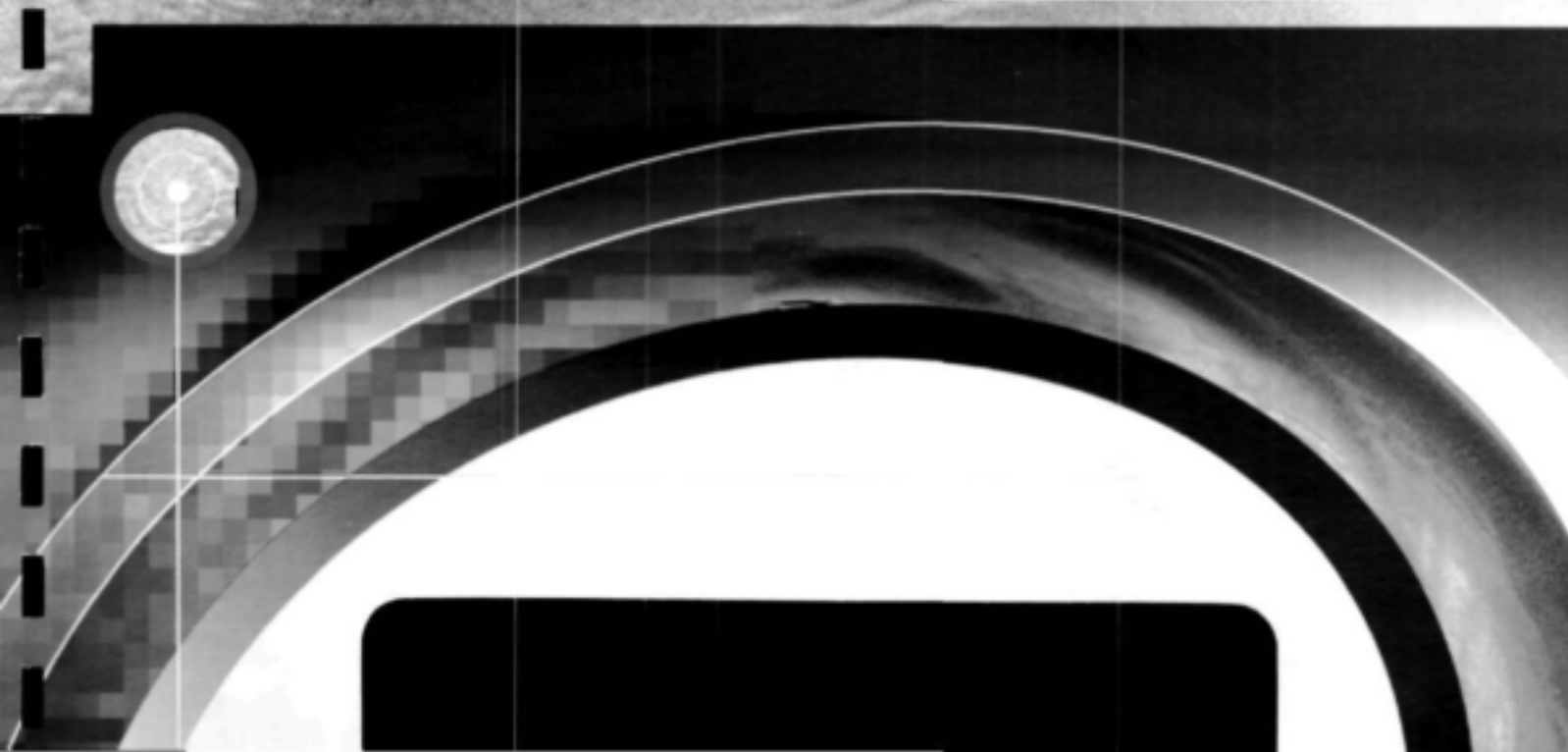

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MEASUREMENT OF COD (ORGANICS) IN DRINKING WATERS AND TERTIARY EFFLUENTS

USE
WRC REPORT NO 833/1/02

RE LOEWENTHAL

MEASUREMENT OF COD (ORGANICS) IN DRINKING WATERS AND TERTIARY EFFLUENTS

by

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Report prepared for
THE WATER RESEARCH COMMISSION

WRC Report No: 833/1/02 **ISBN No: 1 86845 904 7**

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The research is this report emanated from a project funded by the Water Research Commission entitled *"Measurement of COD (organics) in drinking water and tertiary effluents"*.

The Steering Committee responsible for this project consisted of the following persons:

Dr I Msibi
Dr G Offringa
Professor R McCutcheon
Ms M Smuts
Mr J Stow
Mr R E Bartel
Mr D P Theron
Mr D Traut
Mr K Morgan
Dr Katabua
Professor J Haarhoff
Professor C F Schutte

The authors are grateful to Mr I Morrison who prepared the shell for the user friendly computer programme used to determine COD from measurements.

EXECUTIVE SUMMARY

Dissolved (and perhaps suspended) organics invariably are present at low but variable concentrations in tertiary effluents and natural terrestrial waters. Quantifying the concentrations of these is often important: for tertiary effluents, to assess treatment efficiency and aid in process control, and also to effect impact analyses on receiving impoundments; for terresrial waters, in the control of unit processes in drinking water treatment works effecting removal of organics in order to minimise both trihalomethanes (THMs) formation and biogrowth in drinking water distribution systems.

In water treatment practice, accurate measurement of organics at low concentrations (less than ~ 10g C/ℓ) usually is effected using an organic carbon analyser. However, this apparatus is expensive and requires dedicated personnel for both maintenance and quality control. Consequently, only very few laboratories are able to afford the equipment and its effective operation.

In this report an alternative procedure is proposed for assessing dissolved organic carbon (DOC) in water down to concentrations of about 1 mgC/ℓ (i.e. COD of about 3 mg/ℓ). The method involves a novel modification to the conventional COD (chemical oxygen demand) test. It hinges around effecting a potentiometric titration on the digested sample in place of the conventional colourimetric endpoint titration.

The potentiometric titration data is then analyzed using a novel modified Gran function (developed within this project) to yield the COD of the sample. A user friendly computer program GRANCOD is presented to ease such analysis.

Evaluation of the method showed that it is precise and accurate to within 0,3 mℓ of titrant. Furthermore, a closely constant ratio between COD and dissolved organic carbon (DOC) was found for natural terrestial waters (but not those after treatment for humic removal); in the Western and Eastern Cape DOC (mg/ℓ) = 0,35*COD and for the inland waters of the Gauteng region DOC (mg/ℓ) = 0,46*COD.

In conclusion, it is shown that dissolved organics in waters can be quantified rapidly and cheaply by effecting a micro COD digestion on samples. After digestion a potentiometric titration is effected and results analyzed using a modified Gran function to give COD.

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1. INTRODUCTION

Dissolved (and perhaps suspended) organics invariably are present at low but variable concentrations in tertiary effluents and natural terrestrial waters. Quantifying the concentrations of these is often important: for tertiary effluents, to assess treatment efficiency and aid in process control, and also to effect impact analyses on receiving impoundments; for terresrial waters, in the control of unit processes in drinking water treatment works effecting removal of organics in order to minimise both trihalomethanes (THMs) formation and biogrowth in drinking water distribution systems.

