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RESEARCH ARTICLE

Validation of a Modified Procedure for the determination of Chemical Oxygen Demand using standard dichromate method in industrial wastewater samples with high calcium chloride content

A Gnanavelu[1], T S Shanmuganathan[2], V Deepesh[1]*, S Suresh[1]

1 Regional Laboratory, Central Pollution Control Board, Regional Directorate, Bengaluru, 560079, Karnataka, India
2 QA Laboratory, Manali Petrochemicals Ltd, Chennai, India

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* **Corresponding author**.

deepeshv77@yahoo.co.in

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Abstract

Background/ Objectives: Chemical Oxygen Demand (COD) is a widely used aggregate organic pollutant index in national discharge standards and is one of the critical parameters for water quality assessment. The conventional COD determination by wet oxidative method encounters the problem of chloride interference in water samples with high chloride content. The dichromate reflux method oxidizes 85-95% of organic matter and also 100% of chloride ions in the samples, without an appropriate chloride masking strategy. The standard method cannot measure COD accurately in samples containing more than 2000 mg L^{-1} chloride. The present study demonstrates and validates a modified procedure for the determination of COD in industrial sample with high calcium chloride content and low organic load. **Method:** Petrochemical industries manufacturing Propylene Oxide and Propylene Glycol via chlorohydrin route generate wastewater with high calcium chloride content. Due to high chloride content, the standard analysis method could not produce reliable data for COD values with known precision and accuracy. The standard method based on dichromate was modified, with an additional mixing step for a specified time to enhance the chloride masking by mercuric sulphate. Undiluted sample (20 mL) was mixed with the required amount of mercuric sulpahte to maintain 10:1 ratio to chloride content and 10 mL of sulphuric acid at 150-175 RPM for 20 minutes at room temperature to increase the contact time/ chloride masking. Method validation attributes of the modified procedure were assessed and found to be complying with the acceptance criteria. **Findings:** We developed a modified procedure for the standard dichromate based chemical oxygen demand (COD) determination in industrial wastewater samples rich in calcium chloride. An additional mixing step is introduced in the standard procedure to enhance the chloride masking with mercuric sulphate in samples containing high chloride. The amended procedure resulted in accurate COD values in samples with low organic load, rich in calcium chloride and the modified

method was successfully validated. **Novelty**: The modified procedure with mixing step to enhance chloride masking was found to be satisfactory for determining COD in calcium chloride-rich industrial effluent.

Keywords: Chemical Oxygen Demand (COD); Chloride interference; Modification of standard method; Wastewater analysis; Calcium chloride; Validation

1 Introduction

Aggregate organic pollutant load in water can be assessed by measuring the water quality parameter chemical oxygen demand (COD), which is widely used as a national discharge standard to investigate the organic pollution in water [1]. It is used widely as a measure of organic pollutant load in wastewaters [2,3]. In a regulatory perspective, COD is considered as a critical parameter for water quality investigations [4]. The Central Pollution Control Board (CPCB) of India has mandated COD as one of the critical parameters to enforce environmental discharge limits. Typically, COD is defined as the number of oxygen equivalents required to oxidize organic components in a sample [1,5,6] and represents the measure of organic pollutant load in water [4]. COD is considered as a more superior representative of organic matter in water than biochemical oxygen demand (BOD), total organic carbon (TOC) [7], and total oxygen demand (TOD) [8].

The conventional method of COD determination is based on the measurement of an excess oxidizing agent such as dichromate left in the sample-reactant mixture [1] after refluxing. In the conventional COD analytical method, the feasibility of various oxidants like dichromate, permanganate, ceric acid, iodate, persulphate, etc., were already investigated. Because of the easy applicability to a wide range of wastewaters and better oxidation potential, dichromate is the most preferred oxidant for COD determination [7]. Nevertheless, conventional analytical methods have bottlenecks associated with the lengthy procedure, long turnaround time, use of toxic reagents [1,5,9], low detection sensitivity [5], inconsistent oxidation efficiency [10], chloride interference [4], and inherent potential for secondary pollution [4,5,9,11]. However, the most crucial disadvantages of conventional COD analysis are the susceptibility to the presence of interfering substances, inadequate oxidation of certain organic compounds, and substantial error due to oxidant-consuming inorganic matter, especially chloride ion [7]. There are several studies reporting alternate methods for COD analysis. Method free of mercury and chromium (VI), employing manganese (III) as oxidant and silver nitrate as the masking agent for chloride ions was reported by Kolb et al, [12]. The method was tested with the standard potassium hydrogen phthalate (KHP) and different types of wastewater samples with reproducible results in the range of 20–500 mg L^{-1} with a mean recovery rate of 84.1% in the presence of 1000 mg L^{-1} chloride [12].

