



Short communication

# Use of sacrificial anode technology to mitigate non-enzymic Maillard browning



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## ABSTRACT

Experiments were performed to examine the effects of Maillard browning induced in the presence of metallic elements. The rate of brown pigment formation was shown to be reduced in model Maillard reactions performed in the presence of electropositive metals. Experiments involved reactions of D-xylose, D-arabinose and D-ribose with glycine,  $\alpha$ -L- or  $\beta$ -alanine and L-valine in pH 7.0 phosphate buffer at ca. 100 °C. “Browning” measured spectrophotometrically at 420 nm was significantly lower (compared with controls) in selected reactions containing elemental Mg, Al, Mn and Sn particles. It was hypothesized that the metals acted in sacrificial anode redox fashion to reduce or eliminate dehydroreductones believed to be key Maillard intermediates ultimately leading to less browning.

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## 1. Introduction

Control of visual color formation during amine/carbonyl Maillard reactions has been the subject of many investigations (Nursten, 2005). Strategies most often cited involve chemical trapping agents designed to interrupt the Maillard sequence at an early stage. Classic examples include the reversible addition of bisulfite ion or sulfur dioxide in acidic media to form relatively stable adducts of carbonyl reactants like aldose sugars. Under less acidic conditions the browning of hexoses was shown to be moderated by nucleophilic attack of sulfite ion on the  $\alpha,\beta$ -unsaturated linkage in 3,4-dideoxyhexosulos-3-ene intermediates to produce more stable 3,4-dideoxy-4-sulfohexoulose adducts. These sulfonic acid derivatives are believed to be incapable of further reaction leading to colored products. The use of sulfites for food preservation has led to safety concerns in recent years and consequently there is an opportunity to consider additive-free browning prevention. Recent studies have shown that added polyphenolic substances such as flavonols will retard the formation of volatile flavor compounds in model Maillard reactions (Totlani & Peterson, 2007). Conceivably then, additives such as epicatechin may prove to be useful “browning” inhibitors as well.

Recent studies on the electrochemical nature of the Maillard reaction suggested how browning might be minimized by taking advantage of the redox components of the reaction. The most likely

Maillard intermediates responsible for observable redox activity are the nitrogen-free osasones derived from Amadori compound decomposition (Rizzi, Amba, & Heineman, 2010). Chemically, the osasones are formed by  $\beta$ -elimination of an Amadori compound's amino acid moiety to yield 1-deoxyosones (1-DEOs) and 3-deoxyosones (3-DEOs). The 1-DEOs, also known as reductones [RH<sub>2</sub>], contain the readily oxidizable acyl ene-diol structural element  $-\text{CO}-\text{CH}(\text{OH})=\text{C}(\text{OH})-$ . The existence of a measurable galvanic electrical potential during model Maillard reactions provided evidence for an equilibrium between 1-DEOs and their oxidized tricarbonyl counterparts, the dehydroreductones [R],  $-\text{CO}-\text{CO}-\text{CO}-$  (Rizzi, 2013). Dehydroreductones are believed to be key intermediates in brown polymer formation which suggested that their elimination might inhibit non-enzymic browning. Reductones and dehydroreductones have yet to be isolated from foods, however trapping experiments (Smuda & Glomb, 2011) have confirmed their presence in model systems and independent synthesis (Glomb & Pfahler, 2000) has verified their high reactivity and likely contribution to non-enzymic browning.

An electrolytic process was envisioned for prevention or elimination of non-enzymic browning based on certain assumptions. Assuming that (1) dehydroreductones are key browning progenitors and (2) that the reversibility of the  $\text{RH}_2 \rightleftharpoons \text{R} + 2\text{H}^+ + 2\text{e}^-$  equilibrium exists then application of an external electrical potential should theoretically decrease the concentration of dehydroreductone (R) and subsequently lead to reduced browning. As early as 1983 Hekal proposed an electrolytic cell treatment to prolong color and flavor stability in orange juice. The basic idea was to

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employ cathodic reduction to eliminate detrimental oxidized species and/or dissolved oxygen to extend product shelf life (Hekal, 1983). The design reported by Hekal was extended by Marquis in 1995 in an attempt to delay non-enzymic browning in stored lemon juice products (Marquis, 1995). The electrolytic treatment led to reduced levels of dissolved oxygen and an initially lower redox potential in juice but it did not delay eventual browning during storage.

A simpler electrolytic method commonly used to prevent corrosion of iron and ferrous alloys is the sacrificial anode technique. In this technique highly electropositive metals like zinc or magnesium are physically attached to a metal to be protected i.e. such as the iron hull of a ship. The more electropositive metal is preferentially oxidized and transfer of electrons prevents oxygen induced iron deterioration, i.e. the one metal acts as an anode and is sacrificed (converted into cations) for the sake of another. The method is useful since it provides continuous electrolytic protection for a more labile substrate. The technology has yet to find explicit application for food preservation.

