

Iodometric method for the determination of the components of a binary mixture of glucose and sucrose by vanadium(V) in perchloric acid

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Sodium or ammonium metavanadate solution in dilute perchloric acid has been found to be a suitable reagent for the determination of glucose and sucrose in their mixture. After refluxing a blend of glucose and sucrose with an excess of the reagent, the residual metavanadate is determined iodometrically. The amount of each ingredient is determined by using a working formula derived from the standardisation of the vanadate solution by the substrate glucose and sucrose of known strength.

The earliest method of analysis of glucose and sucrose in their mixture was one developed by Fehling¹. The other frequently used titrimetric methods include use of Ost reagent² and oxidation by periodate³. A sensitive colorimetric method was devised⁴. Enzymic⁵ and enzyme electrodes⁶ were also used. Spectrophotometry was used for quantitative determination of glucose and sucrose in their mixture⁷. Estimation based on physical and physicochemical methods like GLC⁸, GC⁹, thermometric titrimetry¹⁰ have found application. Heat of dilution method¹¹, chromatographic polarimetry¹², automated assay method^{13,14} and TLC^{14,15} were also reported.

Vanadium(V) perchloric acid^{16,17} is an excellent reagent for the determination of monosaccharide and disaccharide when present as single component. The present communication describes an accurate and easy-to-handle method for the determination of glucose and sucrose in presence of one another.

Results and Discussion

As reported earlier¹⁶⁻¹⁸, the method of the determination of sugars and related compounds by oxidation with V^V in perchloric acid gives excellent results. The present work has been undertaken with a view to extend and explore further applicability of this reagent for the determination of components of mixture consisting of two oxidisable substrates, viz. glucose and sucrose. In an earlier publication¹⁸, two working formulae were proposed for this purpose.

Formula 1 used was

$$\frac{(Q - W_{OX}^1)}{W_T} (T_1 - T_2) + \frac{W_{OX}^1 (T_1 - T_3)}{W_{OX}} = (T_1 - T_4)$$

oxalic and tartaric acid were taken as the representative of

the two oxidisable substrates in the mixture. Here Q , W_T , W_{OX} , W_{OX}^1 are the quantities (in g) of the binary mixture, tartaric and oxalic acids used to standardise the vanadate solution and oxalic acid (as unknown) respectively, T_1 is the volume of thiosulphate solution (ml) required to titrate V and of V^V and T_2, T_3, T_4 are the volume of thiosulphate required to titrate the residual vanadate from V_{ml} after the oxidation of W_T , W_{OX}^1 and Q respectively.

Working formula 2 employed was

$$\frac{1000 \times W_m}{E_1} + \frac{1000(Q - W_m)}{E_2} = \frac{S_v(T_{im} - T_{fm})}{T_{im}} V_m$$

where Q is the weight of the mixture (g), V_m the volume of known excess of V^V of strength S_v , T_{im} the volume of thiosulphate required for V_m volume of V^V before experiment, T_{fm} the volume of thiosulphate required after the experiment with V_m of V^V , W_m the weight of component 1 of equivalent weight E_1 and $(Q - W_m)$ the weight of the other component of equivalent weight E_2 .

$$S_v = \frac{1000 \times T_i \times W}{V (T_i - T_f) \times E_1}$$

where T_i is the volume of thiosulphate required initially for iodometric standardisation of V^V , T_f the volume of thiosulphate for iodometric determination of V^V after the reaction with the reductant, W the weight of the reductant for the above standardisation, V the volume of V^V added, E_1 the equivalent weight of the reductant.

Method 2 is unsatisfactory due to two reasons. It was found in an earlier report¹⁶ that 1 ml of 0.1 N V^V was equivalent to 170 to 174 mg of glucose indicating a variation in equivalent weight of glucose. So method 1 was employed which does not need the knowledge of equivalent weights.

The oxidising character of V^V also depends on the acid concentration¹⁹. Hence prior standardisation of V^V solution by the substrates and then adopting the proposed working formula 1 seems a better option.

Table 1

No of Expt	Total quantity in the mixture Q (g)	Amount of sucrose (g) Taken/ (Found)	Amount of glucose (g) Taken/ (Found)	Error, based on sucrose
1	0 07680	0 04490 (0 04530)	0 03190 (0 03150)	+1 0%
2	0 06070	0 03370 (0 03340)	0 02730 (0 02700)	-0 7%
3	0 05050	0 03720 (0 03680)	0 01330 (0 01370)	-1 07%
4	0 04040	0 01860 (0 01860)	0 02180 (0 02180)	0 0
5	0 02570	0 00540 (0 00550)	0 02190 (0 02020)	0 28
6	0 03100	0 01600 (0 01590)	0 01500 (0 01510)	0 8
7	0 04904	0 02710 (0 02662)	0 02194 (0 02242)	1 7
8	0 08110	0 05870 (0 06020)	0 02240 (0 02090)	2 5
9	0 02470	0 00234 (0 00229)	0 02236 (0 02241)	2 1
10	0 02925	0 00683 (0 00668)	0 02242 (0 02257)	2 1
11	0 04119	0 01877 (0 01908)	0 02242 (0 02211)	1 6
12	0 05178	0 02936 (0 02990)	0 02242 (0 02188)	1 8
13	0 03735	0 02503 (0 02530)	0 01232 (0 01205)	1 0
14	0 04987	0 02503 (0 02560)	0 02484 (0 02427)	2 2
15	0 05813	0 01877 (0 01885)	0 03936 (0 03928)	0 2
16	1 58480	0 78490 (0 78030)	0 79990 (0 08045)	0 58
17	0 93980	0 63100 (0 64150)	0 30880 (0 29830)	1 6
18	0 02930	0 01732 (0 01696)	0 01198 (0 01234)	2 0
19	0 03901	0 01528 (0 01523)	0 02373 (0 02378)	0 32
20	0 03901	0 01925 (0 01937)	0 01976 (0 01964)	0 6

