

## Quantitative Determination of Mono and Dihydric Alcohols with Ammonium Metavanadate Reagent: Micro Determination of Medicinal Compounds

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**Abstract:** The current study depicts that the determination of methanol, ethanol, n-propanol, n-butanol, 3-pentanol, propane 1,2 diol, butane 1,3 diol, butane 2,3 diol, triethylene glycol and tetraethylene glycol with the use of V(v) reagent. Aliquots containing 1-9 mg of sample are allowed to react with 1 ml of 0.3 N, V(v) reagent and 5 ml of 10 N H<sub>2</sub>SO<sub>4</sub> at water bath maintaining 40°C thermostatically for 20 minutes. A blank experiment also run under identical condition using all the reagent except the sample. The recovery of the sample was calculated. S.D. and C. V. was also calculated. Effect of various variables and interfering substances has also been studied and possible course of reaction was suggested on the basis of stoichiometry as well as previous literature available of the reaction. The accuracy of the method is within + 1% in most of the cases.

**Background:** Drugs are organic substances with a definite physiological activity used in the prevention, diagnosis, treatment or cure of diseases in man or other animals. Physiological activity of a compound is associated with particular structural unit or particular functional groups. These functional groups are biologically active. The determination of these biologically active functional groups is important for the quantitative determination of drugs.

**Materials and Methods:** For testing the quantitative validity of reaction, methanol was taken as test sample, different amounts of sample were allowed to react with varying amount of acidic ammonium metavanadate (v) reagent on boiling water bath for different intervals of the reaction time, the reaction mixture was cooled at room temperature (27°C) and unconsumed ammonium metavanadate (v) was back titrated against ferrous ammonium sulphate using N-phenyl anthranilic acid as indicator. A blank experiment was also run under identical conditions using all the reagent except the sample.

**Results:** The amount of V(v) consumed per mole of dihydric alcohols the following course of reaction may be proposed for the oxidation of propane 1,2 diol, butane 1,3 diol, butane 2, 3 diol with V(v) reagent. The mechanism finds support from literature survey. Polymers of Ethylene glycol like triethylene glycol and tetra ethylene glycol consumes 8 equivalent of V(v) reagent to give corresponding dicarboxylic acids.

**Conclusion:** The current study depicts that the determination of methanol, ethanol, n-propanol, n-butanol, 3-pentanol, propane 1,2 diol, butane 1,3 diol, butane 2,3 diol, triethylene glycol and tetraethylene glycol with the use of V(v) reagent. Aliquots containing 1-9 mg of sample are allowed to react with 1 ml of 0.3 N, V(v) reagent and 5 ml of 10 N H<sub>2</sub>SO<sub>4</sub> at water bath maintaining 40°C thermostatically for 20 minutes. A blank experiment also run under identical condition using all the reagent except the sample. The recovery of the sample was calculated. S.D. and C. V. was also calculated. Effect of various variables and interfering substances has also been studied and possible course of reaction was suggested on the basis of stoichiometry as well as previous literature available of the reaction. The accuracy of the method is within + 1% in most of the cases.

**Key Word:** Ammonium Metavanadate Reagent, Micro Determination, Medicinal Compounds

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### I. Introduction

Drugs are organic substances with a definite physiological activity used in the prevention, diagnosis, treatment or cure of diseases in man or other animals. Physiological activity of a compound is associated with particular structural unit or particular functional groups. These functional groups are biologically active. The determination of these biologically active functional groups is important for the quantitative determination of drugs.

