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# STARCH CHARACTERISATION USING SPECTROPHOTOMETRY AND DIRECT POTENTIOMETRY

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## ABSTRACT

Starch consists of two polymer types; amylose and amylopectine. Their ratio is starch origin-dependent. Triiodide ions bind characteristically to the amylose and amylopectin molecules of the starch. This can be monitored using spectrophotometry, but recently also direct potentiometry with platinum redox sensor. The absorbance and electrical potential change of the starch-triiodide complex were measured for wheat, potato, corn, rye, barley, rice, tapioca and commercial starch. The results showed characteristic curves for each starch type, corresponding to the specific amylose/amylopectine ratio. The curves were used to determinate starch type-specific parameter values; for spectrophotometry: starch-triiodide peak wavelength maximum ($\lambda$max/nm), maximum absorbance change for $\lambda$max ($\Delta$A) and for the direct potentiometry: slope (S) for the linear response region, maximum potential change ($\Delta$E) and relative sensitivity (mV/mg) for potential change in the corresponding starch concentration. Data comparison using these two methods revealed that methods serve to distinguish starch types based on specific triiodide bounding to starch components, but when absolute data changes between starches were compared, no correlation between them has been found.

**Keywords**: spectrophotometry, direct potentiometry, starch triiodide complex

## INTRODUCTION

Starch is a semicrystalline biopolymer and it is stored in various plant locations, such as in cereal grains, roots, tubers, stempiths, leaves, seed, fruit and pollen.

The general properties of a starch, such as gelatinization, solubilization, swelling, granule size, chemical constitution, crystal type, and enzymatic degradation, differ because of the origine of starches. The starch granules from different botanical sources vary in size, shape, and content of amylose and amylopectin, influencing their chemical and physical properties [1].

The interaction of starch and iodine results in the formation of complexes [2] with characteristic colors. The color of the starch–triiodide complex has been shown to vary with starch chain length [3]. Because starch assumes a helical structure, iodine molecules occupy the central cavity of the helical molecule in the complex [4]. Many physicochemical properties of starch, such as its iodine binding capacity and degree of polymerization (DP), depend on the starch's botanical origin [5, 6].

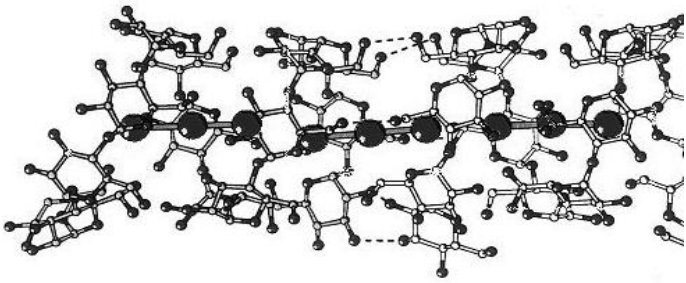

**Figure 1.** Starch-triiodide complex

In our previous paper [7], we described a method for the determination of starch based on direct potentiometric measurements, where the response of the triiodide ion in starch-triiodide complex is measured.

The aim of this work was to deteminate and compare the differences in various staches, concerning amylose/amylopectine ratio and starch-triiodide compex formation by using direct potentiometry and UV-VIS spectrophotometry.

## EXPERIMENTAL

*Reagents and solution preparation*

Starch samples were isolated from wheat (Srpanjka), potato, maize, rye (Barun), barley (Conduct), rice, and tapioca, which were obtained at the local market store in Croatia, and the commercial model (control) starch was obtained from Kemika (Croatia).

The samples' seed coats were peeled off, and an alkali steeping method [8] was used to prepare the puriffied starch samples. The starch solution was prepared in a concentration range of 1-5 g/L. Starch solutions were prepared fresh each day to avoid microbial degradation. Solutions with starch concentrations greater than 5 g/L form a starch gel. As a consequence, such solutions are difficult to manipulate and could cause quantitative errors.

*Apparatus*

Direct potentiometric measurements were performed on 780 Metrohm pH Meter (Metrohm, Switzerland) combined with IJ64 platinum redox electrode (Ionode, Australia) as a detector and a silver/silver (I) chloride reference electrode. Spectrophotometric measurements were performed using AvaSpec 2580 UV–Vis spectrophotometer (Avantes, Netherland).

