

# Determination of Chemical Oxygen Demand in Spent Caustic by Potentiometric Determination

Hamed Harrafi, Masoumeh Khedri, Karim Karaminejad

**Abstract**—Measurement of the COD of a spent caustic solution involves firstly digestion of a test sample with dichromate solution and secondly measurement of dichromate remained by titration by ferrous ammonium sulfate [FAS] to an end point. In this paper we study by a potentiometric end point with Ag/AgCl reference electrode and gold rode electrode. The potentiometric end point is sharp and easily identified especially for the samples with high turbidity and color that other methods such as colorimetric in this type of sample do not result in high precision. Because interim of titration responds quickly to potential changes within the [Cr+6/Cr+3& Fe+2/Fe+3] solution producing stable readings that is lead to accurate COD measurement. Finally results are compared with data determined using colorimetric method for standard samples. It is shown that the potentiometric end point titration with gold rode electrode can be used with equal or better facility

**Keywords**—chemical oxygen demand, spent caustic and potentiometric determination

## I. INTRODUCTION

IN environmental chemistry, the chemical oxygen demand [COD] test is commonly used to indirectly measure the amount of organic compounds in water. Most applications of COD is to determine the amount of organic pollutants found in surface water [e.g. lakes and rivers] or wastewater, making COD a useful measure of water quality. It is expressed in milligrams per liter [mg/L], which indicates the mass of oxygen consumed per liter of solution [1].

Spent caustic is a waste industrial caustic solution that has become exhausted and is no longer useful [or spent]. Spent caustics are made of sodium hydroxide or potassium hydroxide, water, and contaminants. The contaminants have consumed the majority of the sodium [or potassium] hydroxide and thus the caustic liquor is spent, for example, in one common application H<sub>2</sub>S [gas] is scrubbed by the NaOH [aqueous] to form NaHS [aq] and H<sub>2</sub>O [l], thereby the caustic is consumed. Refinery spent caustic comes from multiple sources: the Merox processing of gasoline; the Merox processing of kerosene/jet fuel; and the caustic scrubbing/Merox processing of LPG [2, 3].

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In these streams sulfides and organic acids are removed from the product streams into the caustic phase. The sodium hydroxide is consumed and the resulting wastewaters [cresylic for gasoline; naphthenic for kerosene/jet fuel; sulfide for LPG -spent caustics] are often mixed and called refinery spent caustic [3, 4].

Spent caustic streams from refineries typically have a high chemical oxygen demand [20- 500 g/L] and contain chemicals that are hazardous, inhibitory, and/or bio-refractory. The chemicals of concern in the spent caustic wastewater include reduced sulfur compounds such as sulfides and mercaptans as well as organic species such as the sodium salts of naphthenic and cresylic acids [5].

## II. EXPERIMENTAL

### A. Samples and standards

Spent caustic waste samples from Merox processing of LPG sweetening in gas refinery in Iran South Pars Gas Company in Asaluyeh, were selected for COD analyzing.

The standard solutions were made up on potassium hydrogen phthalate. Therefore to a 1000 ml volumetric flask, add  $3.40 \pm 0.01$  g of potassium hydrogen phthalate [previously dried at 105 °C for 2 hours] to approximately 950 ml of water. Make to 1000 ml with distilled water [theoretical equivalent to 4000 mg/l COD][6].

### B. Reagents and materials

Water used for blank determinations and preparation of control standards should show negligible interference. Water with conductivity of less than 2  $\mu$ S cm<sup>-1</sup> and total organic carbon content of less than 1 mg/l has been shown to be satisfactory. Glassware used for the preparation and storage of water should be cleaned with chromic acid solution. In this study we used the mixed reagent to prepare this reagent, in a 2-litre flat-bottomed borosilicate flask filled with  $250 \pm 10$  ml of water, we added  $6.12 \pm 0.01$  g of potassium dichromate and  $7.5 \pm 0.5$  g of silver sulfate. We whirled the contents of the flask to mix. Cautiously, with frequent swirling of the solution, we added  $750 \pm 25$  ml of sulfuric acid. The contents of the flask should be well swirled, in order to dissolve the silver sulfate completely. This mixed reagent should be stored in the dark in a glass bottle [6].