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In this report an alternative procedure is proposed for assessing the concentration of organics at low concentrations. The method involves measuring COD of the test solution. Although such measurement is not generally linked to organic carbon content (the ratio between COD and organic carbon varies between organic substances), the relative magnitude of the measurement for a particular water will give the desired information. Its measurement involves addition of a known mass of dichromate to a sample of test solution, the mix is then digested under acidic conditions to effect oxidation of organic material; dichromate remaining after the oxidation process is then measured and COD determined by calculation.

Measurement of dichromate remaining usually is effected either by titration with FAS (Fe^{2+}) to a color-indicator end point, or using a colorimetric technique in conjunction with a spectrophotometer (*Standard Methods*, 1992). Alternatively the titration can be carried out to a potentiometric end point using a Pt-calomel electrode system with a conventional pH meter (Bilanovic et al., 1997). For low COD (i.e. low organic concentration) the titrimetric color end-point method is inadequate. Colorimetry possibly can be applied but requires either pre-concentrating samples and/or expensive apparatus. Titration to a potentiometric end point becomes impractical because of the excessive time required by the electrode system to reach stability in the poorly buffered redox zone around the end point (i.e. a relatively slow response for the electrode system). However, an extension to the potentiometric method is possible using an approach parallel to that proposed by Gran (1950) for determination of alkalinity/acidity. He formulated a function(s)from equilibrium and stoichiometric considerations which allows accurate determination of the proton accepting capacity of a solution without the need of titrating to an end point. An analogous function can be developed for determination of the electron donating/accepting capacity of the (Fe^{2+}/Fe^{3+}): (Cr^{6+}/Cr^{3+}) system in aqueous solution.

In this report, a modified Gran function for the potentiometric measurement of COD is developed first. Thereafter, its utilisation in COD determination is evaluated on a variety of solutions. Firstly, on samples containing known concentrations of glucose in a concentration range 4 mg/ℓ < COD < 20 mg/ℓ to test the accuracy of the procedure. Secondly, it is applied to the raw and treated terrestial waters in the W. Cape (which have high humic concentration) and to various waters in the Gauteng region.

2. THEORETICAL CONSIDERATIONS

Smith (1951) observed that the potentiometric end point to the titration of $Cr_2O^{2-}_7$ (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 $Cr_2O^{2-}_7$ (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.

2.1 System equations

Considering the $Cr^{3+}/Cr_2O^{2-}_7$ (i.e. Cr^{6+}) subsystem, for didactic purposes it is useful to express the oxidised Cr species in the form Cr^{6+} rather than $Cr_2O^{2-}_7$. The reaction depicting the interchange between these species can be visualised as:

$$Cr_2O^{2-}_7 + 14H^+ \leftrightarrow 2Cr^{6+} + 7H_2O \qquad (1)$$

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.:

$$Cr^{3+} \leftrightarrow Cr^{6+} + 3e^- \qquad (2)$$

Consequently, the redox equilibrium equation for the subsystem Cr^{3+}/Cr^{6+} (i.e. $Cr_2O^{2-}_7$) 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 molar concentration of species X, i.e. free plus complexed species concentrations.

$[Cr]_t$ = total molar concentrations of Cr species in solution.

(X) = activity of species X.

(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^{2-}_4 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 molar 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

2.2 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 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.

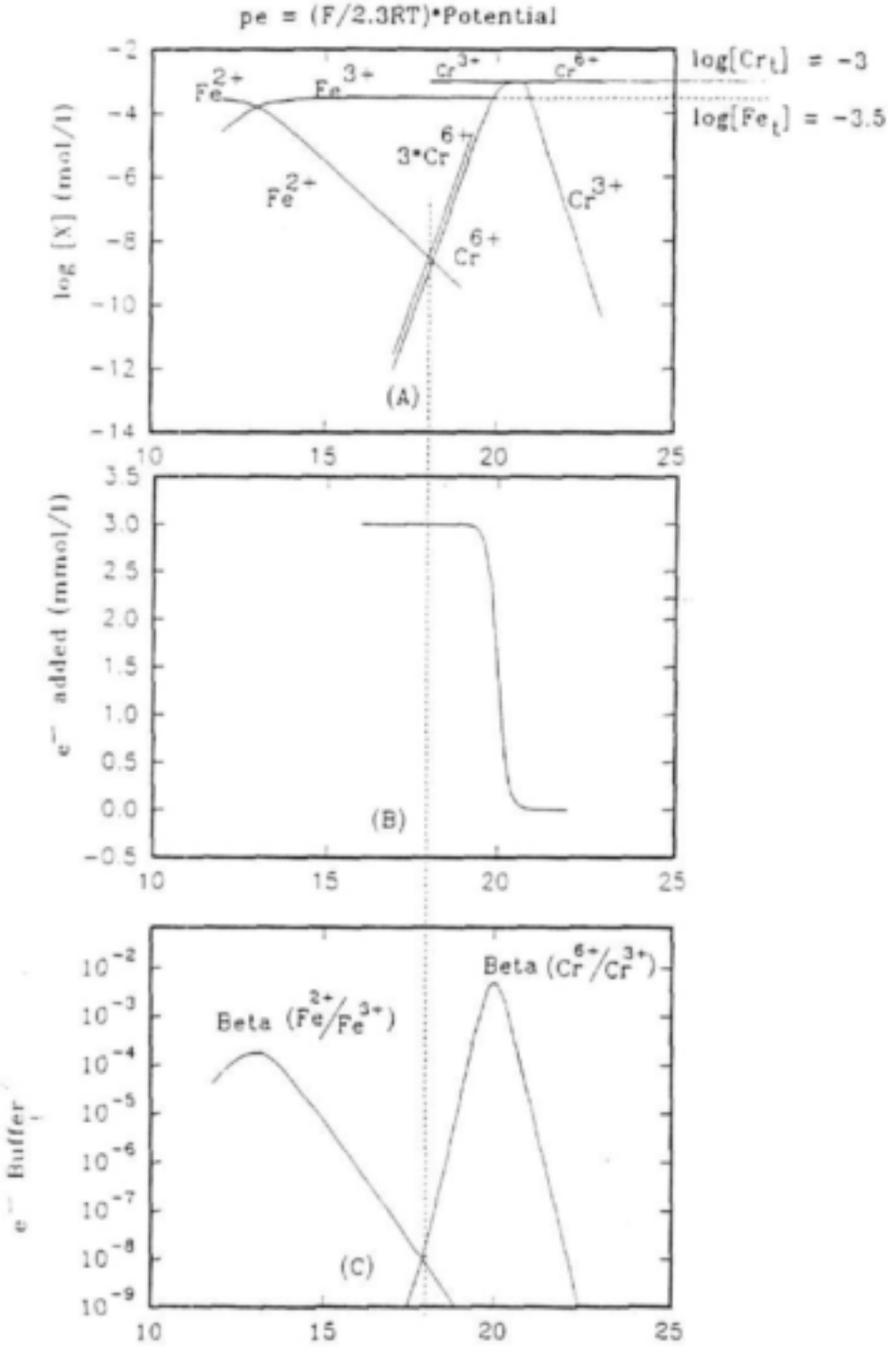


Figure 1: **Theoretical determination of distribution of species, addition of FAS titrant and redox buffer with pe**