Vanadium is a transition metal and hence its penultimate shell is not complete and possess a vacant 'd' orbital. The outer electronic configuration of vanadium is 3d<sup>3</sup>, 4s<sup>2</sup>. It shows oxidation states of +1, +2, +3, +4, +5, 0, —1. The most common oxidation steps are +5 and most uncommon are -1 and 0. The —1 oxidation states occur when 'd' orbital accept one electron and become d's. The zero-oxidation state occur when no electron of vanadium contribute in the

bond formation and all the electron are contributed by the incoming bonding groups. In case of oxidation state of +1, +2, +3, +4 and +5, it is exhibited by gradual removal of electrons from  $4s^2$  and  $3d^3$  orbitals i.e., when one electron is removed from  $4s^2$  it will show +1 oxidation state, +2 oxidation state is shown by the removal of both 4s electrons. +3 oxidation states involve removal of one of the 3d electrons and two of the 4s electron and so on. Vanadium pentaoxide is the most important among all the vanadium oxides and it is generally obtained during the extraction of vanadium from different ores. In laboratory, it is generally obtained by heating ammonium metavanadate. Analytically pure vanadium pentaoxide can also be prepared by decomposing twice crystallised ammonium metavanadate in a platinum crucible in the presence of air at  $400^\circ\text{C}$ -  $450^\circ\text{C}$  and storing the material in a desiccator.

Komers et al proposed a method for the determination of small amount of MeOH and EtOH in aqueous solution. The method based on combination of stripping and gas chromatography technique. Normal  $C_7$ - $C_{16}$  aliphatic alcohols mixture was analysed by gas Chromatography' at  $190^\circ$  on a column packed with 10% polyethyleneglycol. Other chromatographic techniques like liquid chromatography and gas chromatography were also employed for the determination of monohydric and dihydric alcohols. Glycerol was determined spectrophotometrically in its industrial liquors by measuring the absorbance at 580 nm of the violet colour several other spectrophotometric method<sup>1</sup> are also available in the literature for the determination of alcohols. Barkat evolved a titrimetric method using N-bromosuccinimide as oxidant for the determination of primary and secondary alcohols. Kruse et al developed an oxidimetric method for differentiating between three types of saturated alcohols using Nhaloimides.

A similar type of method has also been proposed by Severin. It has been claimed that the method is rapid and accurate compared to the methods proposed by Lucas and Ritter. Litter as well as Jones studied the reaction. Kinetics of oxidation of alcohols using pentavalent vanadium as oxidant and excess vanadate was back titrated with Mohr's salt or with Fe (II) sulphate solution. Various other titrimetric method<sup>23-25</sup> have been proposed from time to time for the determination of alcohols. Dusic<sup>26</sup> determined diols by using  $\text{NaIO}_4$  solution as oxidant excess 10, was determined potentiometrically with  $\text{N}_2\text{H}_4\text{H}_2\text{SO}$ , at platinum electrode. Singh et al oxidised methanol and glycerol with excess amount of permanganate in alkaline solution. The excess reagent was titrated potentiometrically with sodium formate in presence of  $\text{BaCl}_2$ . Beck<sup>2</sup> determined ethylene glycol and glycerol with trivalent copper by potentiometric titration. Stognushko et al developed a potentiometric method for the analysis of phosphorylated product at higher alcohols. A suitable method has been suggested for the determination of Crotyl alcohol with chloramine-T by Naidu et al Haring et al<sup>32</sup> evolved a method for the determination of allyl alcohol with manganese pyrophosphatic. Various metal ions<sup>33-34</sup> were also employed for the determination of alcohols. Oxidation of secondary alcohol as well as allyl alcohol<sup>36</sup> with PFC and Ni(iv) respectively are carried out. Various Methods developed for the determination of alcohols, with different inorganic reagents. In the present work a new titrimetric method has been described for the micro determination of some monohydric and dihydric alcohols with the use of ammonium metavanadate as an oxidising reagent. This is quick, easy and accurate procedure and is of general applicability. The accuracy of the method is within +1% in most of the cases.

## II. Material and Methods

For testing the quantitative validity of reaction, methanol was taken as test sample, different amounts of sample were allowed to react with varying amount of acidic ammonium metavanadate (v) reagent on boiling water bath for different intervals of the reaction time, the reaction mixture was cooled at room temperature ( $27^\circ\text{C}$ ) and unconsumed ammonium metavanadate (v) was back titrated against ferrous ammonium sulphate using N-phenyl anthranilic acid as indicator. A blank experiment was also run under identical conditions using all the reagent except the sample. The stoichiometry of the reaction was established and possible course of reaction was suggested. On the basis of the reaction conditions developed for methanol and determination of other mono and dihydric alcohols like ethanol, n-propanol, n-butanol, 3- pentanol, propane 1 ,2-diol, butane 1,3-diol, triethylene glycol and tetraethylene glycol was carried out.

