*Asian Journal of Chemistry* Vol. 14, No. 2 (2002), 839–843

# Nickel(II) Assisted Determination of Some Reducing Sugars with Alkaline Ferricyanide

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Conditions were developed for titrimetric quantitative detemination of some reducing sugars such as glucose, galactose, fructose, lactose, maltose and inverted sucrose with alkaline ferricyanide as an oxidising agent using nickel(II) sulphate as catalyst and its dimethylglyoxime complex as an indicator. The reaction between glucose and ferricyanide has been found to correspond to a definite stoichiometry. The products obtained by the oxidation of glucose are isolated and identified. The present proposed method is successfully applied to the determination of lactose in milk and sucrose content in commercial cane sugar products.

**Key Words: Reducing sugars, Titrimetry, Ferricyanide**

## INTRODUCTION

Britton and Phillips[1, 2] sought to give a rational and meaningful interpretation to the fact that ferricyanide oxidizes glucose in alkaline solution.Their method involves the detection of the end-point potentiometrically and hence is obviously time consuming compared to a visual titrimetric method. In addition, Fehling's method[3–7] can be considered to be associated with two serious limitations: (i) the method utilizes factor, (ii) detection of end-point with methylene blue indicator needs a trained eye. The other reagents such as iodine[8, 9], periodate[10], vanadate[11] have their own limitations.

Literature survey indicates that there does not seem to be a method reported involving the use of dimethylglyoxime in the presence of nickel(II). The present paper deals with the attempts of a direct visual titrimetric determination of some reducing sugars with alkaline ferricyanide.

## EXPERIMENTAL

0.1 M solution of potassium ferricyanide (Proanalysi, E. Merck) was prepared by weight purity. 0.05 M solution of hydroxylamine hydrochloride (Loba, GR) was prepared and standardized[12]. 0.5 M Nickel(II) sulphate, $NiSO_4 \cdot 7H_2O$ (E. Merck, India) was prepared and standardized. 3% Dimethylglyoxime (DMG) (E. Merck, India) was prepared in 1 M sodium hydroxide solution. 5 M and 2 M sodium hydroxide solutions were prepared. 0.05 M solutions of glucose, galac-

tose, fructose, lactose, maltose and sucrose (Loba, GR) were prepared and standardized[8]. Necessary working range solutions of the above were prepared by appropriate dilution.

A Perkin-Elmer (model-841) double beam infrared spectrophotometer was used for infrared matching of the products resulting in the glucose oxidation with ferricyanide.

## Recommended Procedure

To an aliquot of ferricyanide sufficient sodium hydroxide is added to give a concentration range of 0.5 M to 4 M in overall 50 mL solution. 1 mL of 0.5 M nickel(II) is then added. Then the mixture is brought to 95°C either on a boiling water bath or on a temperature controlled hot plate and is titrated at this temperature with the reducing sugar solution until just before the disappearance of black precipitate (as arrived at by a pilot titration).Then 0.5 mL of 0.5% DMG solution is added. The colour of the solution at this stage is intense red. The titration is continued to the just disappearance of red colour.

The same procedure outlined above is found to be applicable to hydrolysed lactose and maltose and sucrose after inversion.

The parametric conditions mentioned in the recommended procedure are outlined in Table-1.

TABLE-1
EXPERIMENTAL CONDITIONS FOR THE QUANTITATIVE REACTION OF FERRICYANIDE WITH GLUCOSE

Ferricyanide taken 20.0 mL of 0.1042 M; Time of heating 1 min; Temperature 95°C

| Concentration of nickel(II) solution, M | Concentration of NaOH, M | Consumed glucose volume, of 0.0204 M, ml | Moles of ferricyanide per 1 mol. of glucose |
|---|---|---|---|
| 0.1 | 1 | 13.9 | 7.35 |
| $2.08 \times 10^{-3}$ | 1 | 11.6 | 8.81 |
| $2.08 \times 10^{-3}$ | 1 | 10.9 | 7.37 |
| $1.04 \times 10^{-2}$ | 1 | 10.2 | 10.02 |
| $1.66 \times 10^{-2}$ | 1 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 1 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 2 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 3 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 3.6 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 4.0 | 10.1 | 10.11 |
| $3.32 \times 10^{-2}$ | 0.75 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 0.50 | 10.2 | 10.02 |
| $3.32 \times 10^{-2}$ | 0.36 | 10.4 | 9.82 |

## RESULTS AND DISCUSSION

Based on the preliminary studies in the indirect determination of reducing sugars with excess ferricyanide not corresponding to any definite stoichiometry, different transition metal ions were tried as catalysts. Nickel(II) sulphate was found to serve as a suitable one in that the reaction between ferricyanide and reducing sugar proceeded smoothly to a particular stoichiometry.

