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Annals of Advances in Chemistry

Heighten Science PUBLICATIONS Corporation
ISSN
2576-3768

Review Article

Stoichiometric approach to redox back titrations in ethanol analyses

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Submitted: 16 May 2019
Approved: 10 June 2019
Published: 11 June 2019

Keywords: Ethanol analysis; Redox titration; Back titration; Stoichiometry

Abstract

This article refers to calculations involved with determination of ethanol, analyzed according to redox back titration principle. A quantitative reasoning, based on logical sequence of statements, is presented for derivation of the formulas required to calculate the results of chemical analyses according to stoichiometric principles. The titrations are considered as two-step analytical procedures. This way, one can gain an insight into a classical redox titration and get a knowledge on the advantages of back titrations.

Introductory Remarks

The literature designed for analytical laboratory purposes provides more or less detailed description of analytical methods. The description of quantitative nature is often preceded by preliminary information on the analytics. However, the question of the calculation of the results of analysis is commonly presented in the form of a ready formula, into which the data obtained from the experiments are inserted. The knowledge on the derivation of the related formula, based on stoichiometric reaction notations, is then presented as a “dry” information, for assimilation and memorization. This approach can be justified in the case of simple analyses. It is debatable, however, whether the same approach should be applied to more complex analytical procedures.

This paper concerns calculations involved with determination of ethanol contents, taken as interesting examples of classical, titrimetric analysis. Importance of classical determination of this analyte is revealed by the facts that: (1) a variety of analytical procedures were suggested for the ethanol determination [1-11]; (2) the international ethanol reference solution is prepared by the dichromate oxidation method [12].

Ethanol is a component of various alcoholic beverages, which include also other reducing components, considered as interferents in a suitable sample taken for analysis. Therefore, prior to the determination of ethanol in these beverages with use of suitable oxidizing agents, a separation of ethanol by distillation of a sample before the analysis is necessary. This way, less volatile interferents in the sample matrix are eliminated before the titrimetric procedure, realized according to back titration principle.

Titrimetry is one of the oldest analytical methods, frequently applied in analytical practice [13-16]. However, when the rate of reaction between analyte and reagent is slow, or when the standard solution lacks stability, or when the end point cannot be detected in a simple way – direct titration is not possible and resort is made to back-titration. Back-titration is a process in which the excess of a standard solution used to consume an analyte is determined by titration with a second standard solution.

How to cite this article: Michałowska-Kaczmarczyk AM, Michałowski T. Stoichiometric approach to redox back titrations in ethanol analyses. Ann Adv Chem. 2019; 3: 001-006. https://doi.org/10.29328/journal.aac.1001017

Analytics – preliminary data

For clarity of presentation, all volumes are assumed to be expressed in mL units, and all concentrations in mol L^{-1} units. Reagents of at least p.a. quality, and water with a conductivity ≤ 10 μS cm^{-1} should be used during the experiments. For determination of ethanol concentration, standard/ized solutions of potassium dichromate ($K_2Cr_2O_7$), sodium thiosulfate ($Na_2S_2O_3 . 5H_2O$), ammonium iron(II) sulfate ($(NH_4)_2Fe(SO_4)_2 . 6H_2O$) and potassium permanganate ($KMnO_4$) are required, while sulfuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and potassium iodide (KI) solution are added in excess.

End-points of titrations can be determined either potentiometrically or visually. Determination of the end-point of iodine ($I_2 + I_3^{-1}$) titration with sodium thiosulfate can be made more sensitive by adding starch solution as indicator. Phenanthroline or diphenylamine can be used as indicator to determine the end-point of titration in determination of potassium dichromate with ammonium iron (II) sulfate.