Advances in instrumentation and analytical innovations opened up several alternative instrumental methods to determine COD. There are reports on several methods using electrochemical sensors to analyze COD [1]. Alternative methods based on photocatalytic or electrochemical principles have also been experimented, proposed, and probed. Though these alternative methods have several advantages over the conventional analytical methods, they are not foolproof and have several inherent demerits [5]. There are studies on the modification of standard methods with alternative digestion techniques and advanced titration methods. COD determination using ultrasonic digestion and titration based on oxidation-reduction potential (ORP) was reported with COD results well matched with those obtained using conventional methods [13]. The inception of modern detection techniques including chemiluminescence, microwave digestion, and ultrasound dissolution, are yet to yield a breakthrough in developing a feasible and practical COD determination method [9]. Nevertheless, the conventional

dichromate method, in spite of all the drawbacks is still the most preferred method [4] due to rather simple and straightforward approach with bare minimum instrumentation.

Any analytical method that attempts to determine COD by strong oxidative agents in saline water or any water with high chloride content encounters the problem of chloride interference. The standard analytical procedure [14] for the determination of COD by the dichromate reflux method oxidizes roughly 95-100% of organic matter and will also react with chloride ions present in the sample. So, it is not practically possible to measure COD accurately in samples containing chloride more than 2000 mg L^{-1} [15] without an effective chloride masking strategy. Chloride found in the wastewaters reacts with dichromate to form chlorine gas in addition to the interaction with the organic matter [7]. If chloride ions are not masked, silver ions in the COD acid will be scavenged and precipitated as silver chloride by the chloride ions in the sample. This will greatly impair the catalytic effect of silver ions in the acid [7]. Due to these interferences, the presence of chloride in the sample results in positive and/ or negative errors in the determination of the COD parameter [7]. In the standard method, these chloride interferences are circumvented by the addition of mercuric sulphate as a complexing agent in the ratio 10:1. However, the method is applicable only for samples having chloride not more than 2000 mg L^{-1} [15].

M/s. Manali Petrochemicals Limited (MPL), India, is a petrochemical industry engaged in the manufacturing of propylene oxide (PO), propylene glycol (PG), and polyol (PoL) as major products. During the manufacturing process of propylene oxide, propylene vapour is made to react with hypochlorous acid to give propylene chlorohydrin. The solution obtained is saponified with milk of lime to yield propylene oxide. Propylene oxide formed is stripped off using steam and distilled further to separate the final product. Hence the effluent generated from the propylene oxide plant will have high calcium chloride content. The concentration of calcium and chloride ion varies between 15000-16000 and 29,000-30,000 mg L^{-1} respectively. Also, very few amount of propylene oxide will react with water to produce propylene glycol. The organic load in PO industry effluent is due to the presence of propylene glycol and the typical influent COD value varies between 1500-2000 mg L^{-1}. Due to high chloride content, reliable data for COD values of influent and effluent could not be produced with known precision and accuracy. Hence, there is a need for a modified COD procedure for samples containing high calcium chloride content that would produce a satisfactory result with known precision and accuracy. The method so modified also has to satisfy and comply the requirements of industries and the regulatory authorities [16]. Many techniques, including dilution of the sample [7], removal of calcium chloride by addition of sodium hydroxide, or by applying chloride correction [17] were tried. But reproducible, reliable results exemplifying regulatory performance could not be obtained. In the light of more stringent discharge standards prescribed by the regulatory regime, there is a pressing need for an accurate and reproducible method of COD determination to overcome the interference from chloride ions particularly in industrial wastewater samples.

Early studies have shown that the degree of oxidation of chloride is not predictable under practical conditions [17]. If the masking reaction is incomplete, the expected or measured COD value will be always higher than the true value, due to the utilization of oxidizing agent for the conversion of chloride to chlorine gas. Erroneous COD results were reported for bromide-rich industrial wastewater samples using the standard COD determination method [15]. Bromide in water is also reported to interfere with the standard COD determination and masking the interference by mercuric sulphate is reported to be ineffective [15]. Such specific interferences cannot be overcome by lower sample volumes or dilution strategies as it was reported that the major sources of uncertainty in COD analysis is from repeatability at high concentration level and volumetric steps at low concentration level [18].

