| UNIVERSITY OF KWAZULU-NATAL | *Standard Operating Procedure* PRG pollution research group | Effective Date: 14 April 2015 | Version: ***004*** |
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| **SOP_Chem_001 Chemical Analysis_ Chemical Oxygen Demand** | | | Page #: ***1 of 6*** |

# Standard Operation Procedure – Chemical Oxygen Demand Closed Reflux, Titrimetric Method

## 1. Scope and Application

- Chemical Oxygen Demand (COD) measures the oxygen equivalent of that portion of the organic matter in a sample that is easily oxidised by a strong chemical oxidant.
- It is an important and common parameter to measure the amount of organic compounds in streams, industrial waste and in operational control of wastewater treatment plants. It is also applicable for measurements on human excreta.
- The procedure described hereafter is applicable to low COD values 40-400mg/L with sample dilution and high COD values 40-3600mg/L with minimal sample preparation.

## 2. Summary

- The sample is digested for two (2) hours in a strongly acidic dichromate solution, using silver sulphate as a catalyst and mercuric sulphate as a masking agent to prevent chloride interference. The dichromate is partially reduced by the oxidisable material present in the sample. The excess dichromate is titrated with ammonium iron (II) sulphate and the COD value calculated from the amount of dichromate.
- The half reaction for the reduction of dichromate is:
- $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3-} + 7H_2O$
- The remaining dichromate is titrated with a standard ammonium iron(II) sulphate solution:
  - $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 6Fe^{3+} + 7H_2O + 2Cr^{3+}$
- The equivalence point is indicated by the sharp colour change from blue-green to reddish brown as the Ferroin indicator undergoes reduction from iron (III) to the iron (II) complex.

## 3. Apparatus and Glassware

- ETHOS One Milestone microwave
- Carousel of 10 Teflon vessels
- 100 ml Erlenmeyer flasks
- 5ml pipette

- 10ml and 5ml automatic bottle top dispensers
- 1L reagent bottles

## 4. Interferences

- The high levels of chloride (>500mg/L) in the sample undergoes oxidation resulting an increase of COD values. This error is overcome by the addition of mercuric sulphate to samples before digesting. The chloride ion is then eliminated from the reaction by forming a soluble mercuric chloride complex.

## 5. Collection, Preservation and Storage

- Collect samples in 1L plastic buckets.
- Preferably, analyse samples immediately after sampling.
- Store samples at 4 °C or freeze dry samples.
- Preserve wastewater samples by acidifying with concentrated sulphuric acid to pH 2 and faecal samples by freeze drying or freezing.
- Determine COD on well- homogenised samples.

## 6. Safety Precautions

- Handle concentrated sulphuric acid with care.
- Always use safety goggles, gloves and laboratory coat while working in laboratory.
- Wear face shield and protect hands from heat produced when contents of the vessels are mixed.
- After the analysis, clean bottles and beakers with water then dry.
- Dispose used gloves after completion of analysis.
- Clean hands using antiseptic soap.
- Avoid spillage and contact with skin. In the latter case use copious washings with cold water and call for medical attention.

## 7. Sample Preparation –Faecal Sludge

**40-400mg/L COD**

1. Weigh out 2.0000g of well-mixed faecal sludge sample.
2. Blend the weighed sample with 500ml of distilled water in a 1L blender for 30 seconds on the highest speed.
3. Add 250ml distilled water and blend on highest speed until the sample is homogenised (this could range from 30 to 60 seconds).
4. Transfer the blended mixture into a 1L volumetric flask.
5. Add 200ml of blender washings into the flask and top up to 1L with distilled water.
6. Transfer the 1L solution to a plastic bottle and store at 4 °C.

**40-3600mg/L COD**

7. Dilute 0.1g of well-mixed faecal sludge sample with 5ml of distilled water in the digestion vessel.

## 8. Reagents

**Standard Potassium Dichromate $K_2Cr_6O_7$ Digestion Solution: 0.0167M for Wastewater Samples**

- Add 4.913g $K_2Cr_6O_7$, previously dried at 105 °C for 2hrs to approximately 500ml distilled water.
- Add 167ml concentrated Sulphuric acid $H_2SO_4$ and 13.3g Mercuric Sulphate HgSO4.
- Dissolve and cool to room temperature before diluting to 1L.

**Standard Potassium Dichromate $K_2Cr_6O_7$ Digestion Solution: 0.13M for fecal Samples**

- Add 39.93g$K_2Cr_6O_7$, previously dried at 105 °C for 2hrs to about 500ml distilled water.
- Add 167ml concentrated Sulphuric acid $H_2SO_4$ and 13.3g Mercuric Sulphate HgSO4.
- Dissolve and cool to room temperature before diluting to 1L.

**Sulphuric Acid $H_2SO_4$ /Silver Sulphate Reagent $Ag_2SO_4$** (COD Reagent)

- Add **26g of silver sulphate** crystals or powder to 2.5L of concentrated sulphuric acid using a magnetic stirrer. Shake well and leave for 2days for dissolution.