2.3 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

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

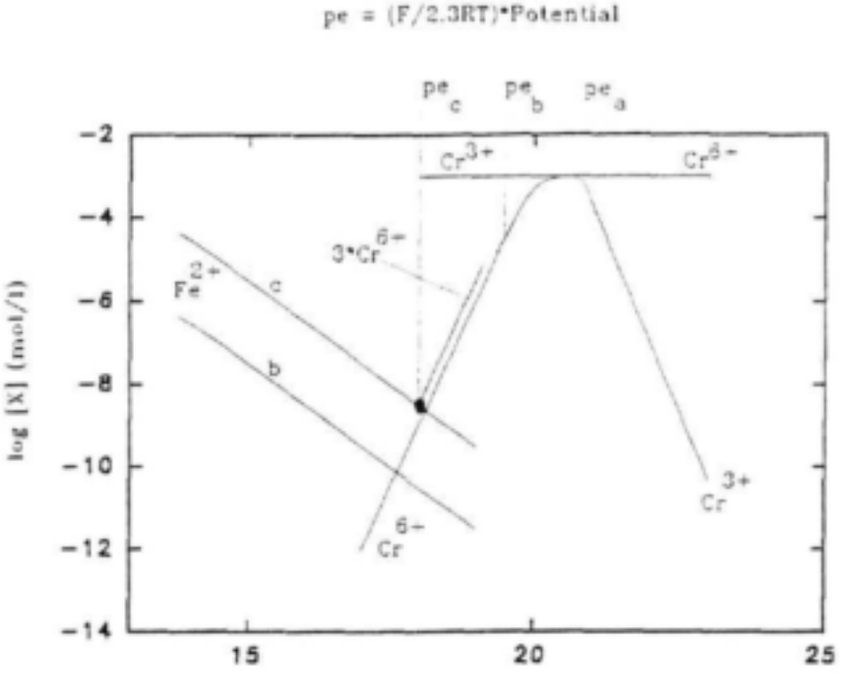


Figure 2: Graphical exposition of potentiometric end-point estimate in the COD titration

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

2.4 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.:

$$(e^- buffer) = \left(\frac{\delta EAC}{\delta pe}\right)[Cr]_t \tag{9a}$$

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

$= e^-$ 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.:

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

where:

e^- buffer has the value determined from Eq (9b) with e^- equal to its estimated value from the potentiometric titration, and
Δpe = estimated difference between assumed and true end-point pe value.
ΔEAC = 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 ΔEAC to be totally negligible.

2.5 Formulation of the alkalimetric Gran function

Gran formulated a semi-graphical technique for determining alkalinity from strong acid titration data without the need of accurate end-point pH detection. The approach hinges on the observation that the mass of alkalinity in a sample (during titration) varies linearly with the volume of titrant (strong acid) added. For example, in the titration of a weak monoprotic acid system (HA/A^-) with standard strong acid, the molar mass of alkalinity (M.Alk) is:

$$M.Alk_x = C_a * (V_e - V_x) \qquad (11)$$

where:

C_a = molarity of titrant
V_e = volume of titrant to the end point (to be determined)
V_x = volume of titrant added
Subscript x = value of parameter after addition of V_x mℓ titrant.

In terms of species concentrations (for alkalinity with reference species HA):

$$M.Alk_x = \{[A^-_x] + [OH^-]_x - [H^+]_x\} * (V_s + V_x) \qquad (12)$$

where:

V_s = initial volume of sample
[Y] = molarity of species Y

Equating Eqs. (11) and (12) and multiplying both sides by the monovalent activity coefficient, f_m, to obtain H^+ in the activity form (which is linked to pH):

$$F_m C_a (V_e - V_x) = [(A_x) + (OH^-)_x - (H^+)_x] (V_s + V_x) \quad (13)$$

where:

(Y) = activity of species Y.

If the titration is continued to well below the end point (i.e. to a pH below the HA equivalence point), the terms $(A^-)_x$ and $(OH^-)_x$ become negligible compared with $(H^+)_x$, leading to an equation for the Gran function F_x, i.e.:

$$F_m C_a (V_e - V_x) = - (H^+)_x (V_s + V_x) \quad (14a)$$
$$= F_x \quad (14b)$$

Values for F_x are obtained using the right-hand side of Eq. (14a) and a series of pH observations (where $pH_x = -\log_{10} (H^+)_x$). A plot of these F_x values against a corresponding value for V_x will be linear, and extrapolation to $F_x = 0$ yields the value of V_e (see left-hand side of Eq. (14a)), and hence alkalinity is calculated.

2.6 Equilibrium chemistry of the ($Cr_2O_7^{2-}/Cr^{3+}$) and (Fe^{2+}/Fe^{3+}) subsystems

For the chromate subsystem in an aqueous solution, the equilibrium reaction and equation can be written as follows:

$$2Cr^{3+} + 7\ H_2O \leftrightarrow Cr_2O^{2-}_7 + 14\ H^+ + 6e^- \quad (15)$$

where:

( ) = activity
K_c^{th} = thermodynamic equilibrium constant

Now in a COD test, the solution is acidified to a pH ~ 0 with concentrated sulphuric acid so that the principal ionic matrix of the solution is comprised of H^+ and SO_4^{2-} species, with the chromate species at a relatively low concentration. Furthermore the solution is titrated with similarly acidified FAS titrant. This has two implications on the above equations. Firstly, pH (i.e. H^+) can be considered constant during the titration and incorporated into the K value on the right-hand side of the Eq. (15). Secondly, there will be significant complexing between the chromate species and SO_4^{2-}. However, because dichromate is not part of a principal ionic matrix, these complexing effects (and short-range Debye-Hückel effects) also can be incorporated into the equilibrium constant to give an apparent constant K_c. In this event, the chromate species concentrations on the left-hand side reflect total molarities (i.e. free plus complexed species). This approach is commonly used for weak acid chemistry in sea water (Loewenthal and Marais, 1986). Rewriting Eq. (15) using this approach yields:

$$\frac{[Cr_2O_7^{2-}](e^-)^6}{(Cr^{3+})^2} = K_c \quad (16)$$

where:

[Y] = molarity of the free plus complexed species Y
(e^-) = electron activity
K_c = an apparent equilibrium constant incorporating complexing, pH and Debye-Hückel effects.

and the mass balance expression is:

$$2\,[Cr_2O_7^{2-}] + [Cr^{3+}] = Cr_t \qquad (17)$$

Similarly for the Fe^{2+}/Fe^{3+} subsystem:

$$\frac{[Fe^{3+}](e^-)}{[Fe^{2+}]} = K_f \qquad (18)$$

where:

K_f = the apparent equilibrium constant for the Fe^{2+}/Fe^{3+} system which incorporates both complexing and Debye-Hückel effects.

and:

$$[Fe^{3+}] + [Fe^{2+}] = Fe_t \qquad (19)$$

The electron activity, $(e^-)_x$, is directly linked to redox potential, E_x,

$$pe_x = \frac{F}{2.303 * RT} E_x \qquad (20)$$

$$= 17.182\ E_x \text{ at } 298K \text{ and } 1 \text{ atm}$$

where:

F = Faraday constant, 23.06 kcal/volt-gram equivalent
R = gas constant, 0.001986 kcal/K
T = absolute temperature, K

These equations are depicted graphically in Fig. (1) in a plot of the log of species concentration vs. pe (i.e. $-\log(e^-)$) for a solution with $Cr_t = 10^{-3}$M and a number of concentrations of Fe_t (lines labeled "b". "c" etc.) to reflect states established in the solution after addition of increasing amounts of FAS titrant (i.e. addition of Fe^{2+}).