*Procedure*

*Spectrophotometric*

For spectrophotometric measurements, five independent series of starch triiodide solutions were prepared. The previously prepared potassium triodide solution was then added to the starch-filled (wt 5%) 50 mL volumetric flasks. The volumetric flasks were filled to the mark with deionized water, stirred in a sonic bath for 5 minutes and were ready for further investigation.

*Potentiometric*

Triiodide solution was transferred to the titration vessel. The responses of the platinum redox electrode were measured by accurate, incremental additions of the prepared starch solutions. The solutions were continuously stirred during the addition of starch and during the measurements. Five independent series of starch triiodide solutions were measured.

## RESULTS AND DISCUSSION

*Spectrophotometric*

Starch samples were characterized by measuring starch triiodide complex absorption spectra. The commercial starch was used as a reference model. The amylose-amylopectin ratio in starch depends directly on botanical starch origin, there is a considerable difference in the starch-triiodide spectra for different starch types. The difference is noticeable in the wavelength area of the starch-triiodide complex where peaks vary in their heights and maximum wavelength values. These parameters from starch-triiodide complex spectra have been used for raw pre-statistical starch type differentiation (Table 1). A model starch was used as a reference for $\lambda$max comparison to other starch types (shown as $\Delta\lambda$). Rye (Conduct) showed the highest positive shift (+71 nm), Waxy corn starch the highest negative (-44) and Potato (Sigma) (+7) the lowest shift towards reference starch. The absorbance increase ($\Delta$A) at each $\lambda$max was calculated. Potato (Sigma) and rice starch showed the highest absorbance increase, 0.474 and 0.422, respectively. This indicates that the highest amount of triiodide is complexed with starch.

**Table 1.** Measured parameters from the absorbance spectra for all starch types

| Starch origin | λmax/nm | ΔĀ(λmax) for 5% starch solution | Δλ/nm (shift λmax) |
|---|---|---|---|
| Model starch | 564 | 0.337 | 0 |
| Potato (Sigma) | 571 | 0.474 | +7 |
| Corn | 610 | 0.321 | +46 |
| Corn waxy | 520 | 0.155 | -44 |
| Tapioca | 600 | 0.398 | +36 |
| Rye (Conduct) | 630 | 0.310 | +66 |
| Wheat (Srpanjka) | 630 | 0.197 | +66 |
| Rice | 590 | 0.422 | +26 |

*Potentiometric*

The platinum redox electrode showed a decrease in the response potential for each starch sample, and the curve shapes and slopes differed between starch samples. This is shown in Table 1; slope (S), linear response region per added starch mass, maximum potential change (ΔE) in linear response area and relative sensitivity (mV/mg) for potential change in the corresponding starch sample. Rye starch showed the highest slope –6.716, maximum potential change 47 mV and the highest relative sensitivity wich indicated it bounded the more triiodide than other starches. Barley starch showed the longest linear response area. Model starch showed the lowest relative sensitivity 2.97 mv/mg. The response data reflect the profile characteristics in the differences in the origins of the starches and amylose amylopectine ratio.

**Table 2.** Measured parameters from the redox electrode potential response change

| Starch origin | slope (S) | linear area / mg starch | Δ E mv / linear | relative sensitivity mV / mg |
|---|---|---|---|---|
| Rice | -4,964 | 9 | 43,2 | 4,80 |
| Rye (Conduct) | -6,716 | 7,5 | 47 | 6,27 |
| Tapioca | -6,381 | 7,5 | 46 | 6,13 |
| Corn | -5,022 | 7,5 | 37 | 4,93 |
| Wheat (Srpanjaka) | -3,542 | 12 | 39,8 | 3,32 |
| Barley (Vanessa) | -3,961 | 10,5 | 39,6 | 3,77 |
| Potato (Sigma) | -5,169 | 7,5 | 37,3 | 4,97 |
| Model starch | -3,035 | 9 | 26,73 | 2,97 |

## CONCLUSIONS

The results showed characteristic data for each starch type, corresponding to the specific amylose/amylopectine ratio, for both techniques.

Data comparison using these two methods revealed that methods serve to distinguish starch types based on specific triiodide bounding to starch components, but when absolute data changes between starches were compared, no correlation between them has been found.

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