**Ferroin Indicator 2 drops**

- Dissolve 1.485g 1:10 phenentroline monohydrate and 0.695g ferrous sulphate ($FeSO_4.7H_2O$) in distilled water and dilute to100ml.

**Ferrous Ammonium Sulphate Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$: 0.10M**

- Dissolve 39.2g Fe $(NH_4)_2$ $(SO_4)_2.6H_2O$ in distilled water.
- Add 20ml concentrated Sulphuric acid $H_2SO_4$ and dilute to 1L.
- Standardize daily against **Standard Potassium Dichromate $K_2Cr_6O_7$ Digestion Solution**

## 9. Calibration

- Prepare a standard K2Cr2O7 solution daily to correct any variation in the concentration of the Ferrous Ammonium Sulphate.
- Prepare a blank with each set of samples consisting of 5ml distilled water in place of sample together with all the reagents and digest together with samples.

### Standard Preparation

- Add 3ml of standard K2Cr2O7 digestion solution to 5 ml of distilled water. Add 7ml COD reagent and cool it down. Titrate with FAS titrant using 2 drops of Ferroin indicator.
- Quality Control: Potassium hydrogen Phthalate (KHP)

- Lightly crush and then dry out KHP to a constant weight at 120°C. Dissolve 0.0425g in distilled water and then dilute to 250ml. This solution has a theoretical COD of 200mg/L. Solution is stable if refrigerated, for a period of 3 months in the absence of biological growth.
- Dissolve 425mg in a litre. KHP has a theoretical COD of 1.176mgO2/mg and this solution has a theoretical COD of 500ug O2/ml. 0.425g = 500mg/L.

## 10. Procedure

### Sample Digestion

1. Add 5ml sample to each Teflon vessel.
2. Add 5ml distilled water to another vessel (blank).
3. Add 3ml potassium dichromate digestion solution into each vessel.
4. Add 7ml sulphuric acid reagent (with silver sulphate) in each vessel.
5. The acid must be poured down the wall of the flask while flask is tilted. If sample is too concentrated it will turn green, and a higher dilution of sample must be used.

### Sample Titration

6. Titrate the excess dichromate in the digest mixture with standard ferrous ammonium sulphate using 2 drops of Ferroin indicator.
7. Titrate from a sharp green/orange to red brown end-point.
8. Take volume reading.

### Digestion Program

- Place Teflon vessels into the rotor, with the temperature probe placed into the Teflon vessel 1.
- Switch on the microwave and select COD METHOD.
- Username/password (Student-9876) (Administrator(123456).
- Name: COD test method (wastewater samples 1h35min).
- Name: COD faecal method (faecal samples 2hr15min).
- Transfer contents from Teflon vessels into 100ml flasks for titrating.

| Wastewater :Time | Power(W) | Temperature(°C) |
|---|---|---|
| **00:05:00** | 1000 | 90 |
| **01:00:00** | 1000 | 130 |
| **00:10:00** | 1000 | 40 |
| **00:20:00** | 0 | 30 |

| Faecal Sludge :Time | Power(W) | Temperature(°C) |
|---|---|---|
| **00:05:00** | 1000 | 90 |
| **01:30:00** | 1000 | 130 |
| **00:10:00** | 1000 | 40 |
| **00:30:00** | 0 | 30 |

## 11. Waste Disposal

- Collect waste in a 2.5L bottle for Waste Tech collection.

## 12. Calculation and Data Analysis

$$COD\ (mg\ O_2/L) = \frac{(Blank - Titration) \times molarity\ of\ FAS \times 8000}{Sample\ (ml)}$$

Where:

8000 = Milliequivalent weight of oxygen × 1000 ml/L

$$Molarity\ of\ FAS = \frac{Volume\ 0.0167M\ K_2Cr_2O_7\ Solution\ Titrated\ (ml)}{Volume\ FAS\ used\ in\ titration\ (ml)} \times 0.10$$

$$COD\ (mg\ O_2/L) = \frac{(Blank - Titration) \times molarity\ of\ FAS \times 8000}{Sample\ (ml)} \times \frac{V}{M}$$

$$COD\ in\ Wet\ Sample\ (g\ O_2/g) = \frac{COD\ (mg\ O_2/L)}{1000}$$

$$COD\ in\ Dry\ Sample\ (g\ O_2/g) = \frac{COD\ in\ Wet\ Sample\ (g\ O_2/g)}{Total\ Solids\ (g/g)}$$

Where:

M = Mass of sludge used in sample preparation (g)
V = Total volume (L)

## 13. Data Quality

| Measurement | mg/l COD |
|---|---|
| Standard Deviation (mg/l COD) | ± 1.1 |
| Confidence Interval (mg/l COD) | ± 3 |

## 14. References


- Standards Methods for the Examination of Water and Wastewater, 18th Edition, p. 5-19, Methods 5220 C. Closed Reflux, Titrimetric Method (1992).
- Milestone Ethos One Operator Manual MA 133, Rev00/2010.


## APPROVAL OF STANDARD OPERATING PROCEDURE

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