3. FORMULATION OF MODIFIED GRAN FUNCTION FOR COD DETERMINATION

In the COD titration of the "excess" $Cr_2O_7^{2+}$, the new species generated in the redox reaction are Cr^{3+} and Fe^{3+} respectively, consequently the end point to the titration corresponds to an equivalent Cr^{3+}/Fe^{3+} solution. The Fe^{2+} added to obtain this condition of equivalence will equal the electron accepting capacity (EAC) of the solution, with reference species Cr^{3+} and Fe^{3+}. To effect this measurement without titrating to the end point, and thereby avoiding end-point errors, a similar technique to that above for alkalinity determination is employed. This involves first formulating an equation for the molar mass EAC in the sample after addition of V_x mℓ titrant, $M.EAC_x$ (which varies linearly with Vx). Thereafter one identifies a region in the titration where $M.EAC_x$ can be determined from the measured redox potential. By analogy with Eq. (11):

$$M.EAC_x = C_f (V_e - V_x) \qquad (21)$$

where:

C_f = molarity of FAS titrant
V_e = unknown volume of FAS to reach the titration end point,
V_x = volume of titrant added.

And, in terms of species concentration, analogous to Eq. (13):

$$M.EAC_x = \{6\,[Cr_2O_7^{2-}]_x - [Fe^{2+}]_x\}\,(V_s - V_x) \qquad (22)$$

Equating Eqs. (21) and (22) gives the desired linear relationship between $M.EAC_x$ and V_x, i.e.:

$$C_f (V_e - V_x) = \{6\,[Cr_2O_7^{2-}]_x - [Fe^{2+}]_x\}\,(V_s - V_x) \qquad (23)$$

From Eq. (22), the end point to the titration corresponds to the condition $M.EAC_x=0$, that is to the state where $6[Cr_2O_7^{2-}]_x = [F^{2+}]_x$ with redox potential pe_e, see Fig. (1). At a redox potential below this point (i.e. the titration is carried out past the endpoint), $[Cr_2O_7^{2-}]_x$ becomes negligible compared with $[Fe^{2+}]_x$ and Eq. (23) approximates to:

$$C_f (V_e - V_x) = [Fe^{2+}]_x (V_s + V_x) \qquad (24a)$$
$$= F_x \qquad (24b)$$

This equation is analogous to the *Gran function* used in alkalinity determination (Eq.(14)) with $(H^+)_x$ now replaced with $[Fe^{2+}]_x$. However, whereas for alkalinity determination values for $(H^+)_x$ could be obtained directly from pH_x data observed in titration, in this case $[Fe^{2+}]_x$ is not directly linked to the redox potential (pe_x) observations, but rather to the molar mass of titrant added (i.e. the total dissolved iron in solution, Fe_t) and redox potential pe_x via Eqs. (24) and (25) i.e.:

$$[Fe^{2+}]_x = \frac{(Fe_t)(e^-)_x}{(K_f + (e^-)_x)} \qquad (25)$$

Now, writing Fe_t in terms of the volume of titrant added:

$$[Fe]_t = \frac{V_s C_f}{V_s + V_x} \qquad (26)$$

Substituting Eqs (25) and (26) into Eq. (24) gives the *modified Gran function,*

$$(V_s - V_x) = \frac{V_s}{1 + 10^{y}} \qquad (27a)$$

$$= F_x \qquad (27b)$$

where:

$$y = pe_x - pK_f$$

$$= \frac{F}{2.303RT} E_x - pK_f$$

E_x = potential reading (Pt-calomel system, see later) in volts after addition of V_x mℓ tirant.

pK_f = negative log of apparent equilibrium constant for the Fe^{2+}/Fe^{3+} subsystem relative to the calomel reference electrode)

From the right-hand side of Eq. (27a) a series of values for F_x can be calculated from corresponding observed data for V_x and E_x in the pe region of the titration below the equivalence point, for example pe_b and pe_c with E_x values E_b and E_c in Fig. 1 (These analyses require that the constant pK_f be known, see below). Furthermore, a plot of V_x vs. F_x will be linear and extrapolation to $F_x = 0$ will intercept V_x at $V^{'}_e$. In order to determine the COD of the test solution, such titration would also have to be carried out on a blank, and the COD could then be calculated as (see *Standard Methods,* 1992):

$$COD\ (mg/\ell) = (V_{eb} - V_e) * C_f * 8000/V_s$$

where:

V_s = volume of sample used in digestion (mℓ)

V_{eb} = volume of titrant to the end point for the blank.

3.1 Determination of equilibrium constant pK_f and numerical determination of V_e

Utilisation of the *modified Gran function* (Eq. (17)) to determine the volume of FAS to the titration end point (i.e. V_e), requires that the apparent equilibrium constant for the Fe^{2+}/Fe^{3+}subsystem (i.e. pK_1) beknown or calculated. Calculation of the constant from thermodynamic data is totally impractical because of the very complex ionic interactions in the digested solution. However, values can be determined very easily from pairs of titration data in the redox region under consideration from the modified Gran function: Rearranging Eq. (27) and solving for V_x:

$$V_{x1} = V_e(1 + 10^{Z1}) \qquad \textbf{(28a)}$$

where:

$$Z_1 = -17.182E_{x1} + pK_f$$

E_{x1} = potential (in V) after addition of V_{x1} mℓ titrant.

Similar equations can be written down for each addition of titrant in the region under consideration, for example after addition of V_{x2} mℓ titrant.

$$V_{x2} = V_e(1 + 10^{Z2}) \qquad \textbf{(28b)}$$

Solving for pK, from Eqs. (28a) and (28b) gives:

$$10^{pK} = \frac{V_{x1} - V_{x2}}{V_{x2}10^{-17.182E_{x1}} - V_{x1}10^{-17.182E_{x2}}} \qquad \textbf{(29)}$$

Examination of Eq. (29) indicates that a number of values for pK_f can be determined in the titration region under consideration simply by considering different pairs of data. This proves useful, because it allows determination of pK_1 through the titration which allows one to ensure that it remains constant (a requirement of the constant ionic medium approach adopted, plus or minus 0.03 units). Note that only data below the equivalence point must be used – at redox potentials above this point the assumptions used in modifying Eq. (23) to give Eq. (24) are not valid.

Examinations of Eqs. (28) and (29) shows that for each pair of data yielding a pK_1 value, one can obtain a corresponding V_e value, for example for V_{x1} (and V_{x2}):

$$V_e = \frac{V_{x1}}{1 + 10^{Z1}} \qquad \textbf{(30)}$$

Usually, in a particular batch of COD determinations the pK_1 value(s) is calculated from the blank and then applied in determinations of *modified Gran function* values for the various samples to obtain corresponding V_e values. For more accurate work, pK_f can be determined for each sample.

4. MATERIALS AND METHODS

In utilising the modified Gran function, digestion is carried out using the "semi-micro" procedures set out under the "Closed reflux colorimetric method" (*Standard Methods*, 1992).

The full procedure adopted and materials used are listed below. However, it is to be noted that these reflect experimentation used here and do not constitute a 'standard method'.

