM</sup>, samples with reasonable contents of chloride and suspended solids will provide more inaccurate results from the PeCOD technique, besides instrumental damage; in such cases, using the dichromate method must be considered. When both methods can be used and no technical restriction exists, environmental, financial, and logistical aspects must take precedence.

Turbidity interference is easier to overcome in the dichromate method than in the PeCOD method. Eventually formed organic flocs are frequently dissolved after two hours of digestion through dichromate method, and the inorganic particles normally settle on the bottom of the reaction vessel, causing little or no interference in spectrophotometric measuring. However, the FI system from PeCOD<sup>TM</sup> can undergo clogging; furthermore, the heterogeneous photocatalysis efficiency is decreased, due to light scattering and the adsorption of solids on the sensor.

#### Conclusions

Both the PeCOD and dichromate methods have well established upper limits for the presence of chloride, but the simultaneous influence of turbidity and chloride underdosing



have not been explored before this study. Recommended doses of chloride or turbidity below 2,300 NTU do not promote significant differences in the COD for KHP or sorbitol. However, a combination of these two effects leads to significant differences in the COD results: the combined interference shows a synergistic effect and critically alters COD recovery, even when the chloride and turbidity are below the recommended limits. The effect is particularly damaging for the analysis of low level COD samples through PeCOD. Under combined interferent condition, the PeCOD method is analytically and financially more greatly affected, because of the frequent wearing of the sensor and pumping system, short-term maintenance and due to the replacement of parts, resulting in high operational costs.

Concerning physicochemical parameters, EC can be used as an inference of high chloride concentration in routine analysis. Apparent color has a non-linear relationship with turbidity but can be used for the estimation of the amount of suspended solids when no turbidimeter is available.

Finally, how to choose the best COD methodology is not an obvious task; consideration of the advantages and limitations of both methods has to be performed before the decision can be made. Unfortunately for the environment, the dichromate method is still widely used and is yet to have been surpassed in terms of usage.

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