



Analytical Methods

Direct potentiometric determination of starch using a platinum redox sensor

Nikola Sakač*, Milan Sak-Bosnar, Marija Horvat

Department of Chemistry, Josip Juraj Strossmayer University of Osijek, F. Kuhača 20, 31000 Osijek, Croatia

ARTICLE INFO

Article history:

Received 17 March 2011
 Received in revised form 19 February 2012
 Accepted 6 October 2012
 Available online 8 November 2012

Keywords:

Starch
 Potentiometric sensor
 Direct potentiometry
 Triiodide

ABSTRACT

Here, we describe the development of a platinum redox sensor for the direct potentiometric quantification of starch in solution. The sensor measures the decrease in free triiodide ion after it complexes with starch to form a starch–triiodide complex. This decrease was, therefore, correlated with starch concentration, and the composition and stability of the potassium triiodide solution were optimised. The starch–triiodide complex was characterized potentiometrically at variable starch and triiodide concentrations. We also propose a response mechanism for the platinum redox sensor towards starch and an appropriate theoretical model. The optimised method exhibited satisfactory accuracy and precision and was in good agreement with a standard spectrophotometric method. The sensor was tested over a range of 0.4–9 mg starch, with recoveries ranging from 97.8% to 103.4% and a detection limit of 0.01 mg starch.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Starch is one of the major polysaccharides produced and used by plants for energy storage. It is commonly found in seeds, roots and tubers, as well as in stems, leaves, fruits and pollen. It is an inexpensive material and has many industrial applications, especially in the food and beverage industry and, recently, in biodegradable applications.

Starch generally consists of two different fractions (Otey & Doane, 1984): amylose, a linear α -1,4 linked polymer, and amylopectin, a highly α -1,6 branched α -1,4 polymer. Starch forms a complex with triiodide that has violet-blue colouration, and the colour depends on the nature of the starch (Murdoch, 1992; Rundle & French, 1943; Saenger, 1984).

The interaction of starch and iodine results in the formation of complexes (Teitelbaum, Ruby, & Marks, 1978, 1980) with characteristic colours. The colour of the starch–triiodide complex has been shown to vary with starch chain length (Bailey & Whelan, 1961). Since starch assumes a helical structure, iodine molecules occupy the central cavity of the helical molecule in the complex (Hinrichs et al., 1987). Many physicochemical properties of starch, such as its iodine binding capacity and degree of polymerization (DP), depend on the botanical origins of the starch and the conditions used for its fractionation and purification.

Many attempts have been made to measure starch directly and quantitatively: HPLC (Boley & Burn, 1990), calorimetry (Acquistucci, Bucci, Magri, & Magri, 1997), flow-injection systems with immobilized enzymes for simultaneous starch and glucose determination (Lim, McDonald, & Hill, 2003), and multi-enzyme elec-

trodes for starch and glucose determination (Hu, Zhang, & Zhang, 1999; Piro, Do, Le, Hedayatullah, & Pham, 2000). However, these methods are typically complicated, expensive or time-consuming.

There are several methods for starch determination. The enzymatic α -amylase/amyloglucosidase (AA/AMG) procedure (McCleary, Gibson, & Mugford, 1997; McCleary, Solah, & Gibson, 1994) is now widely accepted as being reproducible and reliable and has become an American Association of Cereal Chemists (AACC) method. Ewers' polarimetric method is currently the official EC method for the measurement of starch purity (Mitchell, 1990). Finally, there are colorimetric methods based on iodine binding (McCready & Hassid, 1943; Séne, Thévanot, & Prioul, 1997) or the formation of coloured products after chemical degradation (Knutson, 1983) and fluorometric methods like the BioVision Starch assay kit.

The aim of this investigation was to develop a sensor-based method for the fast, reliable, accurate and inexpensive determination of starch in solution. A theoretical model for measuring starch quantity using direct potentiometric sensing principles is also presented. Starch quantification was based on the measured decrease in free triiodide ion after its complexation into a starch–triiodide complex.

Platinum electrode was used as an indicator of the changes of iodide/triiodide redox couple. Its excellent response characteristics towards the redox couple mentioned are described elsewhere (Sakač, Gvozdić, & Sak-Bosnar, 2012; Sakač et al., 2011).

2. Experimental

2.1. Reagents and solutions

Soluble starch was purchased from Kemika (Croatia). Iodine (I_2), purchased from Kemika (Croatia), and potassium iodide (KI), purchased from Sigma–Aldrich (Germany), were used to prepare the

* Corresponding author. Tel.: +385 31495534; fax: +385 31495549.
 E-mail address: nikola.sakac@gmail.com (N. Sakač).

potassium triiodide solution. Glacial acetic acid (CH_3COOH) was purchased from Panreac (Spain), and sodium acetate trihydrate ($\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$) was purchased from J.T. Baker (Holland).

2.1.1. Starch solution preparation

The initial starch solutions were prepared at concentrations of 2, 3 and 5 g/L by adding 0.2, 0.3 and 0.5 g, respectively, of dried soluble starch to a 0.1 M acetate buffer solution (pH 6.0) in a closed 100-mL volumetric flask. After heating and stirring the solution for 10 min., it was allowed to cool to room temperature, then made up to 100 mL with deionized water in a volumetric flask. These solutions were then used for further investigations. Starch solutions were prepared fresh every day to avoid microbial degradation. Solutions with starch concentrations above 5 g/L form a starch gel are difficult to manipulation and possibly cause quantitative errors.

