

# Iodometric Method for the Determination of Malonic Acid by Vanadium (V) in Perchloric acid

**Author: Sanjib Mukherjee**

Affiliation: Technique Polytechnic Institute, Panchrokh, Sugandhya, Hooghly, 712102

E-mail: smchem2510@gmail.com

## ABSTRACT

*A simple iodometric method for the determination of malonic acid has been developed. Sodium (or ammonium) metavanadate solution in dilute perchloric acid and malonic acid are refluxed for 2 hours. The resulting solution was cooled and potassium iodide was added in excess. The liberated iodine was titrated iodometrically.*

**Keywords: Malonic acid, Vanadate in perchloric acid, Iodometric method.**

## 1. INTRODUCTION

Malonic acid is an important biomolecule present in several fruits like apple, beetroot etc. It is present in grapes, strawberries as colourless substances. Malonic acid can be used as an electrolyte additive for anodizing aluminium or as an additive in adhesive composition.

Malonic acid is also used as buffering agent to stabilize the pH of cosmetics.

Recently malonic acid has been used to produce a starch based resin.

Malonic acid can be determined by a number of methods. Pthallimetric oxidation, fluorimetric determination, chromatographic technique and capillary zone electrophoresis.

Vanadium (V) in perchloric acid was found to be an excellent reagent for the iodometric determination of glucose and other monosaccharides. The reagent was successfully employed to determine glycerol and other related compounds.

In this communication, we describe a simple iodometric method for the determination of malonic acid in solution and in solid state.

## 2. EXPERIMENT

Ammonium metavanadate and malonic acid were purchased from Aldrich Chemical Company.

Manganese (II) sulphate dihydrate, potassium iodide, sodium thiosulphate were all of analytical grade. Freshly prepared starch solution was used as indicator. Double distilled water was used during the experiments. The glass apparatus was calibrated in the usual way and general precautions for the analytical work were scrupulously followed. All sorts of weighing were done in digital balance.

Malonic acid was stored over concentrated sulphuric acid for at least one week before use. An accurately weighted quantity of malonic acid was dissolved in volumetric flask in double distilled water.

Ammonium metavanadate solution was prepared according to the procedure described elsewhere. Metavanadate solution was standardized against standard sodium thiosulphate solution iodometrically. Potassium dichromate (N/20) solution was prepared in the usual way. A stock solution of sodium thiosulphate was prepared and it was standardized using standard solution of potassium dichromate.

A definite volume of malonic acid solution and a known excess of metavanadate solution was heated under reflux for a certain period of time. It was cooled. The residual metavanadate was determined iodometrically.

The experiments were continued till time comes when titre values became constant. It was found that oxidation was completed in (110-120) minutes. During determination of malonic acid 120 minutes was fixed for complete oxidation.

For the determination of malonic acid, the following procedure was followed. Two ml of a standard solution of malonic acid (1%) was refluxed under low flame with vanadate (30ml) solution for 120 minutes. The solution was cooled. Solid potassium

Iodide solution was added and the liberated iodine was titrated by standard solution of sodium thiosulphate using freshly prepared starch as indicator.

Another aliquot of malonic acid solution (unknown) was treated similarly. The amount of unknown malonic acid was determined using the formula:

$$S = W (z-y) / (z-x)$$

W = Concentration of malonic acid (gm/dl)

Z = volume of thiosulphate solution required for 30 ml of blank vanadate solution.

Y = Volume of thiosulphate required for the titration of residual vanadate after refluxing with unknown amount of malonic acid.

X = Volume of thiosulphate required for the titration of residual vanadate solution left after refluxing with known amount of malonic acid.

S = Amount of unknown malonic acid.

### 3. RESULTS AND DISCUSSION

#### 3.1. Result

Sl. No.	Malonic acid taken	Malonic acid found ( $\pm$ sd) (gm)
1	0.100	0.10036 $\pm$ 0.011
2	0.150	0.14762 $\pm$ 0.048
3	0.200	0.20043 $\pm$ 0.017
4	0.300	0.28649 $\pm$ 0.081
5	0.500	0.49333 $\pm$ 0.115
6	0.600	0.60063 $\pm$ 0.123
7	0.700	0.73690 $\pm$ 0.374
8	0.800	0.82630 $\pm$ 0.253
9	0.900	0.88381 $\pm$ 0.019
10	1.000	1.06880 $\pm$ 0.343
11	1.110	1.10980 $\pm$ 0.452
12	1.206	1.03861 $\pm$ 0.190
13	1.500	1.59710 $\pm$ 0.245
14	1.800	1.69078 $\pm$ 0.257
15	2.000	2.432 181