The present study aims to modify, optimize the conventional COD analytical method using dichromate to accurately assess the COD in the high chloride wastewater of the propylene oxide manufacturing industry. When the method is tweaked to suit this particular sample matrix, validation of the method is inevitable. Method validation is an important aspect of analytical chemistry to ensure suitability for its intended use [19]. Method validation is essentially a process of testing a measurement procedure to assess its performance and to make sure that performance is acceptable [20]. There are situations when the standardized test method cannot be used for a sample matrix containing particular constituents or characteristics. This warrants method validation or revalidation when modifications are made to a standard method [21] before inducting the modified method in to routine use in accordance with the specific guidelines of validation [22]. The objective of the present study is to demonstrate and validate a modified procedure for the determination of COD with samples having high calcium chloride content and low COD values (< 250 mg L^{-1}).

2 Materials and methods

As per the Standard Methods for the Examination of Water & Wastewater [14] COD test procedure (APHA 5220 B&C), chloride interference is avoided by complexing chloride ion with mercuric sulphate before refluxing the sample. The standard procedure specifies to add 1g mercuric sulphate for 50 mL of a sample containing 2000 mg L^{-1} chloride so that a ratio of 10:1 mercuric

sulphate to chloride is maintained. The sample is refluxed in an acid medium with a known excess of dichromate oxidant and after digestion, remaining un-utilized dichromate is titrated with ferrous ammonium sulphate using ferroin as indicator to determine the amount of dichromate consumed and oxidized organic matter is calculated in terms of oxygen equivalent.

2.1 Standard test procedure

Sample (20 mL) is mixed with 400 mg of mercuric sulphate and 10 mL of sulphuric acid containing silver sulphate (COD acid) is added slowly over an ice bath and mixed thoroughly to dissolve mercuric sulphate. Standard potassium dichromate (10 mL of 0.25 N) oxidant is added followed by 20 mL of COD acid. The mixture is thoroughly mixed and refluxed for 2 hours at 150°C. This procedure is applicable for samples having chloride concentration up to 2000 mg L^{-1}. If the chloride content is higher than 2000 mg L^{-1}, it is recommended to take the lower volume of sample or the sample has to be diluted, which may introduce pipetting and/ or dilution errors. The standard method has not specified any conditions for the masking reaction to circumvent the chloride interference.

In order to overcome the matrix interference, the standard method for the determination of COD is modified to suit effluent samples with high calcium chloride content. In the proposed modification, the sample was taken without any dilution and after adding the required amount of mercuric sulphate, a mixing step is introduced. During the mixing, the sample is subjected for constant agitation/ shaking at room temperature (27°C) on an orbital shaker for a specified period before the addition of the oxidant. After the mixing, standard oxidant is added to the sample mixture and refluxed under the prescribed conditions.

2.2 Modified test procedure

To 20 mL of sample containing 30,000 mg L^{-1} chloride content, 6 g of mercuric sulphate was added to maintain the 10:1 ratio between mercuric sulphate and chloride. To this, 10 mL of sulphuric acid (COD acid) was added slowly over an ice bath and the sample was agitated at 150-175 RPM for 20 minutes over an orbital shaker (Micra, India) to increase the contact time/ reaction between chloride and mercuric sulphate. Then, 10 mL of 0.25 N standard potassium dichromate solution was added to the sample over an ice bath. The remaining 20 mL of COD acid was added to the mixture and subjected to refluxing for 2 hrs. at 150°C. After refluxing, the mixture was diluted twice its volume, cooled and excess dichromate was titrated against 0.1 N standard ferrous ammonium sulphate, using ferroin as indicator.

2.2.1 Mixing time

In order to determine the optimum reaction time for complete masking of chlorides, trials (n=10) were conducted with standard COD solution (150 mg L^{-1}) with a spiked chloride content of 30,000 mg L^{-1} and the reaction time was varied between 5 to 20 minutes with constant agitation/ shaking at 150-175 RPM.