Stoichiometric calculations

Let V_S mL of wine sample (with unknown mass m_{et} of ethanol) be distilled and the distillate is collected in a receiving flask (V_f mL). After complete distillation of ethanol, the receiving flask is filled up to the mark with water and mixed; C_0 mol/L ethanol solution is thus obtained. Subsequently, V_1 mL of the standard $K_2Cr_2O_7$ (C_1 mol/L) solution is placed in a glass-stoppered flask, and a portion of concentrated H_2SO_4 (1.84 g/mL) is added. The mixture is agitated and cooled to room temperature. Then V_0 mL of the C_0 mol/L ethanol solution taken from the receiving flask is added into this mixture; $K_2Cr_2O_7$ is in due excess towards ethanol in this mixture. The flask is stoppered tightly and left to stand for ca. 15 min; it prevents the escape of acetaldehyde, as the intermediate product of this reaction [17]. Further analysis can be performed according to three options, see a flowchart in figure 1.

In Option 1, the excess of $K_2Cr_2O_7$ is reduced by adding an excess of potassium iodide (KI) solution. Iodine formed is subsequently determined in redox titration with standard solution of $Na_2S_2O_3$ (C_2, V_2).

The total number of mmoles of $K_2Cr_2O_7$ added is equal to $C_1 \cdot V_1$, while the number of mmoles (n(Cr)) of $K_2Cr_2O_7$ consumed in the reaction with ethanol is calculated from the stoichiometry of the reaction

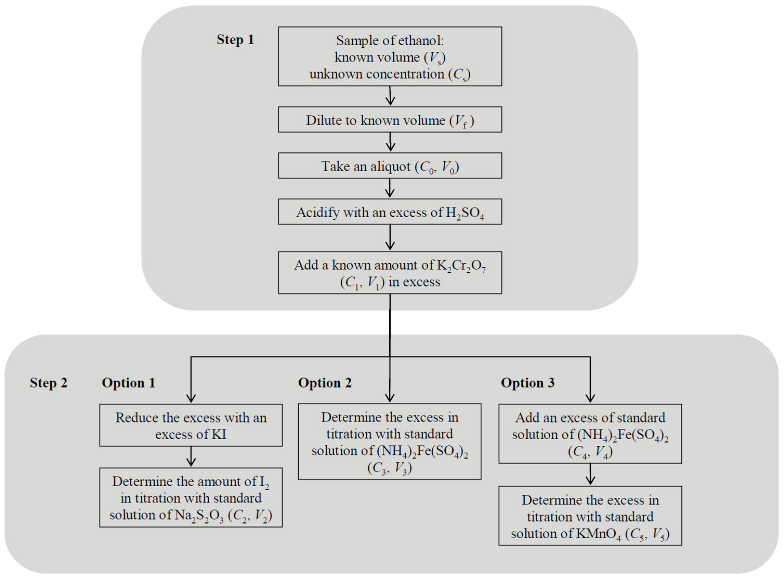

Figure 1: A flowchart of procedures, as suggested in the present paper, for determination of ethanol content.

$$2Cr_2O_7^{-2} + 16H^{+1} + 3C_2H_5OH = 4Cr^{+3} + 3CH_3COOH + 11H_2O \tag{1}$$

$$\begin{array}{cc} 2 & 3 \\ n(Cr) & C_0\cdot V_0 \end{array}$$

i.e. $n(Cr) = \frac{2}{3}\cdot C_0\cdot V_0$. The excess of $K_2Cr_2O_7$, i.e., $C_1\cdot V_1 - \frac{2}{3}\cdot C_0\cdot V_0$, is treated with an excess of KI solution, according to the reaction

$$Cr_2O_7^{-2} + 14H^{+1} + (6,9)I^{-1} = 2Cr^{+3} + 3(I_2, I_3^{-1}) + 7H_2O \tag{2}$$

$$\begin{array}{cc} 1 & 3 \\ C_1\cdot V_1 - \frac{2}{3}\cdot C_0\cdot V_0 & n(I_2) \end{array}$$