**Table-1: Determination of Malonic acid in Aqueous Solution**

For the determination of malonic acid in the solid state, 30ml of vanadate was refluxed with exact amount of malonic acid (less than 30mg) for 120 minutes in a round bottomed flask. Residual

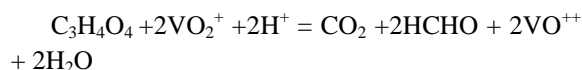
vanadate was titrated iodometrically. Similar procedure was followed for unknown amount of malonic acid. Calculation was done using the formulae... (1). Results are presented in Table 2.

Sl. No.	Malonic acid taken (gm)	Malonic acid found (gm)
1	0.020	0.02120
2	0.030	0.02769
3	0.100	0.10010
4	0.150	0.15380
5	0.200	0.20040
6	0.300	0.29231
7	0.500	0.48148
8	0.600	0.60230
9	0.700	0.73580
10	2.202	2.20600

**Table-2: Determination of Malonic acid in solid state**

#### 3.2. Discussion

It was found that one ml of 1(N) vanadate is equivalent to 62-63 mg of malonic acid. Molecular mass of malonic acid is 104. So it indicates a two electron transfer reaction and in our reaction condition most probable stoichiometry is



We identified the presence of CO<sub>2</sub> and formaldehyde as the reaction product.

Malonic acid was made scrupulously dry in order to achieve accurate results. The method of determination of malonic acid was based on oxidation by vanadium (V) in perchloric acid medium. Now malonic acid was allowed to react with known excess of vanadium (V) solution in perchloric acid under boiling condition for 120 minutes, but overheating should be avoided otherwise vanadium (V) is lost indicated by a red coloured solid precipitation on the wall of round bottle flask. The aqueous solutions of the reagent used were prepared with great care using double distilled water.

When prepared once with single distilled water

slowly turned greenish yellow instead of normal golden colour thus rendering the solution unsuitable for use in analytical purpose. Therefore double distilled water was used throughout the experiment in order to eliminate these undesirable side reactions.

Metavanadate solution was prepared by dissolving the requisite quantity of vanadate in hot double distilled water. This solution was cooled to room temperature with constant stirring and added very slowly to cold dilute perchloric acid; quick addition of vanadate solution could raise the temperature resulting in the formation of a small quantity of brick red precipitation, possibly the oxide of vanadium. This precipitation is undesirable for the present work. The proper concentration of vanadate was important. Since stronger solution readily produced an orange brown precipitate and with very dilute solution the reaction of malonic acid becomes slow and remains incomplete, the concentration of vanadate in perchloric acid should be nearly 0.5(M) and the heating of malonic acid and vanadate mixture should be just 120 minutes.

The strength of the sodium thiosulphate solution should always be determined on the same day of the experiment since its strength slowly changes.

The determination of malonic acid in aqueous solution gives very good result with very high accuracy.

In the determination of malonic acid in aqueous solution, the experiment was repeated for at least nine times.

In the iodometric method of determination addition of vanadate was affected from a burette instead of a pipette in order to avoid the risk of sucking in the vanadate solution in perchloric acid. During the titrations starch solution was used as indicator which must be freshly prepared otherwise the end point would not be sharp and stable. At the end point there was a sharp change of the colour from purple to sky blue with the white crystalline precipitate of potassium perchlorate which settled at the bottom.

#### Malonic acid estimation:

The freshly prepared Malonic acid solution was taken in a clean and dry round bottomed flask, and then added known excess of vanadium (v) in perchloric acid solution. Then the resultant mixture was heated on boiling water bath for 120 minutes, then cooled to room temperature, then added excess KI(solid). Thereafter residual (excess) vanadium (v)

was determined iodometrically.

Solid Malonic acid was weighed accurately and then put into round bottomed flask. Measured volume of vanadate solution was added to it and then treated as before.

#### 4. CALCULATION

The computation used in this paper is done using the working formula ..... (1)

If W is the concentration (g/dl) of the substrate in a solution, Z is the titre value(ml) of thiosulphate solution required for the blank determination of v (ml) of the vanadium(v) and X and Y are the titre values of the same thiosulphate required for the determination of residual vanadium(v) (from V ml) after the oxidation of the substrate of known and unknown strengths respectively, then the concentration of the substrate (S,g/dl) in the solution of unknown strength is given by

$$S=W [(Z-Y)/(Z-X)]$$

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