# Potentiometric measurement of chemical oxygen demand

**Dragoljub Bilanovic[1], Richard E Loewenthal[2]*, Yoram Avnimelech[1] and Michal Green[1]**

[1] *The Lowdermilk Faculty of Agricultural Engineering, Technion- Israel Institute of Technology, Technion City, Haifa 32000, Israel*

[2] *Department of Civil Engineering, University of Cape Town, Rondebosch 7700, South Africa*

## Abstract

Measurement of the COD of an aqueous solution involves firstly digestion of a test sample with dichromate solution, and secondly measurement of the dichromate remaining either by titration by ferrous ammonium sulfate (FAS) to a color indicator endpoint, or via colorimetric determination using a spectrophotometer. In this paper, a potentiometric end-point determination (using FAS titrant) is proposed as a third option for measuring the dichromate remaining. The potentiometric method is based on the observation that the titration end point corresponds to a region of minimum redox buffer. That is, the end point to the titration is sharp and easily identified. Furthermore the platinum-calomel electrode system used in this method responds quickly to potential changes within the ($Fe^{2+}/Fe^{3+}$):($Cr_2O_7^{2-}/Cr^{3+}$) solution producing stable readings. These factors allow rapid and accurate COD measurement. Furthermore the method is based firmly on theoretical considerations allowing extension into a region of low COD.

The method is applied to a broad spectrum of waste waters and dilutions of these, using both macro- and semi-macro techniques. Results are compared with data determined using colorimetric and color indicator end-point methods. It is shown that the potentiometric end-point titration (with FAS titrant) can be used with equal or better facility.

## Introduction

Current practice is to use chemical oxygen demand (COD) as a system parameter both for process design and in the control of waste-water treatment works (Wentzel et al., 1995). The principal advantages of COD over biological oxygen demand (BOD) measurement, are the simplicity of procedure and the fact that the test can be completed very rapidly (within about 3 h).

The COD measurement procedure is based on the observation that under acidic conditions the dichromate ion ($Cr_2O_7^{2-}$) oxidises almost all organic materials ($C_xH_yO_z$) to $CO_2$ and $H_2O$ (Eq. 1).

$$C_xH_yO_z + kCr_2O_7^{2-} + kH^+ \leftrightarrow xCO_2 + \frac{y + 8k}{2} H_2O + 2kCr^{3+} \quad (1)$$

where $k = \frac{2x}{3} + \frac{y}{6} - \frac{z}{3}$

The test involves addition of an excess but known mass of dichromate to ensure complete oxidation of organic material in a digestion process. The COD is then estimated using any of the following routines (*Standard Methods*, 1992):

(a) measurement of dichromate ($Cr_2O_7^{2-}$) remaining via a colorimetric method;
(b) measurement of $Cr^{3+}$ formed, again a colorimetric method;
(c) measurement of $Cr_2O_7^{2-}$ remaining via titration with a ferrous ($Fe^{2+}$) reagent FAS ($Fe(NH_4)_2(SO_4)_26H_2O$) to a colorimetric end point using ferroin indicator (the classical procedure):

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \leftrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad (2)$$

With regard to the colorimetric determinations (i.e. (a) and (b) above) the methods have a number of disadvantages. They require expensive equipment and are relatively time-consuming (the methods only can be applied after digested samples have cooled to room temperature). Furthermore they are affected by stratification in the digested solution (i.e. development of "Schlieren lines" - Messenger, 1981; Jones et al., 1985, Dasgupta and Petersen, 1990). Finally, turbidity interferes with accurate measurement - such turbidity may be present either in the raw samples or generated via precipitation on addition of silver catalyst during the digestion process (Moore et al., 1951; Bertram et al., 1958; Gaudy and Ramanatha, 1964; Messenger, 1981).

With regard to the titration method, disadvantages include use of a titrant $Fe(NH_4)_2(SO_4)_26H_2O$ which degenerates with time and must thus be checked on a daily basis (Gaudy and Ramanatha, 1964). This, however, can be overcome by preparing the titrant using oxygen-free water and storing it in a $CO_2$ atmosphere (Cooke et al., 1951). Furthermore, problems may arise with estimation of the colorimetric end point to the titration. These include:

- masking the color change of the indicator due to presence of turbidity either in the raw sample or generated in the process of digestion (Gaudy and Ramanatha, 1964; Messenger, 1981), and
- an indeterminate error arising from the difference between the true end point to the titration and that reflected by the color change of the indicator used.

Comparing the two methods, colorimetric determination (of either $Cr^{3+}$ or $Cr_2O_7^{2-}$ species) is considered to be faster than the titrimetric color indicator end-point method. Consequently it is preferred in waste-water treatment laboratories handling a large number of COD samples (greater than about 30) per day. Below this number, the colorimetric methods have no advantage over the titration approach. However, recognising that the titration method can be effected using significantly cheaper measurement apparatus, this method is to be preferred for small- to medium-size waste-water treatment laboratories (effecting less than about

* To whom all correspondence should be addressed.
☎ (021) 650-2584; fax (021) 689-7471; e-mail dick@engfac.uct.ac.za
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30 COD tests per day).

It was stated earlier that one of the principal disadvantages of COD measurement by the titration method involves errors arising from end-point estimation, especially where COD has a low value and/or where turbidity is present. Conventionally, the end point is identified using a color indicator (*Standard Methods*, 1992) and it is this which creates the problem. Smith (1951) demonstrated a sharp change in redox potential at the end point of the $Fe^{2+}/Fe^{3+}$ titration using dichromate as oxidant. Raveh and Avnimelech (1972) used this observation to apply potentiometry to determination of organic carbon in soil using a digestion procedure similar to that of the classic COD test; no other work was found in literature survey. The objectives of this investigation were firstly, to compare the potentiometric end-point method (a titration procedure) with recommended standard methods of either colorimetry or titrimetry using a color indicator end point. These comparisons were effected using both "macro" and "semi-micro" procedure (*Standard Methods*, 1992).

