

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 $(\text{Fe}^{2+}/\text{Fe}^{3+})/(\text{Cr}^{6+}/\text{Cr}^{3+})$ 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 $\text{Cr}_2\text{O}_7^{2-}$ 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 $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ subsystems needs to be linked to the stoichiometry of the system to develop the desired function.

Formulation of the alkalimetric Granfunction

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

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