2.3 Method validation

Trials were conducted (n=9) with standard method on synthetic samples with the known concentration of COD, 150 mg L^{-1}, spiked with 4.5% (w/v) calcium chloride. All the results were on the higher side showing the positive interference due to chloride interference. The mean measured value was 309 mg L^{-1}, the standard deviation was 116 and the difference between true and observed value was 106 (%). As per the WHO guidelines [23,24], characteristics that should be considered for the validation of the analytical method are linearity, accuracy, bias, precision, detection limit, system suitability, and robustness [20]. The proposed modified method was validated by determining the following validation attributes.

Linearity: Linearity of an analytical method is the ability to elicit test results directly proportional to the concentration of the analyte in the sample. Recommended, minimum correlation coefficient value for linearity is 0.995 [14].

Precision: It is defined as a measure of the degree of agreement among replicate analysis of a sample, run during a single session by a single analyst, with identical reagents and equipment. Method precision was assessed by replicate (n=10) determinations by varying chloride concentration at different known COD concentrations. Acceptable criteria for method precision is that the relative standard deviation RSD (%) should not be more than 5.0 [14].

Repeatability: It refers to the use of analytical procedure within the laboratory over a short period of time using the same analyst and same equipment. In order to carry out the determination, COD solution of concentration, 250 mg L^{-1} was made with three different concentrations of chloride (25000, 30000, and 35000 mg L^{-1}). Repeatability was evaluated by performing replicate determinations (n=10) and assessment of Horwitz ratio [25].

Recovery: To ascertain method suitability, different concentrations of chloride with different concentrations (n=8) of known COD solution was prepared and recovery (%) efficiency was evaluated as per the standard guidelines [26].

Accuracy: It is the estimate of how close a measured value is to the true value [14] and it is often expressed in terms of recovery (%) and RSD.

Specificity: It is the ability of a method to measure accurately and specifically the analyte of interest in presence of other components that may be expected to be present in the sample matrix. To demonstrate that, the specificity of the analytical method is unaffected due to modification, COD determination was carried out with test samples with known COD concentration and sample blanks spiked with 4.5 % calcium chloride (w/v). Calcium chloride in the industrial wastewater ranges from 2.5-4.5 % and the specificity trials were done with the highest calcium chloride concentration.

Limit of detection (LOD): The detection limit is the smallest quantity of an analyte that can be detected with 99 % confidence [14]. In order to calculate LOD, test samples with different COD concentration were prepared with a chloride concentration of 35000 mg L^{-1}.

Robustness/ ruggedness: It is a test to determine the stability of the result produced when steps in the method are varied [14]. Robustness is an important attribute of a method if it is to be proposed as a standard or reference method. When compared to the original procedure, the only modification introduced is the mixing/ agitation step. Hence to finalize the masking reaction time, trials (n=9) were carried out by preparing a known solution of COD with 4.5 % (w/v) calcium chloride and COD assessments were made using the modified procedure.

3 Results and Discussions

The modification proposed in the standard COD method is the introduction of a mixing/ agitation step and based on the trials conducted, a mixing time of 20 minutes at 150-175 RPM gave reproducible COD values with a mean measured value of 143 mg L^{-1} against the true value of 150 mg L^{-1} [Table 1]. The deviation (%) between the measured and true value is 4.6 which is well within the acceptable difference of 5.0% [14]. Method validation trials for this modified method also yielded a positive outcome. In order to calculate method linearity, test samples (n=8) with varying COD concentration were prepared with chloride content of 35,000 mg L^{-1} and compared the measured value. The linearity trials returned a correlation coefficient (R2) value of 0.998 with a slope of 0.9460 shows that the method is linear [Figure 1].

Table 1. Measured COD value at different mixing time against true value of 150 mg L^{-1} COD

Mixing Time (minutes)	5	10	15	20
Trial 1	260	140	140	140
Trial 2	286	140	140	140
Trial 3	320	136	140	144
Trial 4	196	136	144	144
Trial 5	280	144	140	140
Trial 6	420	140	140	144
Trial 7	560	144	140	145
Trial 8	264	136	140	144
Trial 9	196	140	144	149
Trial 10	188	140	140	144
Mean value (mg L^{-1})	297	140	141	143