In 1985 Rouseff and Ting noted less browning of grapefruit juice stored in tin plated iron cans when compared with product stored in glass and suggested that tin was acting as a sacrificial anode to retard browning (Rouseff & Ting, 1985). More recently packaging containing tin was reported to reduce the loss of ascorbic acid in citrus juices (Robertson, 2012). If true these results are remarkable considering the low reduction potential of tin in acidic solution ( $E^\circ = -0.14$  V vs. standard hydrogen electrode  $E^\circ = 0.0$  V). The conceptual use of galvanic action to prevent non-enzymic browning via oxygen exclusion was the subject of a recent U.S. Patent, however no experimental evidence was reported or cited to support the claims (Del Monte Foods Inc., 2013). Since it is known that some “browning” precursors, i.e. 1-DEOs, are formed in the absence of oxygen it was of interest to investigate the effect of metallic elements on non-enzymic browning in a well defined anaerobic model system.

It was hypothesized that Maillard browning would be suppressed in the presence of sufficiently electropositive metals. Specifically, certain metals could by donating electrons reverse the equilibrium associated with dehydroreductone formation and thereby lead to less browning. Experiments were designed to test the effect of metals on browning intermediates directly without the participation of molecular oxygen.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Amino acids, sugars and inorganic reagents were commonly available commercial samples of >99% purity and used without further purification. Metal samples were of analytical grade purity in various physical forms ranging from 20 mesh particles to thin ribbon (Mg), fine, freshly prepared filings (Fe), freshly pulverized granules (Mn), freshly cut 0.5 mm chips (Al), and fine, reagent grade granules (Zn) and 20 mesh granules (Sn). 0.10 M Phosphate buffer was prepared by adding aqueous 0.10 M potassium dihydrogenphosphate to aqueous 0.10 M potassium monohydrogenphosphate to reach pH 7.0

### 2.2. Experimental procedure

A 100 ml flask was provided with a reflux condenser and an inlet port through which a stainless steel hypodermic needle was inserted. For reactions 40.0 ml of 0.10 M potassium phosphate buffer (pH 7.0) was added to dry ingredients to obtain solutions containing initial concentrations of sugars 0.10 M, amino acids

0.033 M and optionally 12% by weight (of reaction mixture) of metal fragments. Mixtures were rapidly raised to reflux temperature and 1.00 ml liquid samples were withdrawn with a previously ice-cooled plastic syringe. Samples were immediately added to 2.00 ml of water to quench the reaction and diluted solutions were analyzed at 420 nm at ca. 25 °C versus pure water on a Perkin-Elmer Lambda 35 UV/VIS spectrophotometer (slit width 1.00 nm). The experiments were generally run in triplicate. For pH measurements a Fisher Accumet model 955 mini pH meter was employed and calibrated at pH 7.00 with standard buffer. Precision was ca.  $\pm 0.02$  pH unit.

### 2.3. Statistical analysis

Statistical analyses were performed on a Texas Instruments model TI-30Xa hand calculator. SEM values were determined via the  $\delta_{xn-1}$  function key.

## 3. Results and discussion

### 3.1. Development of model system

A convenient model system consisted of a refluxing mixture of reducing sugars and  $\beta$ -alanine in potassium phosphate buffer at pH 7.0. Optionally, metal particles (Mg, Al, Mn, Zn, Fe, and Sn) ranging in size from 20 mesh to 0.5 mm chips were added at 12% of reaction weight. Reactant concentrations and a 50 min. reaction times were adopted to provide an early reaction stage in which dehydroreductones were believed to be present.  $\beta$ -Alanine was chosen initially instead of  $\alpha$ -amino acids to minimize possible metal-amino acid complexation and complications resulting from Strecker degradations. At ca. 100 °C these systems gradually developed a deep yellow-orange color during 50 min. Reactions were done buffered at pH 7.0 to minimize hydrogen generation from metals and other reactants. At reflux temperature oxygen solubility was assumed to be zero rendering the system anaerobic. Experimental results are summarized in Table 1 and Fig. 1.

### 3.2. Reactions of $\beta$ -alanine

Reactions of  $\beta$ -alanine with D-xylose were used to screen the effects produced by six electropositive metals (Table 1, entries 1–7). Predictably, magnesium the most reactive of the six metals ( $E^\circ -2.37$  V) led to visibly less browning after 50 min. reaction ( $A_{420}$  0.665 vs. control  $A_{420}$  0.737). In addition “browning” was significantly suppressed over a wide time range (Fig. 1). Interestingly, tin with the lowest reduction potential of metals examined ( $E^\circ -0.14$  V) was also effective (entry 7) ( $A_{420}$  0.629) thereby confirming the early supposition of its activity by Rouseff and Ting (1985). The magnesium effect (at 50 min) persisted at lower (1.25%) metal addition ( $A_{420}$  0.604  $\pm$  0.021) and with 12.5% thin Mg ribbon ( $A_{420}$  0.609  $\pm$  0.018). Metals with intermediate activity (Al, Mn, Zn and Fe, Table 1, entries 3–6) exhibited directional, but insignificant effects on browning at 50 min. However, mixtures containing Mn and Fe displayed small but significant reduction in browning at shorter reaction times (5, 10, 15, 25 and 35 min, data not shown). Reactions of  $\beta$ -alanine with D-arabinose and D-ribose showed insignificant changes in browning in the presence of magnesium filings (Table 1, entries 8–11). D-Arabinose exhibited less browning than D-xylose at 50 min., but further reduction in color production by Mg appeared to be minimal at best. D-Ribose browned strongly with  $\beta$ -alanine but no lowering effect was observed in the presence of Mg. The absence of reduced browning in D-arabinose or D-ribose reactions may have been due to competitive browning enhancement resulting from the presence of Mg(II) ions (see Section 3.3).

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