## Theoretical considerations

Smith (1951) observed that the potentiometric end point to the titration of $Cr_2O_7^{2-}$ (i.e. $Cr^{6+}$) with $Fe^{2+}$ titrant corresponded to a sharp change in voltage (see later). 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 $Fe^{2+}/Fe^{3+}$ and $Cr_2O_7^{2-}$ (i.e. $Cr^{6+}/Cr^{3+}$) subsystems in aqueous solution. Consequently, any critical evaluation of potentiometric determination (by titration) of COD should be effected from this standpoint.

## System equations

Considering the $Cr^{3+}/Cr_2O_7^{2-}$ (i.e. $Cr^{6+}$) subsystem, for didactic purposes it is useful to express the oxidised Cr species in the form $Cr^{6+}$ rather than $Cr_2O_7^{2-}$. The reaction depicting the interchange between these species can be visualised as:

$$Cr_2O_7^{2-} + 14H^+ \leftrightarrow 2Cr^{6+} + 7H_2O$$

From this reaction it is seen that, provided pH remains constant (which is the case in the COD titration at pH ~ 0), then the assumption that $Cr^{6+}$ is the oxidised species, will have no effect on the redox system because electron transfer is not involved in the reaction. The reaction can be written in terms of $Cr^{3+}$ and $Cr^{6+}$ with the equilibrium constant appropriately adjusted, i.e.:

$$Cr^{3+} \leftrightarrow Cr^{6+} + 3e^-$$

Consequently, the redox equilibrium equation for the subsystem $Cr^{3+}/Cr^{6+}$ (i.e. $Cr_2O_7^{2-}$) is:

$$\frac{[Cr^{6+}]\,(e^-)^3}{[Cr^{3+}]} = K_c \qquad (3)$$

and the mass balance expression is:

$$[Cr]_t = [Cr^{6+}] + [Cr^{3+}] \qquad (4)$$

where:

$K'_c$ = apparent equilibrium constants which incorporates both complexing and ionic strength effects, and the pH of the solution (which is assumed constant).

[X] = total concentration of species X, i.e. free plus complexed species concentrations.

$Cr_t$ = total mass concentrations of Cr species in solution.

$(e^-)$ = electron activity of the solution, and is linked to redox potential ($E_h$).

In the above equations the ionic species are expressed as total species concentration (i.e. free plus complexed ionic species). This is acceptable provided that the principal ionic matrix of the solution is closely constant during the titration. This situation arises in the COD test because the principal ionic matrix is composed of $H^+$ and $SO_4^{2-}$ species (> 1M) and the Cr and Fe species are all at "trace" concentrations (<0.05M).

Considering the $Fe^{2+}/Fe^{3+}$ subsystem, the relevant equilibrium reaction and equation are:

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^-$$

$$\frac{[Fe^{3+}] * (e^-)}{[Fe^{2+}]} = K'_f \qquad (5)$$

and the mass balance expression is:

$$[Fe]_t = [Fe^{2+}] + [Fe^{3+}] \qquad (6)$$

Again, ionic species concentrations are total (free plus complexed) species and the apparent equilibrium constant $K'_f$ incorporates complexing and ionic strength effects.

The electron activity of the solution, $(e^-)$, is linked to pe and redox potential ($E_h$) as follows:

$$-\log(e^-) = pe = \frac{F}{2.3*RT} * E_h \qquad (7)$$

where:

F = Faraday constant, 23.06 kcal/volt-gram equivalent

R = gas constant, 0.001986 Kcal/°K

T = absolute temperature, °K

## Distribution of species with pe (the log species - pe diagram)

From the relationships above, it is possible to determine each of the ionic species concentrations as a function of pe and the respective total species concentration (i.e. either $Fe_t$ or $Cr_t$).

A plot of the logarithm of each of the species concentrations vs. pe is shown in Fig. 1a. for an aqueous solution at pH ~ 0, $Fe_t$ = 0.000316 M, $Cr_t$ equal to 0.001 M, $pK_f$ = 13 and $pK_c$ = 60 (these pK values are only approximate but serve the didactic purposes desired here). Note that the presence of iron species in the diagram together with chrome species indicates that the COD titration has been initiated (i.e. FAS titrant has been added).

Referring to Fig. 1a, it is evident that for pe > 20, $Cr^{6+}$ species totally dominate; in the region 13< pe < 20, $Cr^{3+}$ and $Fe^{3+}$ species dominate with $Fe^{2+}$ and $Cr^{+6}$ at low concentrations; finally in the region pe< 13, $Fe^{2+}$ species dominate and all the remaining species are at relatively very low concentrations. The effects of different total species concentrations (i.e. $Fe_t$ and $Cr_t$) on the distribution of ionic species concentration with pe can be very easily depicted in the diagram - the shapes of the curves remain