An excess of I^{-1} from KI increases the dissolution of the solid iodine; it is readily soluble in KI solution. The number of mmoles, $n(I_2)$, of the oxidized iodine species formed in the reactions (2) is equal to

$$n(I_2) = 3\cdot C_1\cdot V_1 - 2\cdot C_0\cdot V_0 \tag{3}$$

It is quantitatively determined in redox titration with V_2 mL of standardized $Na_2S_2O_3$ (C_2) solution. The reactions occurred here are as follows:

$$2S_2O_3^{-2} + (I_2, I_3^{-1}) = S_4O_6^{-2} + 2I^{-1} \tag{4}$$

$$\begin{array}{cc} 2 & 1 \\ C_2\cdot V_2 & n(I_2) \end{array}$$

At the end of the titration, when nearly all iodine (I_2, I_3^{-1}) is consumed in reaction (4), freshly prepared starch solution (1%) is added. The thiosulfate solution is added until its color turns from dark blue into a clear green blue. Thus the number of mmoles of iodine consumed in reaction (4) is

$$n(I_2) = \frac{1}{2}\, C_2\cdot V_2 \tag{5}$$

After comparing the right sides of equations (3) and (5), the following equation is obtained

$$C_0\cdot V_0 = \frac{1}{4}\cdot(6\cdot C_1\cdot V_1 - C_2\cdot V_2) \tag{6}$$

Mass m_0 [g] of ethanol (molar mass M = 46.07 g mol^{-1}) in the aliquot V_0 of the solution taken for analysis from the flask (V_f) is then calculated by inserting the relation $C_0\cdot V_0 = 10^3\cdot m_0/M$, into equation (6). Then we get

$$m_0 = 10^{-3}\cdot\frac{M}{4}\cdot(6\cdot C_1\cdot V_1 - C_2\cdot V_2) = 1.152\cdot 10^{-2}\cdot(6\cdot C_1\cdot V_1 - C_2\cdot V_2) \tag{7}$$

The mass m_{et} of ethanol in V_f mL of the solution is $m_{et} = m_0\cdot V_f/V_0$. It is assumed that the same mass of ethanol, (i.e., m_{et}) was contained in V_S mL of the sample tested. Then the percentage content of ethanol ($p, \%\frac{m}{V}$) in the sample tested is as follows

$$p = 1.152\cdot(6\cdot C_1\cdot V_1 - C_2\cdot V_2)\cdot\frac{V_f}{V_0\cdot V_S}\left(\%, \frac{m}{V}\right) \tag{8}$$

Second option (Option 2) of the method is a titration of the excess of dichromate with V_3 mL of standard solution of $(NH_4)_2Fe(SO_4)_2$ (C_3). This titration proceeds according to the reaction

$$Cr_2O_7^{-2} + 6Fe^{+2} + 14H^{+1} = 6Fe^{+3} + 2Cr^{+3} + 7H_2O \tag{9}$$

$$\begin{array}{cc} 1 & 6 \\ C_1\cdot V_1 - \frac{2}{3}\cdot C_0\cdot V_0 & C_3\cdot V_3 \end{array}$$

From this proportion we get: $6 \cdot C_1 \cdot V_1 - 4 \cdot C_0 \cdot V_0 = C_3 \cdot V_3$, and then:

$$p = 1.152 \cdot (6 \cdot C_1 \cdot V_1 - C_3 \cdot V_3) \cdot \frac{V_f}{V_0 \cdot V_S} \quad \left(\%, \frac{m}{V}\right) \tag{10}$$

In this titration, when the solution is almost clear-green, o-phenanthroline is added as indicator, that at the end point changes the color of the solution from blue-green to brown [18,19].

