Determination of low chemical oxygen demand using potentiometry and a modified Gran function

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Abstract

The paper presents development and application of a method for determining chemical oxygen demand (COD) in aqueous solutions down to a concentration of 3 mg COD/ℓ (+1 mg/ℓ). The method hinges on the utilisation of a modified Gran function coupled with a potentiometric titration of digested test solutions with ferrous ammonium sulfate (FAS) titrant. Verification is presented using samples of known COD and composition (glucose), and unknown COD and composition, tap water (and dilutions of this) originating from Lake Kinneret (Sea of Galilee), and tertiary effluents from a wetland pilot plant. The latter are compared with measurements of organic concentrations obtained using an organic carbon analyser.

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 terrestrial 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 ~ 5 mg 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 paper 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 totally 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 paper, 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 practical scenario on both tap water from Haifa Municipality (distributing a treated water from Lake Kinneret) and to a tertiary effluent from a wetland pilot plant - diluted to a COD region at which normal methods of COD determination cannot be applied accurately.

Theoretical considerations

A modified Gran function for the redox titration of $Cr_2O_7^{2-}$ with FAS (Fe^{2+}) to determine COD can be formulated using an analogous approach to that adopted by Gran for alkalinity determination of a weak acid system in an aqueous solution. However, in order to effect this formulation two aspects need to be addressed. Firstly, for didactic purposes, the Gran function for alkalinity determination needs to be formulated. Thereafter, the redox equilibrium chemistry of the $Cr_2O_7^{2-}/Cr^{3+}$ and Fe^{2+}/Fe^{3+} subsystems needs to be linked to the stoichiometry of the system to develop the desired function.

Formulation of the alkalimetric Gran function

Gran formulated a semi-graphical technique for determining alkalinity from strong acid titration data without the need of

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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:

$$M.Alk_x = C_a *(V_e - V_x) \quad (1)$$

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):

$$M.Alk_x = \{[A^-_x] + [OH^-]_x - [H^+]_x\} *(V_s + V_x) \quad (2)$$

where:

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

Equating Eqs. (1) and (2) and multiplying both sides by the monovalent activity coefficient, f_m, to obtain H^+ in the activity form (which is linked to pH):

$$f_m C_a(V_e - V_x) = \{(A_x) + (OH^-)_x - (H^+)_x\} (V_s + V_x) \quad (3)$$

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. :

$$f_m C_a(V_e - V_x) = -(H^+)_x\} (V_s + V_x) \quad (4a)$$
$$= F_x \quad (4b)$$

Values for F_x are obtained using the right-hand side of Eq. (4a) 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. (4a)), and hence alkalinity is calculated.

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:

$$2Cr^{3+} + 7\,H_2O \leftrightarrow Cr_2O_7^{2-} + 14\,H^+ + 6e^-$$

$$\frac{Cr_2O_7^{2-}\,(H^+)^{14}\,(e^-)^6}{(Cr^{3+})^2} = K_c^{th} \quad (5)$$

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. (5). 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. (5) using this approach yields:

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

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:

$$2[Cr_2O_7^{2-}] + [Cr^{3+}] = Cr_t \quad (7)$$

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

$$\frac{[Fe^{3+}](e^-)}{[Fe^{2+}]} = K_f \quad (8)$$

where:

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

and:

$$[Fe^{3+}] + [Fe^{2+}] = Fe_t \quad (9)$$

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

$$pe_x = \frac{F}{2.303*RT} E_x \quad (10)$$

$$= 17{,}182\ Ex \text{ at } 298°K \text{ and } 1 \text{ atm}$$

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+}).