4.1 Apparatus used

a. Simax (tall form) 100mℓ and 250mℓ beakers in which titration of digested samples is effected.
b. Custom made pyrex digestion tubes 21,5mm inside diameter and 302mm length together with caps.
c. Automatic titrator – Metrohm 715 Dosimet (or a micro burette).
d. Voltmeter: Hannah pH/mV instrument 8417.
e. Combined platinum electrode:
Metrohm 6.0415.100 (3MKCℓ).
f. Magnetic stirrer and magnetic TFE covered stirrers.
g. Labcon block digester (heating digestion block)
h. 0,45 micron membrane filter paper.

In addition to the above, measurement of dissolved organic carbon was effected using either an ANATOC total organic carbon analyser or a Shimatsu TOC5000A, where available. Absorbance was measured using a Unicam 8625 UV spectophotometer.

4.2 Solutions used

a. FAS titrant: Prepared by adding 1g Fe $(NH_4)_2$ $(SO_4)_2$ $6H_2O$ to distilled water, adding 160mℓ of analar H_2SO_4 and then bring up to 1ℓ with distilled/deionized water.

b. Ferroin indicator: 0,05 mℓ (i.e. one drop) of ferroin indicator added to sample and blank

c. Sulphuric acid/silver catalyst solution:

Add 4,6g/ℓ of Ag_2SO_4 to analar H_2SO_4

d. Dichromate solution: Dissolve 1,226 g analar $K_2Cr_2O_7$ (previously dried for 2 hours at 150°C) in distilled water and bring up to 1000 mℓ. The resultant solution will be 0.00417M $K_2Cr_2O_7$.

4.3 Measurement procedure

a. Sample: Accurately add 10mℓ of filtered sample water (or distilled water for the blank) to digestion tube.

b. Dichromate: 5mℓ of 0,00417M K_2 Cr_2 O_7 is added to the 10mℓ sample (and blank).

c. Sample/blank acidification: 10mℓ of analar H_2SO_4 (containing Ag_2SO_4) is added to the 10mℓ sample/blank dichromate solution(s) in digestion tubes.

d. Add ±0,05g $HgSO_4$ to the samples/blank in digestion tubes.

e. Shake digestion tube samples thoroughly on a rotomix for minimum 10sec.

f. Place tubes in block digester preheated to 150°C for 2 hours.

g. Remove tubes from block digester and cover with parafilm. Allow to cool.

h. Transfer contents of samples and blanks into 100mℓ or 250mℓ glass beakers for titration and add a further about 50ml distilled water.

i. Mixing should be effected using the magnetic stirrer. Add 1 drop ferroin indicator into glass beakers (optional) and cover with parafilm to prevent contamination until the solution is titrated.

j. Titrate each of the samples/blanks with FAS using the automated titrator (or micro burette) at a slow constant flow until either the colour changes or voltage drops very rapidly. Add a further ±1mℓ of FAS.

k. Wait until voltage is stable for at least 1 minute and note the first voltage reading and volume of FAS added.

l. Add a further about half volume of the FAS that was added to obtain the initial (first) voltage reading.

m. Wait until the voltage is stable for a further 1 minute and take the final voltage reading and volume of FAS added.

n. Determine COD either from Equation (30) or using the supplied programme GRANCOD.

4.4 Precautions

a. All glassware should be cleaned as follows: Rinse in hot water before washing with chromic acid. Rinse thoroughly with hot water followed by distilled water and finally deionized water. Leave glassware upside down to dry.

b. The combined platinum electrode should be cleaned with toothpaste and then well rinsed with distilled water before daily use.

5. RESULTS AND DISCUSSION

5.1 Verification

In assessing this approach to measuring COD a number of factors need to be considered. First, the accuracy of the modified Gran function to COD measurement. Second, the precision of the method in the practical scenario. And third, an enquiry into the existence of an empirical link between COD and dissolved organic carbon (DOC) for water from a particular catchment or geographical region.

To assess the accuracy of the Gran function approach, a known mass of organic reductant (glucose) was added to distilled water to create samples with known COD. The COD of these samples (varying from zero to 8 mgCOD/ℓ) was then measured using the method outlined in this report. The results are shown listed in Table 1 below and show excellent agreement. However, it should be noted that in the practical scenario there is no absolute guarantee that all the DOC will necessarily be oxidized by the dichromate in the COD test.

TABLE 1
COMPARISON OF KNOWN COD WITH MEASURED COD

(DETERMINED USING *MODIFIED GRAN FUNCTION*)

Glucose added (mgCOD/ℓ	V_e blank* (mℓ)	V_e sample* (mℓ)	COD measured (mg/ℓ)
0.0	28.9	28.9	0.0
4.3	28.9	27.5	4.9
6.0	28.9	27.3	5.6
8.0	28.9	26.7	7.7

Sample size 2.5 m/ℓ, 1.5.m/ℓ, 0.0003513 M $K_2Cr_2O_7$; 3.5 m/ℓ concentrated H_2SO_4, brought up to total volume of 100 m/ℓ FAS of 0.0001092 M

*pK, determined from the blank 7.18

The precision of the method was assessed in the practical scenario by effecting COD measurement on water samples obtained from numerous sources in the W. Cape. COD measurements on each sample were effected in duplicate and 102 samples were investigated. A statistical analysis of the COD titration differences between duplicate samples is shown in Figure 3.

Referring to Figure 3, analysis would indicate that a standard deviation in the COD titration of about 0,3 mℓ of titrant is to be expected. However, the 'large' number of outliers create some concern. To investigate whether these arose from either the modified Gran theory or potentiometric observations in the titration, an analysis was effected of the difference between colourimetric endpoint and the true equivalence point obtained from the modified Gran technique, see Figure 4. Referring to Figure 4, it is observed that there is a closely constant difference between volume of titrant added determined colourimetrically and potentiometrically. Furthermore, this difference has a very small standard deviation. The low standard deviation indicates that where outliers occur, they probably arise from some organic contamination during the testing regime. In practice such occurrences are easily recognised (provided tests are effected in duplicate) and should be rejected as outliers.