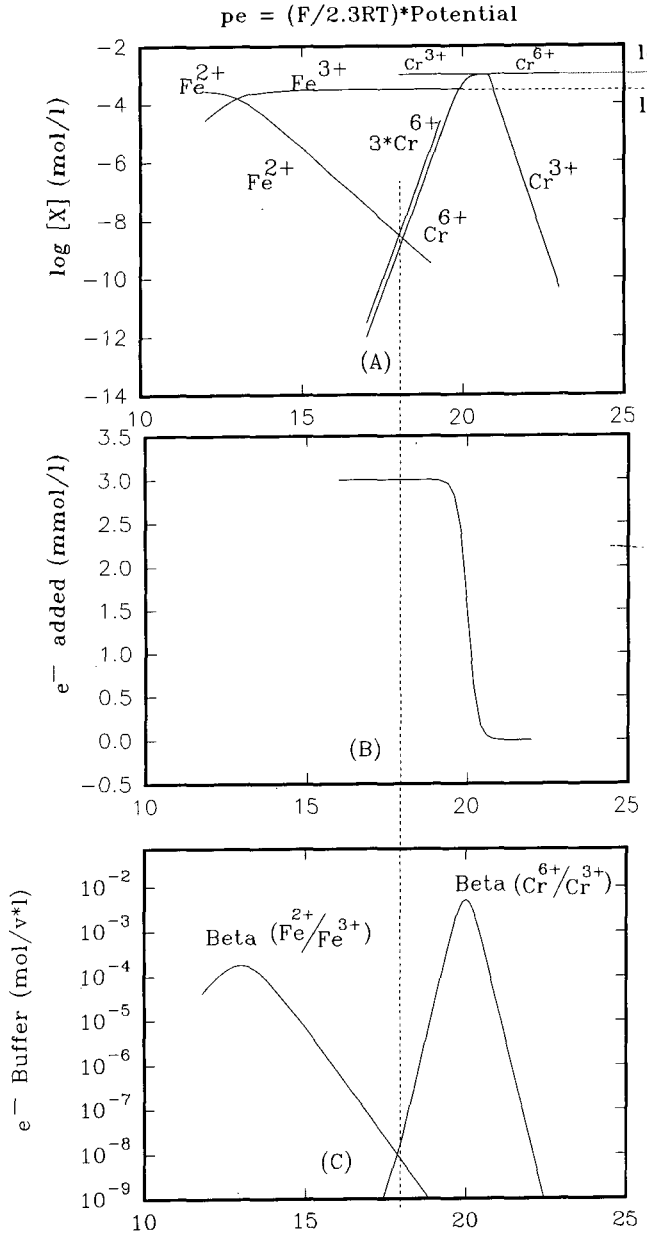


***Figure 1***

*Theoretical determination of distribution of species, addition of FAS titrant and redox buffer with pε (i.e. redox potential). Note: equilibrium constants used are only approximate and relative to the hydrogen half-cell.*

unaltered, they are simply moved vertically upwards or downwards and plotted around new log[Cr]$_t$ and/or log[Fe]$_t$ values. However, perhaps the most important use of this diagram is that it forms a convenient basis for interpreting the redox equilibrium concepts associated with potentiometric FAS titration in COD measurement.

## Capacity parameters and the COD titration

In COD measurement a known total mass of $Cr^{6+}$ species is added to a test solution which is then digested - some pe value will be established, depending on the amount of $Cr^{6+}$ initially added and the organics oxidised in digestion. This post-digestion redox state is depicted as $pe_a$ in the log species - pe plot (Fig. 2). Note that at this point in the test no FAS ($Fe^{2+}$) has been added so that the total dissolved iron in solution initially will be zero (i.e. there is no line "a" representing $Fe^{2+}$ at this initial state), and the solution will possess some electron accepting capacity (EAC) value equal to three times the concentration of $Cr^{6+}$ at $pe_a$ (i.e. each mole of $Cr^{6+}$ can accept 3 electrons in being reduced to $Cr^{3+}$). In equation mode this statement is expressed as follows:

$$EAC\ (Cr^{3+})_a = 3*[Cr^{6+}]_a$$

where:

$EAC\ (Cr^{3+})_a$ is the electron accepting capacity of the solution with respect to reference species $Cr^{3+}$

$[Cr^{6+}]_a$ = concentration of $Cr^{6+}$ at $pe_a$.

In practice the test solution is now titrated with $Fe^{2+}$ (i.e. FAS titrant), the effect of which is to reduce the $Cr^{6+}$ to the $Cr^{3+}$ form and generate $Fe^{3+}$ species. This addition reduces the EAC value thereby establishing some lower pe value, say $pe_b$ in Fig. 2; note that the $Fe^{2+}$ species in solution, with $pe_b$, is now represented by the line "b" in the diagram. An equation for the new EAC value of the solution in terms of species concentration is:

$$EAC\ (Cr^{3+}, Fe^{3+})_b = 3[Cr^{6+}]_b - [Fe^{2+}]_b \qquad (8)$$

where:

$EAC\ (Cr^{3+}, Fe^{3+})_b$ is the electron accepting capacity of the solution with respect to the reference species $Cr^{3+}$ and $Fe^{3+}$ at redox potential $pe_b$.

Note that the reference species selected are the products of the titration of $Cr^{6+}$ with $Fe^{2+}$ (i.e. FAS). Addition of $Fe^{2+}$ is continued until the solution corresponds to an equivalent solution, the pe now corresponds to the equivalence point of the titration ($pe_c$ in Fig. 2) and EAC ($Cr^{3+}$, $Fe^{3+}$) is zero, i.e. at the equivalence point

$$EAC\ (Cr^{3+}, Fe^{3+})_c = 0, \text{ and}$$
$$3[Cr^{6+}]_c = [Fe^{2+}]_c$$

This titration end point occurs at the interception of the lines representing $\log(3[Cr^{6+}]_c)$ and $\log[Fe^{2+}]_c$ (marked line "c"). The difference in EAC between the initial post-digestion state (with redox potential, $pe_a$) and end-point state (characterised by $pe_c$) gives the EAC remaining after digestion. The difference between the EAC derived from chromate added and that remaining after digestion gives the EAC of the organics initially present in the test solution (i.e. COD). Note that in this example, values for $pe_a$ and $pe_b$ are chosen arbitrarily, in practice all we can say is that $pe_b$ will have a value lower than or equal to $pe_a$.