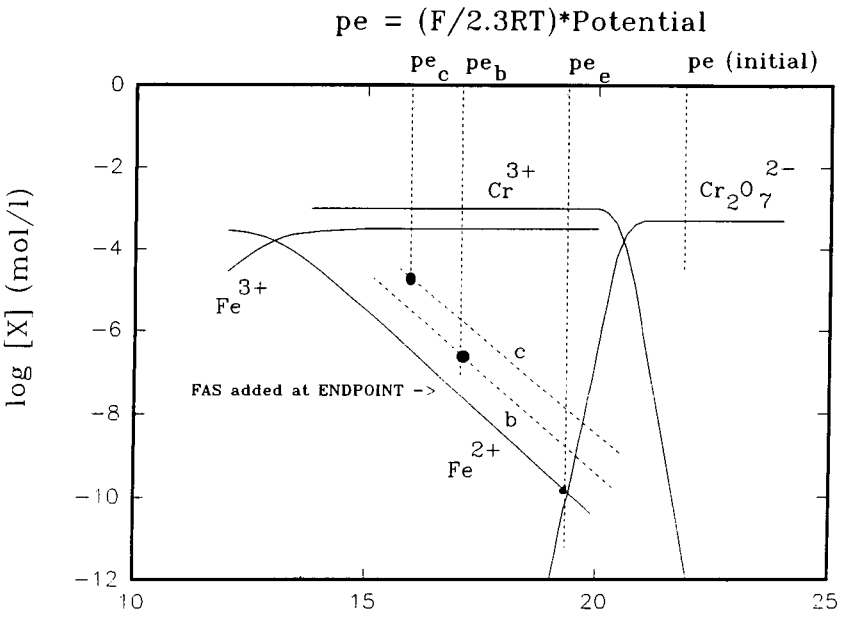

Figure 1

Theoretical plot of the log species concentration vs. pe for a solution with $Cr_t = 10^{-3}$ M. Lines "b" and "c" represent $[Fe^{2+}]$ (from FAS added) below the endpoint (pe_e).

Formulation of modified Gran function for COD determination

In the COD titration of the "excess" $Cr_2O_7^{2-}$ with Fe^{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 (1):

$$M.EAC_x = C_f(V_e - V_x) \qquad (11)$$

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. (3):

$$M.EAC_x = \{6[Cr_2O_7^{2-}]_x - [Fe^{2+}]_x\}(V_s - V_x) \qquad (12)$$

Equating Eqs. (11) and (12) gives the desired linear relationship between $M.EAC_x$ and V_x, i.e.:

$$C_f(V_e - V_x) = \{6[Cr_2O_7^{2-}]_x - [Fe^{2+}]_x\}(V_s - V_x) \qquad (13)$$

From Eq. (12), 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. (13) approximates to:

$$C_f(V_e - V_x) = -[Fe^{2+}]_x(V_s + V_x) \qquad (14a)$$
$$= F_x \qquad (14b)$$

This equation is analogous to the *Gran function* used in alkalinity determination (Eq. (4)) 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. (14) and (15) i.e.:

$$[Fe^{2+}]_x = \frac{(Fe_t)(e^-)_x}{(K_f + (e^-)_x)} \qquad (15)$$

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

$$[Fe]_t = \frac{V_x C_f}{V_s + V_x} \qquad (16)$$

Substituting Eqs (15) and (16) into Eq. (14) gives the *modified Gran function*,

$$(V_x - V_e) = \frac{V_x}{1 + 10^y} \qquad (17a)$$
$$= F_x \qquad (17b)$$

where:

$y = pe_x - pk_f$

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

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

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. (17a) 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.

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_f) be known 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. (17) and solving for V_x :

$$V_{x1} = V_e(1 + 10^{z1}) \qquad (18a)$$

where:

$z_1 = -17{,}182\ E_{x1} + pK_f$

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.

$$V_{x2} = V_e(1 + 10^{z2}) \qquad (18b)$$

Solving for pK_f from Eqs. (18a) and (18b) gives:

$$10^{pKf} = \frac{V_{x1} - V_{x2}}{V_{x2}\,10^{-17.182Ex1} - V_{x1}\,10^{-17.182Ex2}} \qquad (19)$$

Examination of Eq. (19) 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_f 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. (13) to give Eq. (14) are not valid.

Examination of Eqs. (18) and (19) shows that for each pair of data yielding a pK_f value, one can obtain a corresponding V_e value, for example for V_{x1} (and V_{x2}) :

$$V_e = \frac{V_{x1}}{1 + 10^{z1}} \qquad (20)$$

Usually, in a particular batch of COD determinations the pK_f 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.

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 to adopt and materials to be used are listed below.

Digestion procedure

Use 5220 (C or D) procedure as described in *Standard Methods* (1992) with the following suggestions: Sample size 2.5 mℓ; Dichromate digestion solution 1.5 mℓ of dichromate in concentration range 0.001 to 0.005 M; sulphuric acid reagent 3.5 mℓ. Reagents should be added using "high precision pipettors", and digested in sample tubes (either supplied by HACH or Pyrex screw-cap test tubes). Digestion should be effected for 2 h at 152°C using "Hach COD reactor" (1990) or an Al-block (Bilanovic et al., 1997) placed on a hotplate with a thermostat controller.