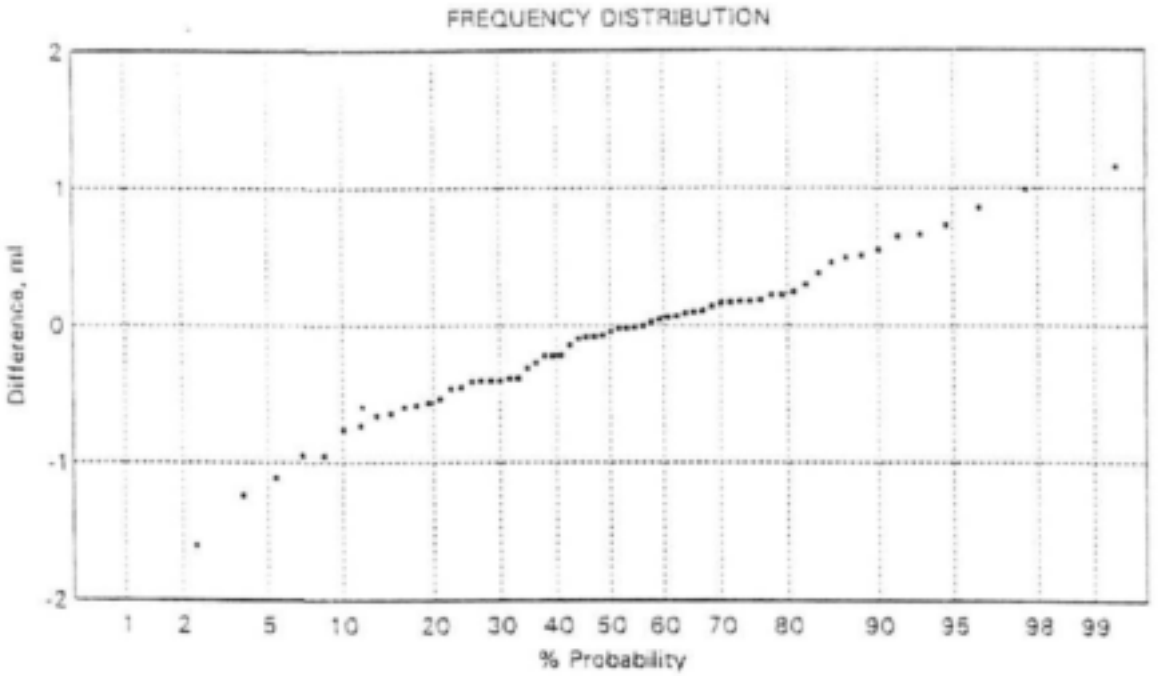


Figure 3: Statistical analyses of COD titration on duplicate samples

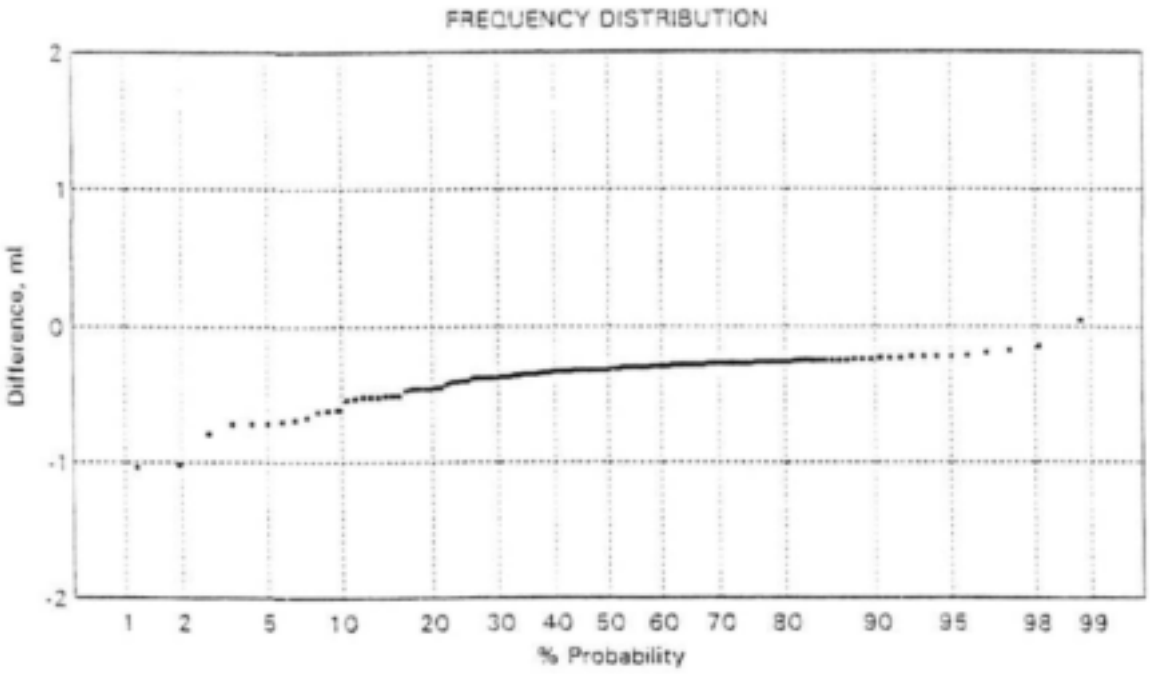


Figure 4: Statistical analyses of COD titration using colourimetric and potentiometric endpoints

Third, with regard to a link between COD and DOC, waters from a wide geographical terrain in the W.Cape and four sources in the Gauteng region were investigated. DOC measurement was effected using an ANATOC DOC analyser which required substantial modifications to obtain reasonable accuracy.

Waters from ten sources in the W. and E.Cape (Churchill Dam, PE; Plettenberg Bay; Knysna; Sedgefield; George; Sandhoogte; Mossel Bay; Kleinbrak; Duivenshok; Swellendam; Simonstown) were analysed. These analyses were effected during both summer and winter seasons. A plot of COD versus DOC and DOC versus UV absorbance (at 254 nm) is shown in Figure 5. The plot shows a meaningful empirical relationship between these parameters, i.e. DOC (mg/ℓ) = 0,35*COD.

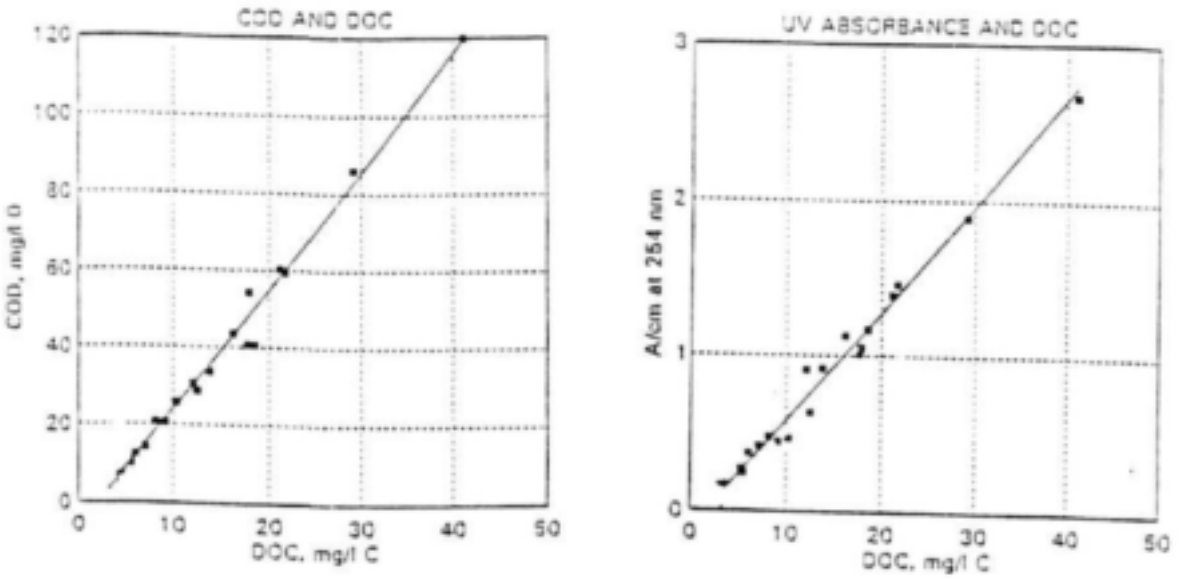


Figure 5: COD versus DOC and absorbance (at 254 nm) for raw surface waters from W.Cape

For the Gauteng region, four water sources were analysed (Vaal Dam, Rietvlei, raw tap water and a river water). Results from analyses gave:

	DOC (mg/ℓ)	COD (mg/ℓ)
Vaal Dam	5,15	10,81
Rietvlei	7,32	16,10
Tap Water	7,33	16,12
River Water	6,99	15,38

For these waters the relationship linking DOC and COD gave:

DOC (mg/ℓ) = 0,46*COD

One may conclude that the nature of the dissolved organics present in W.Cape and Gauteng waters has different oxidation states.