Aliquots, containing 1-5 mg of the sample were taken in 100 ml Erlenmeyer flask followed by the addition of 1 ml of 0.3 N, V(v) reagent and 5 ml of 10 N sulphuric acid. The reaction contents were shaken gently and kept on a boiling water bath for 20 minutes. After the reaction was over the reaction mixture was cooled at room temperature.

The unconsumed V(v) reagent was titrated against 0.025 N ferrous I ammonium sulphate using N-phenyl anthranilic acid as an indicator. A blank experiment was also run under identical condition, using all the reagents except the sample. Recovery of the sample was calculated by following expression.

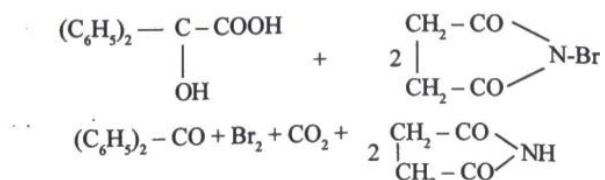
$$\text{mg of the sample} = \frac{M \times N (B - S)}{n}$$

Where M = Molecular weight of the sample, N = Normality of Fe(II) solution, B=Volume of Fe(II) consumed to titrate with the blank experiment, S = Volume of Fe(II) consumed to titrate with the sample experiment and n=Number of moles of V(v) reagent consumed per mole of the sample.

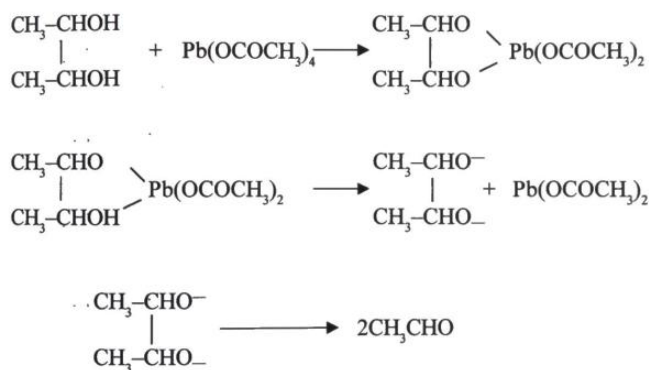
### III. Result and Discussion

With the recommended procedure the determination of mono and dihydric alcohols has successfully been achieved on 1 - 10 mg of sample size within the accuracy of + 1%. Taking methanol and propane 1, 2 diol as the representative compounds the effect of various variables was studied. 1 ml of 0.3 N vanadium (v) reagent was found to be sufficient for quantitative oxidation of mono & dihydric alcohols. A more concentrated solution does not give any improvement either in the recovery of the sample or the reaction time. The lower concentration gives inaccurate results. Therefore, the prescribed amount of V(v) reagent was employed for the general procedure. It was also observed that the quantitative oxidation of mono and dihydric alcohols like methanol, ethanol, n-propanol, n-butanol, require 10 minutes of reaction time. While secondary alcohols like 3-pentanol require 15 minutes reaction time. A lower reaction of 3-pentanol may be due to its oxidation via formation of ketone which then breaks to give a mixture of acids with lesser number of carbon atoms. Propane 1, 2 diol, butane 1,3 diol, butane 2,3 diol, triethylene glycol & tetra ethylene glycol require 20 minutes of reaction time for accurate and concordant results. Beyond this reaction time there was no improvement in the recovery of sample. The reaction time lesser than this gives inconsistent and lower results indicating incomplete reaction.