Since the earlier reports indicated the reaction between ferricyanide and glucose to be considerably slow at room temperature, we sought first to determine glucose by the indirect method using the ferricyanide—hydroxylamine visual titrimetric method[13] as monitor to asses the excess ferricyanide. The procedure revealed the following points:

1. The reaction between ferricyanide and glucose in the presence of nickel(II) is stoichiometrically complete at 95°C within 1 minute.
2. Nickel(II) served as a catalyst.
3. DMG in the presence of nickel(II) served as an indicator in the reaction of ferricyanide-hydroxylamine reaction.

Based on the above points, a direct titrimetric method for the determination of glucose is reported.

The relevant mole ratio data of other reducing sugars with the mean errors are given in Table-2.

TABLE-2
DETERMINATION OF SOME REDUCING SUGARS

| Name of the sugar | Moles of ferricyanide per one mole of sugar | Pooled standard deviation*, mg |
|---|---|---|
| Glucose | 10.00 | 0.06 |
| Galactose | 10.00 | 0.05 |
| Fructose | 8.66 | 0.09 |
| Hydrolyzed lactose | 20.00 | 0.08 |
| Hydrolyzed maltose | 20.00 | 0.07 |
| Inverted sucrose | 18.66 | 0.09 |

*Average of four determinations for each six replicates.

The above recommended procedure is applied to the determination of lactose in milk samples. The conventional procedure[14] is applied to remove the protein and fat contents. The results (Table-3) are compared well with the earlier methods[1, 2]. The purity of sucrose content in some commercial samples of cane sugar is determined using the recommended procedure.

Since a definite stoichiometry is obtained in the case of glucose it may sound logical to probe into investigation related to product identification which is given hereunder.

The different products of oxidized glucose that can be envisaged are collected

from the literature and various combinations have been tried to correspond to the mole ratio of 10. Such attempts led to malic acid and oxalic acid as the most probable ones.

TABLE-3
DETERMINATION OF LACTOSE IN MILK SAMPLES AND SUCROSE IN COMMERCIAL CANE SUGAR PRODUCTS

| Sample | Present method (%) | Standard method (%) |
|---|---|---|
| (a) *Lactose in milk* | | |
| Bufffalo milk | 4.39 | 4.36 |
| Cow milk | 4.68 | 4.60 |
| Visakha Dairy milk | 4.94 | 4.92 |
| Dolphin Dairy milk | 4.84 | 4.84 |
| Vijaya Dairy milk | 5.06 | 5.02 |
| (b) *Sucrose in commercial cane sugar product* | | |
| Sample-1 | 98.4 | 98.2 |
| Sample-2 | 99.6 | 99.4 |
| Sample-3 | 99.0 | 99.0 |
| Sample-4 | 98.2 | 98.1 |

The identification tests[15] for malic and oxalic acid are positive. Identification of products is further followed up by isolation and IR spectral studies.

After the titration is completed, the resulting titrated recipe is filtered. The filtrate is neutralized with dilute sulphuric acid to litmus paper and treated with

TABLE-4
COMPARISON OF INFRARED SPECTRA OF THE KNOWN AND UNKNOWN MIXTURES OF ETHYL OXALATE AND ETHYL MALATE

| Functional group expected to be | Wave number ($cm^{-1}$) | | | |
|---|---|---|---|---|
| | Unknown product | | Known mixture | |
| | Sample 1 | Sample 2 | Sample 1 | Sample 2 |
| —OH | 3451 | 3445 | 3450 | 3450 |
| —C=O | 1618 | 1621 | 1628 | 1628 |
| —C—O | 1205 | 1195 | 1195 | 1201 |
| —C—O | 1046 | 1050 | 1051 | 1050 |

zinc sulphate (equivalent to ferrocyanide content) and filtered. The filtrate containing products is preconcentrated on a water bath and finally a white solid (I) is obtained. The components identified in the obtained product are malic acid and oxalic acid in a mixture, which could not be separated with the facilities available. But the corroboration of the suggestion of malic acid and oxalic acid was tried in (I) by esterification and subsequent identification with infrared spectral matching with authentic malic acid and oxalic acid mixture similarly esterified (Table-4). Based on the results obtained by the analysis, the stoichiometry can, therefore,be represented as:

$$C_6H_{12}O_6 + 10Fe(CN)_6^{3-} + 10OH^- \longrightarrow (COOH)_2 + (COOH)_2CH_2CHOH + 10Fe(CN)_6^{3-} + 7H_2O$$

## ACKNOWLEDGEMENTS

The authors are thankful to UGC, India for financial assistance. One of the authors (ASRK) is thankful to Dr. G.V. Prasad for his encouragement.

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(*Received*: 27 October 2001; *Accepted*: 8 February 2002) AJC-2596