Pre-titration procedure

If the full digested sample (7.5 mℓ is to be titrated, transfer the sample into a total volume of 100 mℓ H_2O, adjusted for final H_2SO_4 concentration of 7% (i.e. to the 7.5 mℓ sample add a further 3.5 mℓ H_2SO_4 and bring up to 100 mℓ with H_2O). If only a fraction of the digested sample (say 3.0 mℓ) is to be used, then add a further 2.3 mℓ concentrated H_2SO_4 and bring up to 50 mℓ with distilled water. This constitutes part of the procedure needed to ensure a constant ionic matrix (and closely constant pH) during the titration. All additions (except distilled water) should be effected using a "high precision pipettor".

FAS titration

FAS titrant

Molarity of FAS titrant should be in the range 0.005 to 0.001 M. Oxygen-free distilled water is recommended for preparation of titrant $Fe(NH_4)_2(SO_4)_26H_2O$. If need be, FAS titrant can be kept in a dark bottle under an inert atmosphere.

Titration equipment

Microburette 1 to 5 mℓ with 0.02 mℓ divisions or a "high precision pipettor" were used for addition of FAS; sample and titrant were mixed by means of a magnetic stirrer; Pt-calomel electrode system linked to a pH meter with a digital output was used for measuring potential. "Radiometer Copenhagen" pH meter and "El-Hama Instruments" pH meter.

Note: all potentiometric readings are relative to a calomel reference electrode (not to the hydrogen reference cell). To obtain fast, stable and meaningful readings, a "plate" type Pt electrode should be used (i.e. Radiometer K401) and not the "button" or "wire" type electrodes (Garrels and Christ, 1965).

Titration procedure

Place the Pt-Calomel electrode system into the diluted, digested solution (the test solution) and then add sufficient FAS to bring the potential reading down to ~ 480 mV, the sign depending on the polarity set-up (in this event the titration has proceeded past the end point). Allow 5 min for electrode stabilisation in the solution. Continue the titration adding FAS aliquots of between 1 and 5 mℓ, to effect a change in potential greater than ~ 5 mV. After addition of each aliquot, wait 60 s and then note the potential. Obtain 4 to 6 potential observations in the region down to about 430 mV. An example of the procedure is set out in detail in **Appendix I**.

TABLE 1
COMPARISON OF KNOWN COD WITH MEASURED COD (DETERMINED USING A *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 mℓ, 1.5 mℓ 0.003513 M $K_2Cr_2O_7$; 3.5 mℓ concentrated H_2SO_4, brought up to total volume of 100 mℓ FAS of 0.001092 M
*pK_f determined from the blank 7.18

TABLE 2
COD MEASURED (USING A *MODIFIED GRAN FUNCTION*) VS. NON-PURGEABLE ORGANIC CARBON

Sample	Non-purgeable organic carbon*-mgC/ℓ(A)	COD (mg/ℓ) by "Gran titration" (B)	Ratio B/A
Tap water - undiluted	3.04	10.85	3.57
Tap water - diluted 2 times	1.80	5.60	3.11
Wetland effluent - diluted 40 times	1.05	3.22	3.06
Wetland influent - diluted 20 times	2.14	6.76	3.16

* Determined on "Shimatzu TOC-5000 A" analyser.

Results and discussion

Verification

The modified Gran function method for analysing low COD waters was assessed from various standpoints. Firstly, solutions were prepared containing known COD (glucose) and diluted down into the range 4 to 8 mg COD/ℓ with distilled water (i.e. organic carbon content 1.60 to 3.00 mg C/ℓ). The objective here being to assess the accuracy of the method on defined samples known to be completely oxidised by the digestion process. Analyses were effected as set out above and in **Appendix I**. A detailed sample calculation of a typical test is set out in **Appendix I** for a glucose sample containing 6 mg COD/ℓ. Table 1 lists a summary of the results obtained. In all cases close agreement was obtained between the known input and measured values.

A second set of experiments were effected to measure COD and compare it with "organic carbon" in natural and tertiary treated waters. The *modified Gran function* was used to asses COD, and a Shimatzu TOC-5000A analyser for measurement of organic carbon. Samples were either undiluted or diluted with double distilled water into a COD range 1 to ~ 10 mg COD/ℓ. Table 2 lists a summary of the results obtained. With regard to the tap water samples, the measured diluted and undiluted values indicate that the method gives a consistent estimate of COD. The ratio of COD to "organic carbon" appears to be approximately constant in both tap water and tertiary effluents. This observation is probably a chance event - there is no reason to suppose that the nature of organic material in treated waters and tertiary effluents should have similar oxidation states. However, the observed trend (that COD increases with an increase in organic carbon) would appear to have application in monitoring organic carbon in effluents from a particular water treatment works. Further, the fact that COD can be measured accurately down to a low concentration, would have importance in quality control of terrestrial water resources. In these, discharges are usually grossly diluted and great difficulty is encountered in detecting discharges. Furthermore, COD measurement coupled with organic carbon measurement allows determination of the average oxidation state of carbon in the system - changes in this can possibly be useful in pollution monitoring.