Two problems in particular arise from the discussion above. Firstly, the digestion process and titration are carried out on a sample which has been acidified to pH~0 with sulphuric acid - inevitably this contains $Fe^{2+}$ impurities which will introduce an error in the determination. To bypass this problem, normally an acidified distilled water blank (at pH ~ 0) is digested and titrated in parallel, and used to determine the initial dichromate value thereby nullifying the $Fe^{2+}$ impurity problem. Secondly, it was stated that the FAS (i.e. COD) titration is carried out to an "end point"; however, this end point changes depending on initial chromate present, the amount of organics in the test solution and the mass concentration of FAS titrant added (this can be appreciated from the log species - pe plot). With regard to the estimate of the

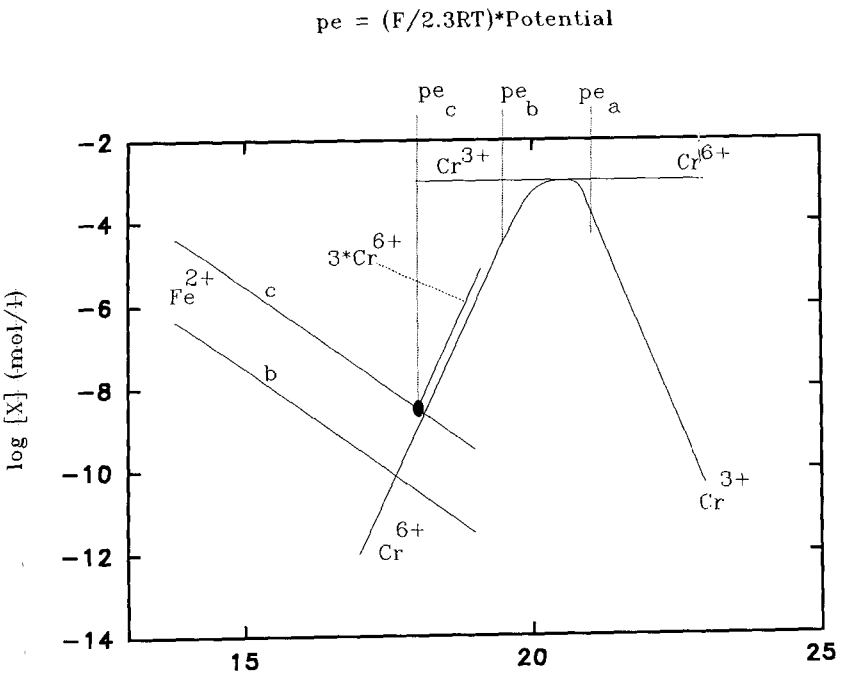


**Figure 2**

*Graphical exposition of potentiometric end-point estimate in the COD titration. Note: equilibrium constants used are only approximate and relative to the hydrogen half-cell*

end point in a potentiometric titration, this is best illustrated using a typical potentiometric titration curve.

## Potentiometric end-point determination and redox buffering capacity

Determination of the end point in the potentiometric titration is best illustrated by developing a theoretical potentiometric titration curve. Such development is easily effected using the EAC parameter developed above. This arises because EAC is a capacity parameter and hence changes in a simple stoichiometric fashion on addition of oxidant or reductant (i.e. addition of either FAS or $Cr^{6+}$).

For the initial conditions, after digestion but prior to titration, from Eq. (8):

$$EAC\ (Fe^{3+},Cr^{3+})_a = 3[Cr^{6+}]_a - 0$$

and writing $Cr^{6+}$ in terms of $[Cr]_T$ and electron activity after digestion, i.e. $pe_a$ in Fig. 2.:

$$EAC\ (Fe^{3+},Cr^{3+})_a = \frac{3[Cr]_t\ K_c}{K_c + (e^-)_a^3}$$

where:

$[Cr]_t$ = total chromate added before digestion

$(e^-)_a$ is linked to the redox potential after digestion, i.e. $pe_a$.

For any point during the titration with some measured pe value, say $pe_b$:

$$EAC\ (Fe^{3+},Cr^{3+})_b = \frac{3[Cr]_t\ K_c}{K_c + (e^-)_b^3} - \frac{[Fe]_t(e^-)_b}{K_f + (e^-)_b}$$

The titrant added is simply the change in EAC between initial and intratitration pe values (see Fig. 1b). Figure 1b shows a theoretical titration curve of solution with $[Cr]_t = 0.001M$. Referring to this diagram the slope of the titration curve is very steep in the pe region where $\log[Cr^{3+}] \sim \log[Cr^{6+}]$, and almost horizontal out of the region. Furthermore it is clear from Figs. 1a and 1b that the end point to the titration occurs in a region of very low slope (later, the sharp change will be explained in terms of redox buffering). Consequently, it is to be expected that in the practical titration the end point is identified where a sudden, sharp and large change in pe occurs on addition of a very small aliquot of titrant. The error arising in this end-point estimate will be very small (see Fig. 1b). An estimate of the error arising from this estimate can be effected through the concept of redox buffering.

The slope of the titration curve introduces the concept of redox buffering capacity ($e^-$buffer), which is defined as the slope of the titration curve i.e.:

$$(e^-buffer) = \left(\frac{\delta EAC}{\delta pe}\right)_{Cr_t} \qquad (9a)$$

$$= \frac{(2.3[Fe]_t K_f(e^-))}{(K_f + (e^-))^2} + \frac{(2.3*9[Cr]_t K_c(e^-)^3)}{(K_c + (e^-)^3)^2} \qquad (9b)$$

$$= e^-buffer\ (Fe^{2+}/Fe^{3+}) + e^-buffer\ (Cr^{3+}/Cr^{6+})$$

These buffer curves are shown plotted in Fig. 1c for a solution with $[Cr]_t = 0.001M$ and $[Fe]_t = 0.000316M$. Referring to this plot, $e^-$ buffer has a maximum value in the region where the redox species concentrations for a particular subsystem are equal, and the total $e^-$ buffer has a minimum value in the region where the $e^-$ buffer values for the two subsystems are equal.