The third option (Option 3) of ethanol contents determination is based on the reaction of the dichromate excess with standard $(NH_4)_2Fe(SO_4)_2$ (C_4, V_4) solution, added in excess; this excess is titrated with V_5 of standard $KMnO_4$ (C_5) solution. From the proportion

$$\begin{array}{ll} 1 & 6 \\ C_1 \cdot V_1 - \frac{2}{3} \cdot C_0 \cdot V_0 & n(Fe) \end{array}$$

resulting from reaction (9) we get

$$n(Fe) = 6 \cdot C_1 \cdot V_1 - 4 \cdot C_0 \cdot V_0 \tag{11}$$

From the reaction

$$\begin{array}{lll} MnO_4^{-1} & + & 5Fe^{+2} + 8H^{+1} = 5Fe^{+3} + Mn^{+2} + 4H_2O \\ 1 & & 5 \\ C_5 \cdot V_5 & & C_4 \cdot V_4 - n(Fe) \end{array} \tag{12}$$

we get

$$C_4 \cdot V_4 - n(Fe) = 5 \cdot C_5 \cdot V_5 \tag{13}$$

From (11) and (13)

$$C_0 \cdot V_0 = \frac{2}{3} \; (6 \cdot C_1 \cdot V_1 - C_4 \cdot V_4 + 5 \cdot C_5 \cdot V_5) \tag{14}$$

and the content of ethanol in the analyzed sample is calculated from the formula:

$$p = 1.152 \cdot (6 \cdot C_1 \cdot V_1 - C_4 \cdot V_4 + 5 \cdot C_5 \cdot V_5) \cdot \frac{V_f}{V_0 \cdot V_S} \quad \left(\%, \frac{m}{V}\right) \tag{15}$$

Historically, the Option 3, involving three standard(ised) solutions, was the first one, introduced by Nicloux in 1896 [20].

A note on the principle of stoichiometric excess

The limiting reagent can be explained as the reactant that requires more moles to react than are available in the experiment. The term “stoichiometric excess” refers to the reagent, which remains in excess in the reaction mixture, after the reaction is completed. The minor component (in stoichiometric sense) defines the quantity (the number of mmoles) of the product formed.

An excess of the reagent can play different roles. For example, an excess of H_2SO_4 assures the right course of a chemical reaction; an excess of iodide increases dissolution of iodine, I_2, moderately soluble in aqueous media.

To apply the reasonable/moderate quantities of the corresponding reagents, the stoichiometry of a chemical reaction should be considered before starting the experiment. In other words, stoichiometric amount of a reactant/product should be adequate for the reaction to proceed. Such a procedure is valid for the systems where the reaction leads to completion, as in the analysis specified in this paper. In general case, in particular when this requirement is not fulfilled, a use of a more advantageous simulating approach, which involves all prior physicochemical knowledge about the system tested, is suggested; its use was illustrated in the authors' papers cited in [13-16].

Final Comments

This paper is an illustration how to teach complex classical analytical procedures, referred to determination of ethanol contents. These determinations, based on redox back titrations, are presented from the viewpoint of the stoichiometric calculations involved. Combination of different redox titrations for determination of the same analyte, in which prior students' knowledge is engaged, is presented. The principle of stoichiometric excess is considered. Importance of classical analysis is highlighted.

Stoichiometry is an essential part of chemistry education; it is the science aiming to study how compounds react one with the other. It is easy to find students who are competent in calculations at particular steps of an analytical procedure, but it is difficult to find a large number of students able to link all these steps in a logical whole. Starting from this viewpoint, we consider the derivations presented in this paper as not trivial ones. As a matter of fact, a solving of stoichiometric problems encountered some problems for many students attending in introductory courses of chemistry. Certainly, the description of experimental procedure (analytical measurement) has here a prominent place. We must help the students to develop a systematic approach to solve such problems; this is the main aim of this paper. The drawback of use memorized formulas to solve problems is that they are shortcuts only, and thus a systematic reasoning is not involved in a didactics. The method presented here helps the students to calculate the results obtained from titration data in a systematic way.

The example considered is important in chemical analysis. In particular, quantitative determination of ethanol from blood samples is used for scientific research made in the forensic laboratory. An international reference solution of ethanol is prepared according to the dichromate oxidation method. Quantitative determination of ethanol in wine and liquors may be also carried out by the dichromate method. And last but not least, the costs of the related analyses are relatively low.

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