The effect of temperature as mentioned earlier was also studied and it was noticed that 40°C is sufficient for quantitative oxidation. Beyond 50°C inaccurate results are obtained and a sharp end point is not obtained. The stoichiometry of the reaction was also established for each compound and is equivalent to methanol, ethanol, n-propanol, nbutanol, 3-pentanol, propane, 1,2 diol, butane 1-3 diol, butane 2,3 diol, triethylene glycol & tetraethylene glycol consumes 4, 4, 4, 4, 8, 6, 12, 6, 8 and 8 equivalent of V(v) reagent respectively. It is well known that primary and secondary alcohols are oxidised to aldehydes and ketones respectively by the use of a mixture

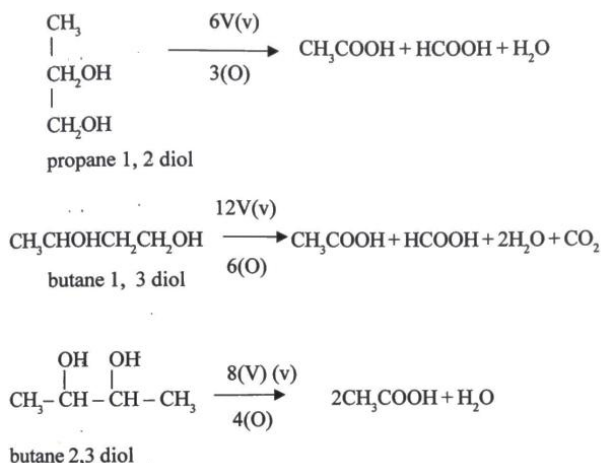


In view of above oxidation reaction and considering the amount of V (v) consumed per mole of the primary and secondary alcohols the following course of reaction may be proposed for the oxidation of methanol, ethanol, n-propanol, n-butanol & 3-pentanol with the use of V (v) reagent. In the above oxidation reaction primary alcohols after oxidation with V (v) gives corresponding carboxylic acid and secondary alcohol produces a mixture of acids. Aldehydes and Ketones are produced in case of 1, 2-glycol as well with certain reagents, notably periodic acid and lead tetraacetate. The reaction affords one of the few ways in which a carbon - carbon single bond can be cleaved readily various theory have been proposed to explain the cleavage, one of which postulates that the glycol is changed to 1, 4-Zwitter ions, which in turn breaks down to form two carboxyl groups. According to this theory the cleavage of 2,3 butane diol with lead tetraacetate<sup>48</sup> may be depicted as follows.

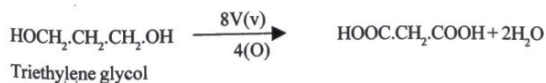


Cleavage of olefins to aldehydes through corresponding glycol can be accomplished by treatment with periodate in the presence of catalytic amounts of osmium tetroxide<sup>49</sup>. Cleavage of glycol, can also be affected with the sodium bismuthate and diethyltartrate.<sup>50</sup>

In view of above reactions and considering the amount of V(v) consumed per mole of dihydric alcohols the following course of reaction may be proposed for the oxidation of propane 1,2 diol, butane 1,3 diol, butane 2, 3 diol with V(v) reagent.



The above mechanism finds support from previous workers.<sup>51</sup> Polymers of Ethylene glycol like triethylene glycol and tetra ethylene glycol consumes 8 equivalent of V(v) reagent to give corresponding dicarboxylic acids.



#### IV. Conclusion

The current study depicts that the determination of methanol, ethanol, n-propanol, n-butanol, 3-pentanol, propane 1,2 diol, butane 1,3 diol, butane 2,3 diol, triethylene glycol and tetraethylene glycol with the use of V(v) reagent. Aliquots containing 1-9 mg of sample are allowed to react with 1 ml of 0.3 N, V(v) reagent and 5 ml of 10 N H<sub>2</sub>SO<sub>4</sub> at water bath maintaining 40°C thermostatically for 20 minutes. After the reaction was over, the contents were cooled at room temperature and unreacted V(v) reagent was determined titrimetrically with 0.025 N ferrous ammonium sulphate solution using N-phenyl anthranilic acid as indicator. A blank experiment also run under identical condition using all the reagent except the sample. The recovery of the sample was calculated. S.D. and C. V. was also calculated. Effect of various variables and interfering substances has also been studied and possible course of reaction was suggested on the basis of stoichiometry as well as previous literature available of the reaction. The accuracy of the method is within + 1% in most of the cases.

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