Attempts to expand sensitivity

Conventionally, excess dichromate is used to ensure complete digestion and dichromate remaining is measured. In order to increase sensitivity of observations either or both of two strategies currently are used:

(a) Diluting the FAS titrant to expand the difference between volume of titrant added to the blank (V_b) and that added to the same)V_e)

(b) Minimising the excess dichromate, the effect of which is to increase the ratio of (FAS added to the blank)/(FAS added to the sample). This approach involves addition of less dichromate prior to digestion.

With regard to (a) above, titrations were carried out on low COD waters (and blanks) with FAS concentrations diluted approximately three times that used in the previous experiments (see Tables 1 and 2). Samples of known mass of dichromate were titrated with FAS (~0.0004 M). The observation was, the lower the mass of dichromate present the higher the error in the estimated mass of dichromate used. Furthermore, the time required for the Pt-calomel electrode system to reach a stable potential after each addition of titrant, increased with decreasing mass of dichromate. In order to assess whether these problems arose because of the low mass of dichromate used, or because of the low concentration of iron in the titration solution, a further series of investigations were effected. In these, a low mass of dichromate was used (i.e. (b) above) but the FAS concentration was increased by a factor of two (FAS – 0.00088M). In these experiments the error in dichromate determination was minimal, provided the electrode system was allowed to stabilise for 5 min after the first addition of FAS to obtain a potential below the equivalence point and the electrode system was allowed 1 min to stabilise after each subsequent addition of titrant.

The tentative conclusion was that the time for the electrode system to reach stability becomes excessively long when the concentration of dissolved iron in the titration solution is too low. These observations formed the basis for the proposed methodology to be adopted in the measurement of low COD samples in the field (see **Materials and methods**). That is, in utilising the modified Gran function method the concentration of dissolved iron in a titration solution should be sufficiently high so that good coupling is obtained with the electrode system. This can be achieved by preparing the solution to be digested as follows: 2.5 mℓ sample with COD<20mg/ℓ, addition of 1.5mℓ of dichromate of molarity ~ 0.001 M, addition of 3.5mℓ concentrated H_2SO_4; diluting the digested solution before titration with not more than 100mℓ distilled water and titrating with FAS titrant of concentration greater than ~ 0.0007 M.

REFERENCES

Loewenthal, R., Bilanovic, D., Thebe, T. and Green, M. (1997). Determination of low chemical oxygen demand using a modified Gran function, Water SA 23 (4), 293-299.

Smith, F.G. (1951). Determination of formal oxidation potentials of ferric-ferrous and dichromate-chromic systems, Anal. Chem. 23 (6), 925-927.

Standard Methods (1992). Standard Methods of the Examination of Water and Waste Water, AWWA, WPCF, Washington DC.

APPENDIX A

GRANCOD

USER MANUAL

GRANCOD

USER MANUAL

PURPOSE

GranCod calculates the end points and COD concentrations for titrations carried out using the gran method.

USING GRANCOD

1. To start the program: Key iN **grancod** on the command line and press **Enter.**

2. From the Main Menu: Run any of the displayed actions, until the job is complete.

3. To exit the program: Choose **Quit Program** from the menu and press **Enter.**

MAIN MENU

The main menu allows a choice of the following actions, which may be carried out in the order appropriate to the problem in hand:

Open Data Files: Allows naming of input and output files. Not essential.

Enter Batch Data: Data common to a batch of titrations, e.g. dichromate volume.

Enter Sample Data: Sample names and volumes, titrant volumes and potentials.

Print Data: Send data and results, for all samples in the batch, to the printer.

Choose Printer Port: Choice of lpt1: or lpt2:

Help on Files: Information about use of files for input and output.

Quit Program: Terminates the program.

INPUT AND OUTPUT FILES

You can run the program without making use of data files, but:

Data files are useful for:	Storing results. Re-use of batch data and sample names.
To read in an existing file, at any time:	Select the **Open Data Files** item from the menu.
	Enter a name for the **Input File** field or Press **Enter** and select a file from the resultant Menu of names in the current director.
	Note: data entered during the current session will be saved before the new file is opened,

provided an output file has been named, otherwise it will be lost.

If you want data to be saved: Supply an output file name. Entered data and results will automatically be saved, on exiting or when a new input file is named, if changes have been made.

Routine analysis of a set of sample points: If you want to re-use sample names or batch data, supply the name of a suitable existing file as an input file. You can clear old titration values by pressing **F8** or by overwriting them.

The output file can be the same as the input file if you don't want long-term storage, otherwise use a new output file name each time.

BATCH DATA

To move up and down the batch-details Page: Use the arrow keys.

Some are fields that are unchanging and are skipped by the cursor.

To enter new values or make changes: Key in the new values
or
With items that end in … press **Enter** to display a menu of commonly used values. Select the desired item and press **Enter.**

Commonly used values are supplied as defaults, where possible. Take care to change these if necessary.

Sample Volume: The value entered in this field will be used as the default volume for individual samples, on the sample data page.

If individual sample volumes differ, enter their values – which will be used in the calculations – on the Sample Data page.

SAMPLE DATA

There are three panels on this page, namely **Samples, Input** and **Quality Control**:

SAMPLES PANEL: a list of samples, initially containing only two items named Blank

To move up and down this list: Use the **PageUp** and **PageDown** keys

To add a new item, after the current item:	Press **Cntrl-Insert**.
	The default name for a newly inserted sample line is *Blank*. If the sample is not meant to be a COD blank, the name **must** be changed to something else, on the input panel.
	Note: Any name starting with *Blank* is taken to signify a COD blank. Names such as *Blank1, Blank 2* etc may be used. There must be at least one blank in any batch of samples to allow COD to be calculated.
To delete the current item:	Press **Ctrl-Delete**.
INPUT PANEL:	The data entry panel, which displays and allows editing of the details of the current sample.
To enter new value in a field:	Key in the value and press one of the **Enter, up-arrow, down-arrow, PageUp** or **Pagedown** keys to confirm the entry.
	Note: The normal action when you start to enter data into a field is that the previous content is cleared. However, if you merely wish to alter part of the existing content you can avoid this loss by first pressing **Del** or **Backspace** and then editing the field.
To recover the previous field value:	Press **Esc** – only works if you have not yet confirmed the new entry, otherwise **Esc** gives you the main menu.
To move between fields:	Use the **up** and **down** arrow keys.
To move inside a field:	Use the **left** and **right** arrow keys.
To delete characters:	Use the **Backspace** or **Delete** keys.
To toggle Insert Mode on/off:	Use the **Insert** key.
To exit to the main menu:	Press **Esc**, if not busy editing a field.
Sample volume:	The default volume is that given in the Batch Data page. Alter it as desired.
Titration data:	Enter titrant volumes and electrical potential readings in rows **V1, V2** and **V3.** Only two sets are required, for an end-point volume to be

calculated and displayed, but a third may also be provided.

Calculated end point volume and COD:

Displayed at the bottom of the panel, once enough data has been entered. Will be updated each time a change is made.