Attempts to expand sensitivity

Conventionally, excess dichromate is used to ensure complete digestion and dichromate remaining 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 sample (V_c)
(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. 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 < 20 mg/ℓ, addition of 1.5 mℓ of dichromate of molarity ~ 0.001 M, addition of 3.5 mℓ concentrated H_2SO_4; diluting the digested solution before titration with not more than 100 mℓ distilled water and titrating with FAS titrant of concentration greater than ~ 0.0007 M.

Conclusions

Dissolved organics invariably are present in terrestrial waters and tertiary effluents at low but variable concentrations. Present-day methods for measuring these requires utilising a carbon analyser which very few laboratories can afford. In this paper an alternative method is proposed which utilises potentiometry (Pt-calomel electrode system) and measures COD. The method follows the semi-micro COD test procedure set out in *Standard Methods* (1992), except that the titration is now effected using an alternative procedure allowing greater accuracy. The alternative procedure involves utilising a modified Gran function for the redox titration of dichromate with FAS titrant. The principal advantage of the method is that it allows detection of the volume of titrant to the end point without the problematic identification of this point.

The basic redox equilibrium chemistry underlying the development of the *modified Gran function* is presented. Application of the function to COD measurement of aqueous solutions was tested by experiment. Firstly on waters with known COD and organic carbon composition (glucose) down to COD ~ 3 mg/ℓ and organic carbon content ~ 1 mg/ℓ. Secondly on a tap water (and dilutions of this) from Haifa Municipality drinking water distribution system which is obtained from Lake Kinneret. Thirdly, on tertiary effluents (and dilutions of these) from a wetland pilot-plant unit process at the Technion, Haifa, Israel. In all cases the expected COD and observed values where within 1 mg/ℓ.

A crucial factor in utilising the modified Gran function method is that 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 < 20 mg/ℓ, addition of 1.5 mℓ of dichromate of molarity ~ 0,001 M, addition of 3.5 mℓ concentrated H_2SO_4; diluting the digested solution before titration with not more than 100 ml distilled water and titrating with FAS titrant of concentration greater than ~ 0.0007 M.

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Appendix I
Sample calculation

An example of the utilisation of the modified Gran function for determining COD is set out below. The example given is for a water with low COD where conventional methods for COD measurement can not be used. Two approaches to using the modified Gran function are given, (A) a semi-graphical procedure, and (B) a numerical procedure.

(A) Semi-graphical procedure

(a) Digestion sample: 2,5 mℓ water sample (or 2.5 mℓ double distilled water for the blank), plus 1.5 mℓ of 0.003513 M $K_2Cr_2O_7$, plus 3.5 mℓ H_2SO_4.

(b) Titration sample: The full 7.5 mℓ of digested sample was brought up to 50 mℓ with distilled water.

(c) FAS titrant: This was prepared to be approximately 0.003 M and to contain 7% by volume of H_2SO_4.

(d) Titration: The electrode system was placed in the stirred "titration sample" (i.e. (b.) above) and the titrant was added to obtain a potential that was well below the equivalence point (i.e. 0.46 V after 34 mℓ of titrant was added). After 5 min in this solution, the potential was noted. Thereafter, 2 mℓ aliquots of titrant were added and the potential observed 60 s after each addition (see columns 2 and 3 in Table A for the blank, and in Table C for the test solution sample).

(e) pK_f was calculated from the titration data for the blank as follows:
Pairs of V_x and E_x data listed in Table A were used together with Eq. (19) to determine corresponding pKf values. The pairs selected are listed in column 1, Table B, and the corresponding pK_f values determined using Eq. (19) in column 2, giving a mean value pK_f = 7.18. This value was then assumed to be valid for test samples digested and titrated in parallel with the blank.

(f) Determine values for F_x using Eq. (17) (with pK_f = 7.18) and V_x vs. E_x data listed in Table A for the blank and Table C for the test solutions. These F_x values are listed in column 4 of the respective tables.