The error arising in EAC determination can be estimated from Eqs. (9a and b), i.e.:

$$\Delta EAC = (e^-buffer)*\Delta pe \qquad (10)$$

where:

e-buffer has the value determined from Eq (9b) with $e^-$ equal to its estimated value from the potentiometric titration, and

$\Delta pe$ = estimated difference between assumed and true end-point pe value.

$\Delta EAC$ = estimated titration error.

For example, in the theoretical titration shown in Fig. 1, if the end point is estimated to occur at pe = 17, but the actual value may be one pe unit on either side of this, then $\Delta pe = 2$. Substituting $[Cr]_t = 0.001M$, $[Fe]_t = 0.000316M$ and $\Delta pe = 2$ into Eq. (10) gives $\Delta EAC$ to be totally negligible.

## Materials and methods

Potentiometric end-point titration for COD measurement was tested against colorimetric and titrimetric color end-point methods firstly on samples digested using the "macro" procedure (all steps were in accordance with the "open reflux method", *Standard Methods*, 1992); and secondly on samples digested using the

**TABLE 1**
**REAGENTS AND SAMPLES USED**

| Reagent or sample | Procedure (volume mℓ, concentration, remark) | |
|---|---|---|
| | Macro | Semi-micro |
| $K_2Cr_2O_7$ | 0.0417 M, 25 mℓ | 0.0167 - 0.0347 M, 1.5 mℓ** |
| $Ag_2SO_4$ in $H_2SO_4$ | 0.0325 M, 75 mℓ | 0.0325 M, 3.5 mℓ |
| Ferroin indicator | 2 - 3 drops | 0 - 2 drops |
| $Fe(NH_4)_2(SO_4)_26H_2O$ | 0.025 - 0.25 M | 0.001 - 0.10 M |
| $HgSO_4$ | 1 g | 0.1123M, 1.5 mℓ** |
| $CO_2$ or $N_2$ | No addition, sample open to air | Sample digested under $CO_2$ or $N_2$ |
| $H_2O$ | b. 150 - 200 mℓ | a. 0-2.5 mℓ; b. 20 - 40 mℓ |
| One of the following samples or reagents | | |
| Raw sewage | up to 50 mℓ | 0 - 2.5 mℓ |
| Primary settler effluent | up to 50 mℓ | 0 - 2.5 mℓ |
| Activated sludge effluent | up to 50 mℓ | 0 - 2.5 mℓ |
| Wetland effluent | up to 50 mℓ | 0 - 2.5 mℓ |
| Algae pond effluent | up to 50 mℓ | 0 - 2.5 mℓ |
| Fish pond effluent | up to 50 mℓ | 0 - 2.5 mℓ |
| Glucose Standard | up to 50 mℓ | 0 - 2.5 mℓ |
| K-hydrogen phtalate | up to 50 mℓ | 0 - 2.5 mℓ |
| Sample volume | | |
| - after digestion | 150 mℓ | 7.5 mℓ |
| - after COD measurement | 300 - 400 mℓ | 15 - 100 mℓ |

a = distilled "make-up" $H_2O$ added to sample before digestion. b = distilled $H_2O$ used for cooling of sample and dilution, ** = added together with **

**TABLE 2**
**EXPERIMENTAL PROCEDURES**

| Step | Procedure | |
|---|---|---|
| | Macro | Semi-micro |
| 1. Place sample in: | 500 mℓ refluxing flask | 16 * 130 mm tube |
| 2. Add reagents: | see Table 1 | see Table 1 |
| 3. Digest under $CO_2$ or $N_2$<br>Digestion time & temp. | no<br>2 h at 150°C | yes<br>2 h at 150°C |
| 4. Cool to room temp. | Colorimetric quantification: YES. Potentiometry and Indicator: NO. | |
| 5. Take aliquot | yes | yes |
| 6. Dilute aliquot with $H_2O$ | yes | yes |
| 7. Measurement | Potentiometric, color-indicator endpoint, colorimetric | |

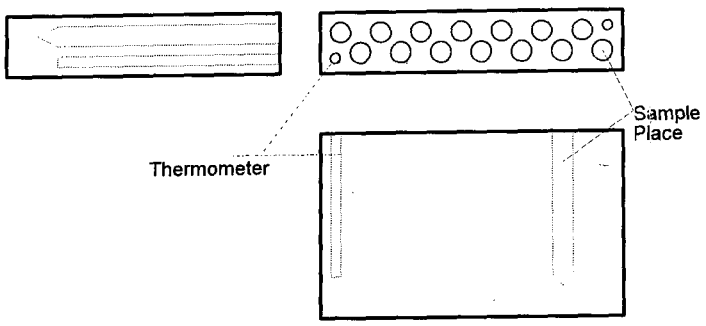


***Figure 3***
*Aluminium digestion block*

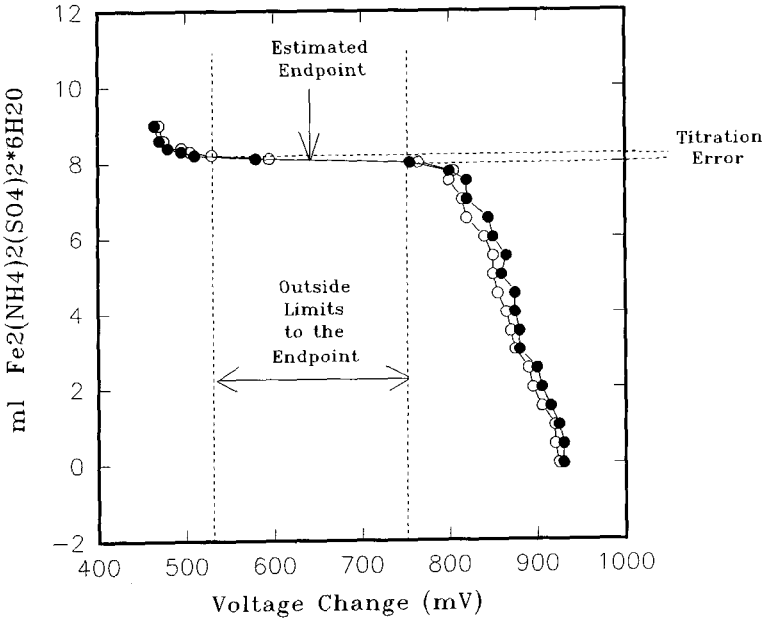


***Figure 4***
*Potentiometric titration of Neve Shaanan primary settler effluent indicating the range of the end-point estimate*