In the present method refluxing for 1 h is recommended instead of 40 min as was employed for single component determination.

The results (Table 1) reveals that accuracy is better in comparison with the other methods available in the literature. Very accurate results were obtained if the total concentration of sugar used remained around 1%. It was observed that accuracy of the present method depends largely on the following facts : (i) the substrate must be anhydrous and pure, (ii) starch solution must be freshly prepared, (iii) Double-distilled water is an absolute necessity and (iv) time of reflux must be maintained carefully. The merit of this method involves simple iodometric titration which gives stable and sharp end-point. In view of accuracy and operation the method scores over that of Fehling's.

Experimental

Both glucose and sucrose (Merck) were stored over concentrated sulphuric acid in a desiccator for at least one week before use. Sodium (or ammonium) metavanadate, perchloric acid (70%), potassium iodide, potassium dichromate (all G.R., Merck), sodium thiosulphate and hydrochloric acid (A.R., Biosol) were used. A freshly prepared starch solution was used as indicator. Double-distilled water was used throughout.

Preparation and standardisation of thiosulphate solution were carried out as described elsewhere^{10,11}. Vanadium(V) was prepared in the following manner. The clear yellow solution obtained by dissolving sodium (or ammonium) metavanadate (0.05 mol) in hot water (200 ml) was allowed to cool to room temperature. It was then poured slowly into a cold solution of perchloric acid (70%; 170 ml) in water (200 ml) with stirring, whereupon a transparent yellow solution of the metavanadate (approximately, 1 mol dm⁻³, caused by the reduction of V^V to V^{IV}) was obtained. The solution was standardised iodometrically.

Standardisation of metavanadate solution with standard glucose solution : A solution of glucose (0.9842 g dl⁻¹) was prepared. A mixture of this solution (2.0 ml) and the metavanadate solution (30 ml) was refluxed for 1 h. The resulting green-blue solution was cooled to room temperature. The reflux condenser was washed with water (10 ml). The residual metavanadate was determined iodometrically.

In another experiment the metavanadate solution was standardised by a standard sucrose solution (1.0098 g dl⁻¹), following the procedure as described above.

Derivation of the working formula : Formula used for the determination of monosaccharides is

$$S = \frac{W(Z - Y)}{(Z - X)}$$

where W is the concentration (g dl^{-1}) of sugar content in a solution of known strength, Z the titre value of thiosulphate solution required for a blank titration of the vanadium(V) solution (taken), X and Y are the titre values of the same thiosulphate solution required for determination of residual vanadate of known and unknown strengths respectively and S represents the concentration (g dl^{-1}) of unknown solution.

For glucose the equation used be

$$S_1 = \frac{W_1(Z_1 - Y_1)}{(Z_1 - X_1)} \quad (1)$$

and for sucrose the equation be

$$S_2 = \frac{W_2(Z_2 - Y_2)}{(Z_2 - X_2)} \quad (2)$$

From eqn. (1), one can write,

$$\frac{S_1(Z_1 - X_1)}{W_1} = (Z_1 - Y_1) \quad (3)$$

Similarly, from eqn. (2) one can write,

$$\frac{S_2(Z_2 - X_2)}{W_2} = (Z_2 - Y_2) \quad (4)$$

Summation of (3) and (4) leads to the derivation,

$$\frac{S_1(Z_1 - X_1)}{W_1} + \frac{S_2(Z_2 - X_2)}{W_2} = Z_1 - Y_1 + Z_2 - Y_2$$

putting $Z_1 + Z_2 = Z$ and $Y_1 + Y_2 = T$, one can get,

$$\frac{S_1(Z_1 - X_1)}{W_1} + \frac{S_2(Z_2 - X_2)}{W_2} = (Z - T)$$

or,
$$\frac{(Q - W_2)(Z_1 - X_1)}{W_1} + \frac{S_2(Z_2 - X_2)}{W_2} = (Z - T)$$

where, Z_1 , Z_2 and Z represent the volume of thiosulphate solution for blank titration and Q represents total quantity in the mixture. Since Z_1 , Z_2 and Z all represent the volume of thiosulphate solution for titrating blank vanadate solution, they can be replaced by Z . Thus the formula assume the form,

$$\frac{(Q - W_2)(Z - X_1)}{W_1} + \frac{S_2(Z - X_2)}{W_2} = (Z - T)$$

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