The mean of all blank volumes in the batch is used in the calculation of COD's. Therefore, COD values will be adjusted as entry of data progresses.

QUALITY CONTROL PANEL:

Displays calculated endpoints and pKf values for all possible pairs of titrant volumes V1, V2 and V3. If only V1 and V2 are entered, only one result will be available. For three pairs, three results are calculated and used for the sample average.

EXAMPLE

Two waters, A and B, are to be analysed for COD. For each water two 10 mℓ samples, A1 and A2 and B1 and B2, together with two blanks have been digested with 5 mℓ of 0.00417 molar dichromate.

FAS titrant (0.00255 molar, i.e. 1 g/ℓ) was added to the samples such that the titration endpoint was passed by about 1 mℓ of titrant, the volume of titrant V1 (mℓ) and redox reading E_1 (m volts) was noted; a further volume of titrant was then added and potential measured to give V_2, E_2. This data was then used with GRANCOD to determine COD as follows:

Select 'Enter batch data'

The screen then displays 'Batch details'.

For our example type say 'DICK' for sample set name and either accept default data or change this information.

In our example change the default value for 'dichromate volume' from 2.0 to 5.0.

Press 'ESC' to return to main menu.

Select 'Enter sample data'
You will now be working on the middle screen under 'input':

Give 'name' the name 'blank1'
Give 'sample volume' (mℓ), the value 10

Enter to	'volume of titrant'	'Potential'
V1	42.0	607
V2	63.0	513

Above right screen for calculation and middle screen below data for endpoint data.

Now press 'page down' and then 'enter' to get to the next sample; also a blank.

Repeat as in previous blank, naming this one 'Blank2' with a 'sample volume' of 10.0.

Enter measured data.

	Volume	Potential
V_2	41.5	606
V_2	62.25	519

Observe 'endpoint data' and 'quality control' screen.

Press 'CTRL Insert' for sample A1.
Type 'A1' and enter the relevant data, i.e. sample volume of 10.0 mℓ and

	Sample Volume	Potential
V_1	38.5	632
V_2	57.75	532

Read off COD of sample on the 'endpoint' screen (below, middle), i.e. COD = 7,10 mg/ℓ.

Press 'CTRL INSERT' for sample A2.
Type 'A2' and enter the relevant data, i.e. sample volume of 10.0 mℓ and

	Volume	Potential
V_1	38.5	635
V_2	57.75	535

The 'Endpoint screen' gives COD = 7.10 mg/ℓ (i.e. identical to sample A1).

Press 'CTRL INSERT' for sample B1.
Type 'B1' and enter the relevant data, i.e. sample volume of 10.0 mℓ and

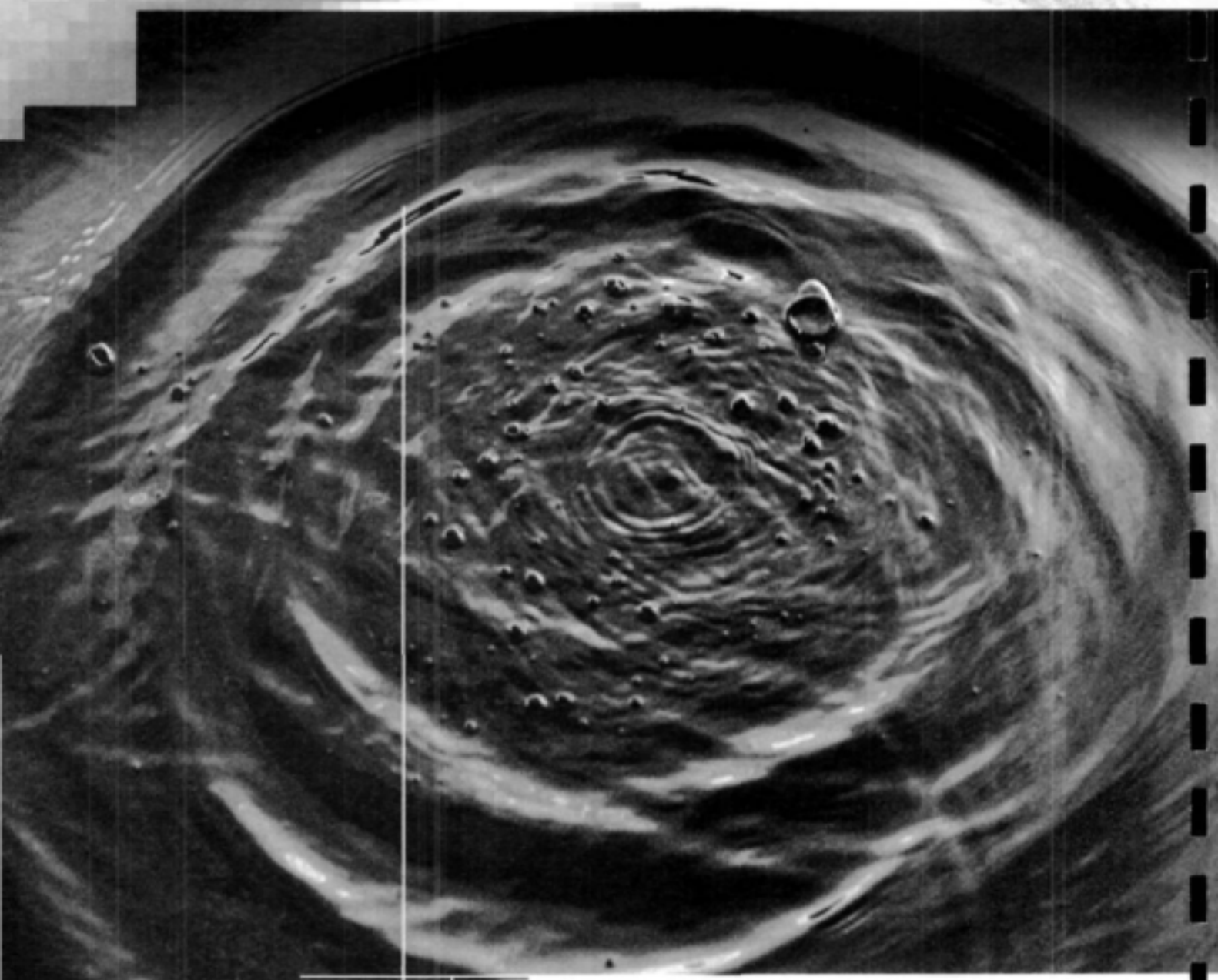
	Volume	Potential
V_1	37.5	660
V_2	56.25	579

The 'endpoint screen' gives for sample B1 a COD = 10.5 mg/ℓ.

Press 'CTRL INSERT' for sample B2.
Type 'B2' and enter the relevant data, i.e. sample volume of 10.0 mℓ and

	Volume	Potential
V_1	37.5	658
V_2	56.25	583

This gives a COD for sample B2 = 11.1 mg/ℓ (cw 10.6 for B1).



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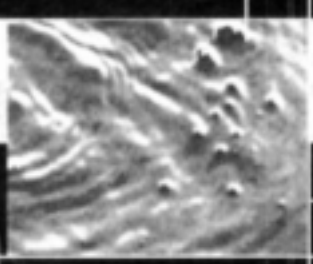

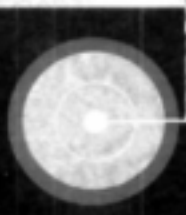

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