**TABLE 3**
**POTENTIOMETRIC VS. COLORIMETRIC AND TITRIMETRIC COD DETERMINATION**

| Method | Average COD (mg/ℓ)* | Deviation (mg/ℓ) |
|---|---|---|
| Colorimetry | 691 | + 53 |
| Potentiometric end point | 645 | + 34 |
| Colour-indicator end point | 678 | + 51 |

* Average of three determinations.

"semi-micro" procedure in accordance with "closed reflux colorimetric method" (*Standard Methods*, 1992).

Reagents and samples were prepared in accordance with Standard Methods (1992); changes concerning preparation of reagents and procedures are listed in Tables 1 and 2. COD measurement was conducted by all of the following methods: colorimetry, potentiometric end-point titration and color indicator end-point titration at macro and semi-micro sample size (see Tables 1 and 2). Oxygen-free distilled water was used in the preparation of $Fe(NH_4)_2(SO_4)_26H_2O$ titrant (FAS) which was then stored in a dark bottle.

Effluent samples were taken from the Technion's waste-water pilot plant which is operating on raw sewage (RS) from Haifa's suburb of Neve Shaanan. The plant produces primary settlement effluent (PSE), two activated sludge unit effluents (ASE), a number of high rate algal pond effluents (APE), two wetland effluents (WE) and other effluents not relevant to this work. Within the pilot plant two small fish ponds are also operated and their effluents used (FPE). "Semi-micro" sampling was effected by mixing approximately 500 mℓ of effluent in a food blender and samples of desired volume taken while blender was operated at maximal speed.

Samples were digested in capped culture tubes ("Purex" 16*130 mm, No. 9825) in the "semi-micro" procedure; the tubes containing samples were placed in a dur-aluminium block (Fig. 3) and digestion effected using a thermostatically controlled electrical heating device. Temperature difference across the Al-block was always less than about +1°K. Potentiometric and/or titrimetric measurements were made immediately after digestion; colorimetric measurement was effected only after samples reached room temperature.

Instruments used: "El-Hama Instruments" spectrophotometer S-12; "Radiometer Copenhagen" pH meter and "El-Hama Instruments" pH meter; in-house built platinum and calomel electrode system; "Fried electric" hotplate with temperature regulation.

With regard to the Pt electrode, this functions best if it has a large surface area, so that the "plate" and "thimble" types electrodes generally are more reliable than the "button" type and "single platinum wire" electrodes (Garrels and Christ, 1965)

## Results and discussion

Four samples of primary settled effluent (2 000 mℓ each) were obtained from Haifa's suburb of Neve Shaanan. After homogenisation in a food blender, aliquots were digested following procedures set out in Tables 1 and 2. COD was measured colorimetrically and titrimetrically to both color-indicator (ferroin) and potentiometric end points (Table 3). Curves depicting the potentiometric titration with FAS are shown in Figs. 4 and 5.

A sharp drop in voltage reading signals the end point to the potentiometric titration (see Figs. 4 and 5). A plot of the titration (Fig. 4) indicates that the error associated with the end-point estimate can be determined easily (Note: The estimate of error in COD measurement shown in Figs. 4 and 5 is ~ 7 mg, approximately 1.%; this is very much greater than would be expected from the theoretical analysis above. A possible reason for this is that the in-house Pt electrode used had a slow response time when pe buffering was low (i.e. in the region of the end point)). No experimental allowance was made in these experiments as the error was not considered significant in this set of experiments.

This type of estimate is not possible when the titration is effected to the color-indicator end point. Average COD values determined potentiometrically are slightly lower than those determined using the color-indicator end-point method and colorimetry. Perhaps this is because the end point to the potentiometric titration offers a method with greater accuracy and precision (see Tables 3 to 5).

The potentiometric method was tested further using duplicate samples of effluent from the various unit processes in the wastewater treatment plant. To broaden the COD range investigated some samples were diluted with distilled water prior to digestion. COD test was conducted according to the "classic" and "semi-micro" methods. The COD was quantified colorimetrically, and by titration to potentiometric and color-indicator end point. Results are listed in Tables 4 and 5. The average values obtained using the three methods are all in close agreement. Good agreement was also found for the samples using glucose and potassium hydrogen phthalate standards.

In order to estimate limiting concentrations to which potentiometric titration can be applied, and to estimate the minimum sample size which would not affect either accuracy or reliability of COD determination, a number of experiments were effected using samples of the same volume but with different COD concentrations. In these experiments PSE, having original COD of 493 mg/ℓ, was diluted stepwise with double-distilled water down to 1/50. For each dilution duplicate samples with volume 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mℓ were placed in digestion tubes and then double-distilled water added to a volume of 2.5 mℓ. After addition of digestion chemicals, the COD test was conducted according to the "semi-micro" method. COD was measured both colorimetricaly and potentiometrically. The colour-indicator end-point measurement was effected in this series of tests without pre-concentration as suggested for low COD samples, see *Standard Methods* (1992). The colorimetric readings were conducted only after samples had cooled to room temperature. This usually takes up to one hour thereby increasing the detection time significantly. The results are listed in Tables 6A and 6B.