We employ additional mercury [II] sulfate for removing of chloride interferences when the 2-ml aliquot taken for analysis contains more than 1 mg of chloride such that the ratio of mercury [II] sulfate to chloride is 40 to 1[7].

### C. Apparatus

Thermostatically controlled [WTW CR3200] heating block capable of accommodating the digestion tubes such that the level of the liquid in the tube is coincident with or below the surface of the block. The block should be controlled to give a digest temperature sufficient to gently reflux the oxidation mixture. A temperature of  $150 \pm 3$  °C is suitable.

Potentiometric titration was performed with a computer-controlled digital Metrohm 888 titrator with a combined electrode Au/Ag- AgCl system.

All absorbance measurements were made with a Hach DR2800 digital spectrophotometer.

### D. Sample preparation

We Placed 2 ml of sample [or standard and blank water] in a 10 ml refluxing tube or in a special COD tube [close digestion tube] and after that added some powder of HgSO<sub>4</sub> [depend on the chloride content]. Then we whirled and mixed well. And finally added 3.7 ml mixed reagent solution to the tube placed in ice cubes.

We closed the tube securely, whirled the tube to mix the contents and placed in the heating source. Reflux was done for  $120 \pm 10$  minutes. Then we removed the tubes out and allowed the contents to be cooled to below 20 °C, approximately 5 minutes under running water [6].

### E. Measurement

Colorimetric analysis works because the two chromium ions absorb in the visible range but at different wavelengths. The dichromate ion does not absorb at the Cr<sup>3+</sup> ion wavelength, and the Cr<sup>3+</sup> ion absorbs only a small, correctable amount of the wavelength in the dichromate range. This slight interference is zeroed out in the calibration step. For the 160 mg /l range greater sensitivity is achieved by measuring reduction in yellow colour at 420 - 450 nm, and determining remaining Cr<sup>6+</sup>. For the 1600 mg/l range, the increase in blue colour at 600 - 620 nm determines the amount of Cr<sup>3+</sup> produced.

In this study because the COD range of dilution sample was 0-1600 mg/L, we used 620nm wavelength [6, 8].

The resulting mixture is refluxed for two hours and residual dichromate is determined by titration with standardized iron [II] ammonium sulphate solution. The amount of dichromate reduced is expressed as COD in the form of milligrams of oxygen consumed per liter of sample. Blank and analytical quality control determinations should always be undertaken with every batch of samples.

The COD of the sample is given by [8]:

$$\text{COD [mg /L]} = 8000 \times \text{DF} \times \text{M} [\text{Vb} - \text{Vs}] / \text{sample size}$$

Where

Vb is the average volume [ml] of iron [II] ammonium sulphate solution used in the titration of blank solution;

Vs is the volume [ml] of iron [II] ammonium sulphate solution used in the titration of the sample;

DF is the dilution factor, if appropriate;

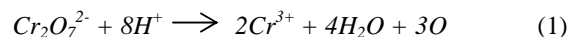
M is the molarity of standardized iron [II] ammonium sulphate solution.

### III. RESULT AND DISCUSSION

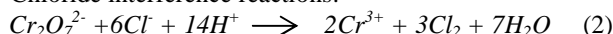
After homogenization, samples were digested in closed reflux tubes. The method was applied to standards and dilution spent caustic waste waters, using both potentiometric and colorimetric methods.

The reactions taking place during the oxidation can be expressed by the following series of equations [6]:

Oxidation reaction:



Chloride interference reactions:



Organic matter contained in a water sample is oxidized in 50% sulfuric acid, by a known excess of potassium dichromate. After digestion, the content of tube in a beaker was stirred magnetically and the titrant was added from microburette. Near the equivalence point, the titrant was added in 0.1 ml increment. The addition of titrant was continued until was no significant change in potential on further addition of titrant. After digestion, remaining unreduced dichromate is determined by potentiometric titration using a Fe [II] solution according to the equation [3].

Iron [II]/dichromate titration:

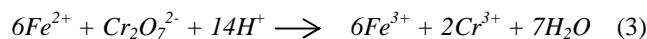


Table I shows the results of COD that is measured by colorimetric and potentiometric titration with FAS. Figs 1 [blank] and 2 [sample] show the changes potential via volume of titrant. A sharp slope is observed in potential changes while titrating [see figs 1 and 2].