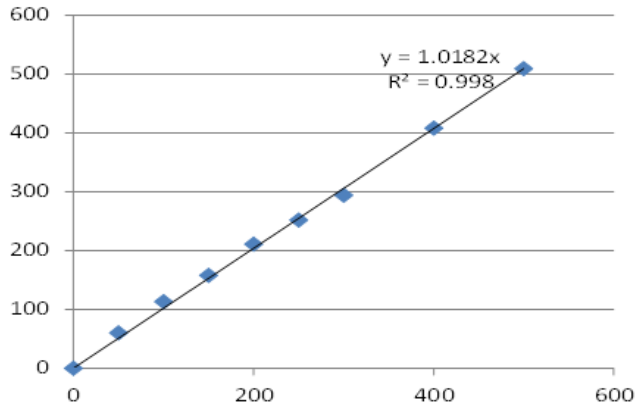

Fig 1. Method linearity

The outcome of trials to determine the precision of the modified method, in terms of RSD, show that sample precision was within 5.0% [Table 2].

Table 2. Trials to determine precision, reproducibility & recovery of the modified method

COD true value (mg L^{-1}) / Chloride (mg L^{-1})	50	100	150	200	250	300	400	500
2000	53.4	103	142	202	247	301	396	493
5000	50.8	102	151	205	246	289	392	486
10000	54	108	153	204	255	293	399	495
20000	55	103	160	196	249	292	405	493
25000	52	108	149	200	260	313	407	510
30000	53	113	158	199	252	294	401	509
35000	58	112	153	214	263	316	409	510
Mean	53.7	107.0	152.3	202.9	253.1	299.7	401.3	499.4
SD	2.3	4.5	5.9	5.8	6.5	10.8	6.1	10.0
RSD	4.3	4.2	3.9	2.9	2.6	3.6	1.5	2.0
Recovery (%)	104	103	95	101	99	100	99	99

Repeatability was calculated by determining COD values of different concentrations of chloride solutions spiked with a known amount of COD primary standard. Repeatability trials show that Horwitz ratio (HorRat) is within the acceptable limit of 2.0% [Table 3]. The trials for reproducibility also show that Horwitz ratio (HorRat) is within the acceptable limit of 2.0% [Table 3].

Table 3. Repeatability of the modified method

Determinants	Chloride concentration (mg L^{-1})		
	25000	30000	35000
Mean value	260	251	263
Std. Deviation	3.5	5.0	2.76
Observed RSD	1.38	1.99	1.05
Calculated RSD	6.93	6.96	6.91
Horwitz ratio (HorRat)	0.2	0.29	0.15

The recovery (%) efficiency for various combinations of chloride and COD concentrations were found to be between 95 to 105% [Table 2]. Assessment of method accuracy trials in terms of recovery (%) was within 95-105 and the RSD (%) was below 5.0 [Table 2]. From the specificity trials, it was observed that the sample blanks were not yielding any positive response for COD. This exemplifies, that there is no interference from calcium chloride and the method is very specific for COD in samples with high calcium chloride content. The limit of detection (LOD) of the method was calculated from the standard deviation of regression line/ slope as 17.8 mg L^{-1}. In order to find the stability of the result produced when steps in the method

are varied, the method ruggedness (Robustness) test was carried out by varying the reaction time. Test results shows that the mixing of the reaction mixture in an orbital shaker with 150-175 RPM for 15-20 minutes is essential for completion of the reaction. It was observed that, optimum chloride masking happened around 150 RPM and optimum agitation was fixed between 150-175 RPM for 20 minutes for the proper mixing and to avoid spillage of sample. The method validation attributes like repeatability, reproducibility, linearity, accuracy, precision, and recovery of the modified method were reviewed, checked, and are in compliance as per the guidelines and method validation criteria [Table 4].

Table 4. Summary of compliance to validation criteria

Parameter	Acceptance criteria	Result	Remarks
Repeatability	HorRat <2.0	< 2.0	Complied
Reproducibility	HorRat < 2.0	< 2.0	
Recovery	95-105 %	95-104 %	
Linearity	> 0.995	0.998	
Precision	RSD < 5.0 %	< 5.0 %	
Accuracy	RSD < 5.0 %	< 5.0 %	

The present study proposes a modified procedure of COD determination especially for industrial wastewaters containing high calcium chloride content and low organic load. The modified procedure inducts a step for agitation/ mixing to enhance the reaction between chloride ions and mercuric sulphate. A similar strategy was earlier reported [27], the mixing/ pretreatment step was introduced in the standard procedures using silver sulphate in seawater for removing halides. The study reported a 60-90 minutes mixing step at room temperature and 5-10 minutes settling time as pretreatment for removing halides from seawater samples [27]. The modified procedure was subjected to several trials and various method validation attributes were assessed and found to be complying the validation acceptance criteria. However, the use of mercuric sulphate for masking chloride interference as per the standard method is used in this modified procedure and the precautions to recover and safe disposal of the toxic remnants from the spent reaction mixture has to be followed as per the national and international regulatory guidelines.