(g) Determine the volumes of FAS titrant to the respective endpoints (V_b and V_e for the blank and test solutions respectively). The corresponding F_x and V_x values for the blank (from Table A) and test solution (from Table C) are shown plotted in Fig. A1. Extrapolation of the straight line plot to F_x = 0 gives V_b = 27.3 mℓ

(h) Determine molarity of FAS
[FAS] = (1.5* 0,003513*6)/28.9 = 0.00109= 5,6 mg/ℓ

(B) Numerical Procedure

Steps (a) to (d) are the same as in (A) above.

(e) pK_f values were determined from the titration data for the blank as set out in (A) above. The same procedure was than adopted to determine a series of pK_f values for the test solution. That is, pairs of V_x and E_x data listed in Table C were used together with Eq. (19) to determine corresponding pK_f values. The pairs selected are listed in column 1, Table D and the corresponding calculated pK_f values in column 2.

(f) Determine volumes of FAS titrant to the respective end points (V_b and V_e for the blank and test solutions respectively) using Eq. (20) (see column 3, Table B for the blank and Table D for the test solution).

(g) Determine molarity of FAS as in (h) above.

(h) Determine COD as in (i) above.

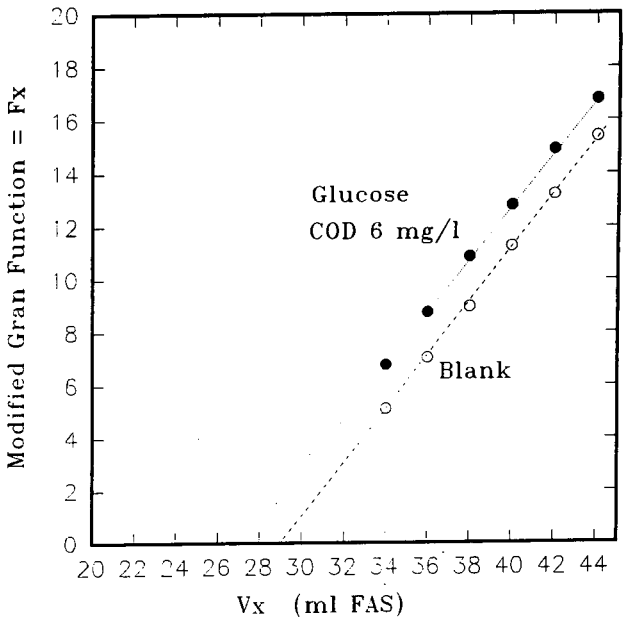

Figure A1
Plot of modified Gran function values for determination of COD; semi-graphical procedure

TABLE A
TITRATION DATA AND THE *MODIFIED GRAN FUNCTION* VALUES FOR THE BLANK SAMPLE

V_x (1)	V_x (mℓ) (2)	E_x (V) (3)	F_x (4)
V_{x1}	34	0.460	5.3
V_{x2}	36	0.452	7.3
V_{x3}	38	0.446	9.2
V_{x4}	40	0.441	11.3
V_{5x}	42	0.437	13.2
V_{x6}	44	0.433	15.4

TABLE C
TITRATION DATA AND THE *MODIFIED GRAN FUNCTION* VALUES FOR THE TEST SOLUTION

V_x (1)	V_x (mℓ) (2)	E_x (V) (3)	F_x (4)
V_{x1}	34	0.453	6.78
V_{x2}	36	0.446	8.77
V_{x3}	38	0.441	10.87
V_{x4}	40	0.437	12.78
V_{5x}	42	0.433	14.90
V_{x6}	44	0.430	16.80

TABLE B
DETERMINATION OF PK_F FROM THE BLANK TITRATION DATA (AND NUMERICAL DETERMINATION OF V_B)

V_x pair (1)	pK_f Eq. (19)) (2.0)	V_b (Eq. (20)) (3.0)
V_{x1}:V_{x6}	7.17	29.0
V_{x2}:V_{x5}	7.18	29.0
V_{x1}:V_{x4}	7.17	29.0
V_{x1}:V_{x5}	7.18	28.6
Mean	7.18	28.9

TABLE D
DETERMINATION OF PK_F FROM THE TEST SOLUTION TITRATION DATA (AND NUMERICAL DETERMINATION OF V_E)

V_x pair (1)	pK_f Eq. (19)) (2)	V_b (Eq. (20)) (3)
V_{x1}:V_{x6}	7.18	27.2
V_{x2}:V_{x5}	7.15	27.8
V_{x1}:V_{x4}	7.19	27.1
V_{x1}:V_{x5}	7.18	27.1
Mean		27.3