Smith observed that the potentiometric end point to the titration of dichromate [i.e. Cr<sup>6+</sup>] with Fe<sup>2+</sup> titrant corresponded to a sharp change in potential [9]. This observation forms the basis for the potentiometric determination of COD presented here. The observed change in voltage with addition of titrant reflects the equilibrium chemistry of the Fe<sup>2+</sup>/Fe<sup>3+</sup> and Cr<sup>6+</sup>/Cr<sup>3+</sup> subsystems in aqueous solution [9].

Average COD values determined potentiometrically are lower than those determined using the colorimetry method [see Table I]. Our idea, this is because the end point to the potentiometric titration offers a method with greater accuracy and precision [see Table II].

Furthermore, the colorimetric method cannot be applied on turbid samples, such turbidity may be present in raw samples or generated in the digestion process. In addition, colored sample especially the samples that can absorb in 620nm wavelength like this spent caustic waste have positive errors.

TABLE I  
COD VALUES DETERMINED BY POTENTIOMETRIC AND COLORIMETRIC METHOD

Spent caustic waste water	Colorimetric COD [mg/l]	Potentiometric COD[mg/l]
1	9693	7747
2	11233	9286
3	9255	8847
4	10120	7771
5	9140	8592
6	9730	7739
7	9330	8651
8	9770	7774
9	11720	11430
10	9921	8205
11	9454	8080
12	9319	8210

high turbidity and colored samples such as spent caustic waste water. In addition, to make use of closed reflex digestion instead of open reflex digestion is easy and rapid.

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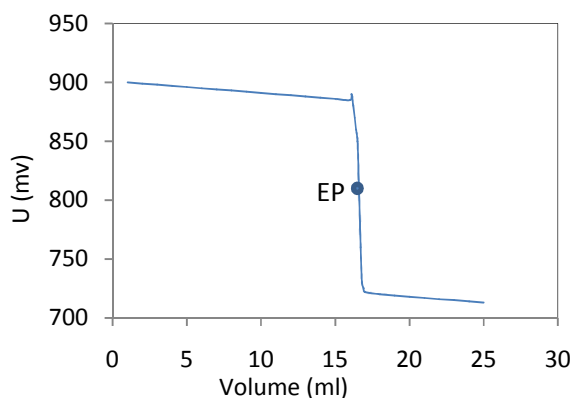


Fig. 1 potentiometric titration curve for blank

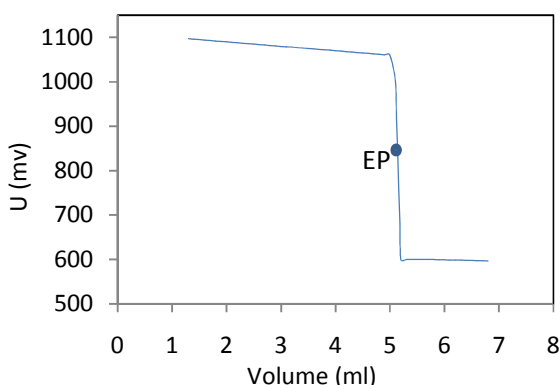


Fig. 2 potentiometric titration curve for sample

TABLE II  
POTENTIOMETRIC AND COLORIMETRIC COD DETERMINATION OF STANDARD 1000[MG/L] KHP

Potentiometric	colorimetric
998	1016
1002	1019
1001	1015
998	1012
STD:1.81	STD:2.88
LOQ: 18.1	LOQ:28.8
Average Error:0.25	Average Error:15.5

#### IV. CONCLUSION

The potentiometric method is based on the observation that the end point corresponds to a redox region of minimum redox buffer. That is, the end point of titration is sharp and easily identified. Furthermore, the Au-Ag/AgCl system used in this method responds quickly to potential changes within the [Fe<sup>3+</sup>/Fe<sup>2+</sup>]: [Cr<sup>+6</sup>/Cr<sup>+3</sup>] solution producing a stable reading. These factors allow rapid and accurate identification of the true end point and this method is very useful especially for the