Referring to the results listed in Table 6A, the potentiometric and the colorimetric methods show excellent agreement down to COD close to 20 mg/ℓ; at lower COD values the potentiometric method appears superior. Comparing the two methods, each has its disadvantages for the lower COD measurements. The colorimetric method becomes time- consuming and more expensive because of the need

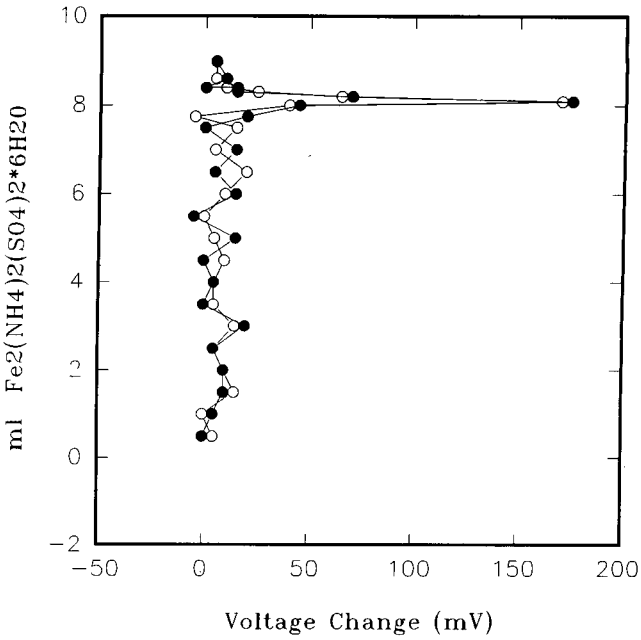


***Figure 5***
*Slope of the observed voltage changes in a potentiometric titration of Neve Shaanan primary settler effluent*

**TABLE 4**
**COD DETERMINATION BY CLASSIC METHOD - SAMPLE VOLUME LARGE**

| Sample | COD (mg/ℓ) | | |
|---|---|---|---|
| | Colorimetry | Potentiometry | Colour Indicator |
| Raw sewage | 1903 + 7.5% | 1706 + 4.6% | 1781 + 7.9% |
| Primary settler effluent | 684 + 7.8 % | 635 + 5.1% | 668 + 8.3% |
| Glucose standard (added 512 mg COD/ℓ) | 528 + 4.5% | 509 + 3.1% | 521 + 4.8% |
| K-hydrogen phtalate (added 504 mg COD/ℓ) | 515 + 4.8% | 508 + 4.4% | 499 + 5.7% |
| Wetland effluent | N.D. | 73 + 4.6% | 79 + 6.2% |
| Fish-pond effluent | N.D. | 41 + 4.4% | 39 + 7.3% |

N.D. = No data because of excessive precipitation.

**TABLE 5**
**COD DETERMINATION BY SEMI-MICRO METHOD - SAMPLE VOLUME SMALL**

| Sample | COD (mg/ℓ) | | |
|---|---|---|---|
| | Colorimetry | Potentiometry | Colour Indicator |
| Raw sewage | 1976 + 8.4% | 1754 + 5.4% | 1854 + 6.7% |
| Primary settler effluent | 688 + 8.9% | 593 + 5.0% | 683 + 8.4% |
| Glucose standard (added 512 mg COD/ℓ) | 523 + 4.6% | 515 + 2.1% | 524 + 5.9% |
| K-hydrogen phtalate (added 504 mg COD/ℓ) | 507 + 4.9% | 501 + 4.9% | 509 + 6.4% |
| Wetland effluent | 72 + 6.0% | 70 + 7.0% | 76 + 5.5% |
| Fish-pond effluent | N.D. | 43 + 3.1% | 43 + 4.7% |

N.D. = No data because of excessive precipitation.

**TABLE 6A**
**POTENTIOMETRIC VS. COLORIMETRIC COD DETERMINATION**

| Potentiometric COD (mg/ℓ) | Expected* COD (mg/ℓ) | Colorimetric COD (mg/ℓ) |
|---|---|---|
| 500 | 493 | 506 |
| 387 | 394 | 386 |
| 298 | 296 | 289 |
| 199 | 197 | 206 |
| 104 | 99 | 101 |
| 46 | 49 | 49 |
| 38 | 39 | 41 |
| 29 | 29 | 32 |
| 21 | 20 | 24 |
| 11 | 10 | 8 |

*Calculated from dilution based on the average of four samples giving COD = 493 mg/ℓ at zero dilution.

**TABLE 6B**
**POTENTIOMETRIC VS. TITRIMETRIC COD DETERMINATION**

| Potentiometric COD COD (mg/ℓ) | Expected* COD (mg/ℓ) | Color indicator mg/ℓ |
|---|---|---|
| 583 | 598 | 585 |
| 452 | 478 | 490 |
| 350 | 348 | 378 |
| 240 | 239 | 253 |
| 131 | 119 | 149 |
| 75 | 75 | 92 |
| 62 | 60 | |
| 49 | 45 | 57 |
| 32 | 30 | |
| 14 | 15 | 22 |

*Calculated from dilution based on the average of four samples giving COD = 598 mg/ℓ at zero dilution.

to use cuvettes with longer light path, and it would appear increasingly less accurate. The potentiometric method at low COD concentration suffers from a relatively slow electrode response in the poorly redox-buffered zone.

Referring to Table 6B the colour-indicator (i.e. ferroin) end-point method is certainly not acceptable at COD values of less than about 100 mg/ℓ.

Additional experiments were effected to assess the effect of both sample size and COD concentration on the accuracy of potentiometric titration method. These were effected on RS, APE and WE, all without dilution using the "semi-micro" method of analysis. Results are shown plotted in Fig. 6 and indicate that the potentiometric method is closely independent of both sample size (in the range 0.5 to 2.5 mℓ) and COD.