Due to the critical nature of the COD parameter in environmental compliance monitoring, it is one of the commonly used indexes to assess environmental water quality [11] and COD is a widely used surrogate measure for carbon bioavailability in environmental matrices [28]. COD determination in complex industrial wastewater has been a challenge due to the interference from components inherent in the sample matrix and there is an urgent need for a simple, reliable, and fast method [9] to overcome the issues with several industrial wastewaters. Unlike chloride interference, there is no satisfactory approach to circumvent bromide interference in COD determination of bromide-rich industrial wastewater [15]. In a study, strategies like masking and correction were investigated for the effectiveness in suppressing bromide interference during COD analysis and suggested the correction strategy to eliminate bromide interference in standard COD determination [15]. In chloride-rich oilfield wastewater, TOC was proposed as an alternate index for COD and studies reported an acceptable correlation between TOC and COD in oilfield wastewater [11]. A study by Zhang et al, reported the feasibility of dichromate method using low concentration oxidant for high chloride oilfield wastewater [29]. When COD determination on several wastewater was done with manganese (III) as oxidant and silver nitrate for chloride removal, a high correlation (R2 = 0.9935) to the standard method with a mean recovery rate of 78.1% (±5.2%) was reported [12]. However, the precipitation of silver chloride warranted separate oxidation of the suspended/ colloid matters and the dissolved organic substances in the supernatant. It was reported that, this benign alternate method yielded high correlation and reproducibility with existing instrumentation [12]. Another study reported the removal of chloride ion as hydrochloric acid gas from acidified sample solutions at 150°C in a closed reaction tube and captured by a bismuth-based adsorbent suspended above the heated solution [30].

Research on alternate COD determination methodology has put forth several alternatives. The research and development activities emphasized on new innovative methods using a high degree of instrumentation and modification to the conventional method including a proposal to use other related aggregate organic indexes like TOC in place of COD. Report on COD determination of wastewater using ultrasonic digestion followed by ORP based titration resulted in COD values within 80-90% of those obtained using standard methods [13]. Special electrodes developed for organic electro-catalytical oxidation was used as an amperometric sensor, coupled with flow injection, to determine the COD of wastewater. This method under optimized conditions exhibited a linear range of 50–2000 mg L^{-1} with LOD of 20.0 mg L^{-1} and the COD values were within ±5% of those values given by the conventional COD method. This method was reported to have a short analysis time, simplicity, low secondary pollution, low reagent consumption, no pretreatment step, easy automation, and long sensor life [31].

There are promising innovative methods of COD determination which are better than the standard method in terms of simplicity, automation opportunities, avoidance of hazardous chemicals, low secondary pollution potential, etc. However, there is considerable dependence on a medium to a high degree of instrumentation and the associated resource requirements and maintenance. There is a need to develop a clean method of COD determination from the available option of alternate methods and has to be harmonized as a standard method after the mandatory validation trials and feasibility checks.

4 Conclusion

At present, there are no harmonized, clean, alternate COD determination method and as long as COD is considered as a critical index for environmental quality, standard method of COD determination has to be employed. In this study, a modification to the standard method is proposed to circumvent the chloride interference in calcium chloride-rich industrial wastewater from the propylene oxide industry. It is emphasized that such a modified procedure has to be employed for COD determination in industrial wastewater with inherent matrix interferences till harmonized, alternate methods are made available. The secondary pollution potential from the standard methods and its modified versions need to be addressed properly and the toxic wastes are to be managed as per the prevailing environmental regulations for waste disposal. The modified dichromate procedure using mercuric sulphate as a masking agent, with a well-defined mixing step effectively masked the chloride interference in the tune of 35000 mg L^{-1} (as calcium chloride) in industrial wastewater and resulted in validated COD estimation with known precision, accuracy and reproducibility.

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