2.1.2. Triiodide solution preparation

The potassium triiodide solution was prepared by dissolving solid iodine (100 μM) in a 0.05-M potassium iodide solution.

2.2. Apparatus

A Metrohm 780 pH meter, 728 Stirrer, 765 Dosimat (all from Metrohm, Switzerland) were used along with custom software made in house and a platinum redox electrode IJ64 (Ionode, Australia) for the response measurements. A silver/silver (I) chloride electrode (Metrohm, Switzerland) served as the reference electrode. Direct potentiometric measurements were performed on an eDAQ 186 Quad Amp pH/mV amplifier, eDAQ e-corder 821 8-channel data acquisition system, eDAQ EChem1.5 software (all from eDAQ, Australia), IJ64 platinum redox electrode and a silver/silver (I) chloride reference electrode.

2.3. Procedure

2.3.1. Preparation and optimization of potassium triiodide solution

Potassium triiodide solutions were prepared by dissolving fixed iodine (5 mM) and different amounts of potassium iodide in ultrapure deionized water to yield final concentrations of 0.02, 0.05, 0.1 and 0.5 M. The above solutions were prepared separately.

The responses of the platinum redox electrode were measured by accurate, incremental additions of the prepared triiodide solutions to 20 mL of a potassium iodide solution, with the same potassium iodide concentration as the prepared triiodide solution. Solutions were continuously stirred during triiodide addition and measurement.

2.3.2. Selection and optimization of the starch–triiodide complex

To measure the response of the platinum redox electrode, the starch solutions (2, 3 and 5 g/L) were added incrementally to 8 mL of potassium triiodide solutions that had different triiodide concentrations but constant iodide concentrations (0.05 M).

2.3.3. Measurement of starch concentration

A known amount of starch solution was added to 8 mL of a standard potassium triiodide solution with a constant iodide concentration of 0.05 M. After stirring, the redox potential of the platinum sensor was measured. The starch concentration was determined from the calibration graph or from the regression equation. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Optimization of the iodide/triiodide composition

Potassium triiodide is obtained by dissolving iodine in potassium iodide solution:



The equilibrium constant of the above reaction is given by Eq. (2):

$$K = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} \quad (2)$$

A large excess of iodide is needed to hold the triiodide concentration constant due to the low value of the above equilibrium constant.

The equilibrium concentrations of iodine and iodide from Eq. (2) are as follows:

$$[\text{I}_2] = [\text{I}_2]_0 - [\text{I}_3^-] \quad (3)$$

$$[\text{I}^-] = [\text{I}^-]_0 - [\text{I}_3^-] \quad (4)$$

After inserting Eqs. (3) and (4) into Eq. (2), the following expression is obtained:

$$K = \frac{[\text{I}_3^-]}{([\text{I}_2]_0 - [\text{I}_3^-])([\text{I}^-]_0 - [\text{I}_3^-])} \quad (5)$$

where the subscript, 0, relates to the initial concentrations of iodine and iodide.

The equilibrium triiodide concentration can be calculated by solving the quadratic Eq. (5), whose real solution is given by Eq. (6):

$$[\text{I}_3^-]_{1,2} = \frac{[K([\text{I}^-]_0 + [\text{I}_2]_0) + 1] - \sqrt{[K([\text{I}^-]_0 + [\text{I}_2]_0) + 1]^2 - 4K^2[\text{I}^-]_0[\text{I}_2]_0}}{2K} \quad (6)$$

The surface 3D plot in Fig. 1 shows the conversion of iodine to triiodide, expressed as the percentage of triiodide formed, in relation to the initial iodide/iodine ratio and iodine concentration. Maximum conversion occurred at lower iodine concentrations, higher iodide concentrations (i.e., >0.1 M) and iodide/iodine ratios greater than 100.

3.1.1. Response of the platinum redox sensor against triiodide



For the reaction in Eq. (7), the corresponding redox potential can be described by the Nernst equation:

$$E = E^\circ + \frac{RT}{2F} \ln \frac{[\text{I}_3^-]}{[\text{I}^-]^3} = E^\circ S \log \frac{[\text{I}_3^-]}{[\text{I}^-]^3} \quad (8)$$

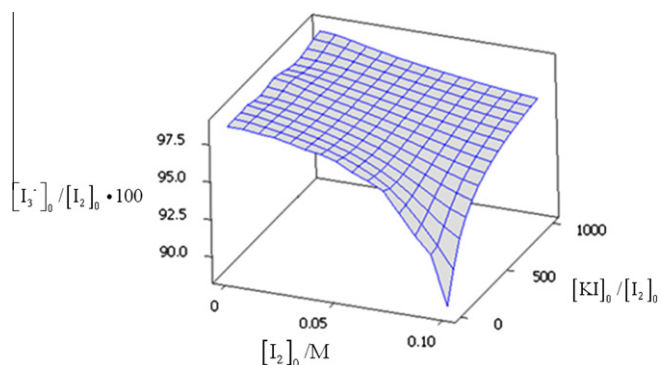


Fig. 1. Conversion rate of iodine to triiodide as a function of the initial iodide/iodine ratio and iodine concentration.

Download English Version:

<https://daneshyari.com/en/article/10538529>

Download Persian Version:

<https://daneshyari.com/article/10538529>

[Daneshyari.com](https://daneshyari.com)