## Conclusions

Present-day measurement of the COD of an aqueous solution involves firstly digestion of a test sample with dichromate solution, and secondly measurement of the dichromate remaining

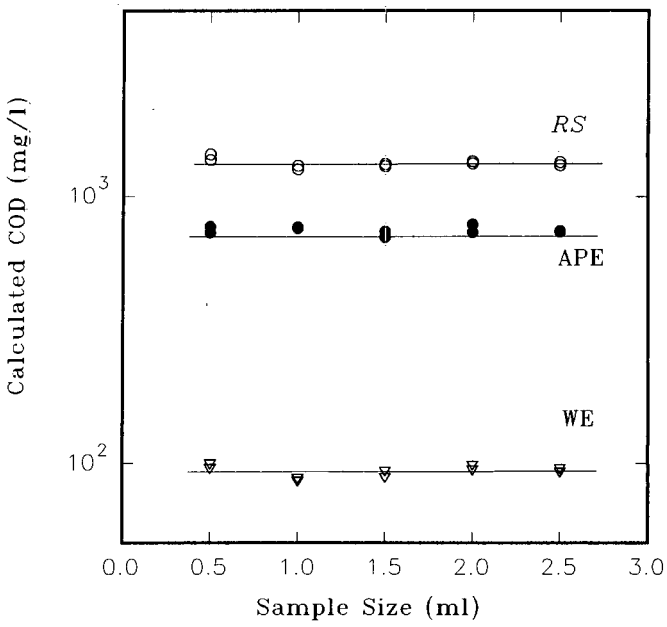


***Figure 6***
*Effect of sample size on potentiometric COD quantification on waste water from various sources*

(after digestion) either by titration with FAS to a colorimetric end point, or via a colorimetric determination using a spectrophotometer. In this paper, a third option for measuring dichromate remaining is proposed. It is shown that a potentiometric end-point titration (with FAS titrant) can be used with equal or better facility. It should be mentioned that all three methods of COD determination addressed in this paper require a digestion step, and in this regard they are all equally affected by the deficiencies of incomplete digestion. Such an error cannot be assessed on samples of unknown organic composition.

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 the titration is sharp and easily identified. Furthermore, the Pt-calomel system used in this method responds quickly to potential changes within the ($Fe^{3+}$/$Fe^{2+}$):($Cr^{6+}$/$Cr^{3+}$) solution producing a stable reading. These factors allow rapid and accurate identification of the true end point. In contrast, the conventionally used colour indicator end-point method, reflects an end point prescribed *a priori* by the chemical characteristics of the indicator. Furthermore, the method is based firmly on theoretical considerations allowing extension of potentiometry into a region of low COD (the lower limits are present elsewhere (Loewenthal et al., 1997).

The method was applied to a broad spectrum of waste waters and dilutions of these, using both macro and semi-micro digestion techniques. Results were compared with data determined using the colorimetric and colour-indicator end-point methods. For all samples colorimetric and potentiometric methods gave closely the same results. However, it should be mentioned that for the low COD values the colorimetric method requires expensive cuvettes and/or pre-concentration of samples, increasing the cost and time involved. Furthermore, the colorimetric method cannot be applied on turbid samples, such turbidity may be present in raw samples or generated in the digestion process. With respect to the colour indicator end-point method, results indicate that it is comparable to the above methods only down to a COD of approximately 50 mg/ℓ.

## References


BERTRAM WF, CARLISLE TO, MURRAY EJ and WARREN WG (1958) Chemical oxygen demand of petrochemical wastes. *Anal. Chem.* **30** (9) 1482 - 1485.

COOKE WD, REILLEY CN and FURMAN NH (1951) Sensitive end-point procedure for coloumetric titrations. *Anal. Chem.* **23** (11) 1662 - 1665.

GAUDY FA (Jr.) and RAMANATHA M (1964) A colorimetric method for determining chemical oxygen demand. *JWPCF* **32** (12) 1479-1487.

GARRELS MR and CHRIST LC (1965) *Solution, Minerals and Equilibria*. Harper & Row, New York.

DASGUPTA PK and PETERSEN K (1990) Kinetic approach to the measurement of chemical oxygen demand with an automated micro batch analyzer. *Anal. Chem.* **62** (4) 395 - 402.

JONES MB, SAKAJI HR and DAUGHTON GC (1985) Comparison of microcolorimetric and macrotitrimetric methods for chemical oxygen demand of oil shale wastewaters. *Anal. Chem.* **57** (12) 2334 -2337.

LOEWENTHAL RE, GREEN M and BILANOVIC D (1997) Determination of low chemical oxygen demand using potentiometry and a modified Gran function. *Water SA* **23** (3) pp to come.

MESSENGER LA (1981) Comparison of sealed digestion chamber and standard method COD tests. *JWPCF* **53** (2) 232 -236.

MOORE WA, LUDZACH FJ and RUCHHOFT CC (1951) Determination of oxygen-consumed values of organic wastes. *Anal. Chem.* **23** (9) 1297 - 1300.

RAVE HA and AVNIMELECH Y (1972) Potentiometric determination of soil organic matter. *Soil. Sci. Soc. Am. Proc.* **36** (6) 967.

SMITH FG (1951) Determination of formal oxidation potentials of ferric-ferrous and dichromate - chromic systems. *Anal. Chem.* **23** (6) 925-927.

STANDARD METHODS (1992) *Standard Methods for the Examination of Water and Wastewater* (18th edn.), Method 5220 C&D, pp 5.6 to 5.10 APHA, AWWA, WPCF, Washington DC.

WENTZEL MC, MBEWE A and EKAMA GA (1995) Batch test for measurement of readily biodegradable COD and active organism concentrations in municipal waste waters. *Water SA* **21** (2) 117-124.