Gluten Content of Some Commercial American Silica-Stabilized Beers

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Abstract:

A number of commercially available American beers *already stabilized against chill haze with silica gel* were analyzed for gluten using the R5 competitive ELISA test. The beers were also analyzed for Chapon Chill Haze, Sensitive Protein, Tannoids, alcohol, conductivity, and pH. Rough correlations were found between: silica gel use and initial gluten level; Sensitive Protein and gluten content; and Chapon Chill Haze and gluten content. Several commercial silica-treated beers were found to have less than 20 mg/kg gluten. This level allows certain government-specified gluten reduction verbiage on a label and in advertising.

The Beers:

All were chillproofed using silica gel.

- 4 American lagers
- 2 Light beers
- 2 Bocks
- 1 Export-type lager
- 1 Ale
- 1 Wheat beer

Background:

Some but not all beers have been found to be gluten-free due to either normal protein-reducing steps in the brewing process or due to silica gel stabilization(1, 2). Previous work has demonstrated the tight adsorption of beer gluten to silica gel(3). Whether or not the dose needed to bring gluten down to the trigger level of 20 mg/kg(4) was the same as the dose needed to stabilize the beer to prevent chill haze depended on the beer. The doses did not seem that different, though.

The present work examines some finished beers to see whether commercial beers adequately stabilized by silica gel were “automatically” gluten-acceptable. The present work improves the reliability of the previous conclusions by using the quantitative R5 competitive ELISA test instead of a qualitative G12 dipstick test.

The relationship between gluten and chill haze protein is expected to be one of identity. The present work seeks to show this relationship by comparing standard measurements of chill haze protein to the measurement of gluten.

Measurements were made of the haze active protein and Chapon Chill Haze, but not forced beer haze. It has been found that forcing results did not have a simple dependence on haze-active protein, and so forcing results were considered too complex for the present work(3). Air, metals, polyphenol types, polyphenol amounts, and carbohydrates can all affect chill haze. Even without these extra factors, it has already been shown that protein-polyphenol haze is strongly affected by salts, pH, and alcohol in complex ways(5). The present empirical approach tries to take all of these protein-polyphenol solubility factors into account.

The most recent U.S. government ruling(4) does not allow the phrase "gluten-free" to be used for a barley-based beer even if it is below 20 mg/kg for basically three reasons: 1) the gluten-containing ingredient (barley malt) is not itself being processed to reduce gluten, but rather the food is being processed; 2) the R5 competitive ELISA test is not considered accurate enough in fermented beverages; and 3) gluten content is of such a severe health risk to some people that these uncertainties present too much risk to the consumer for "gluten-free" to be non-deceiving for barley-based beers. The same ruling, however, does describe verbiage for beers measuring less than 20 mg/kg gluten that is considered non-deceitful and adequately disclosing.

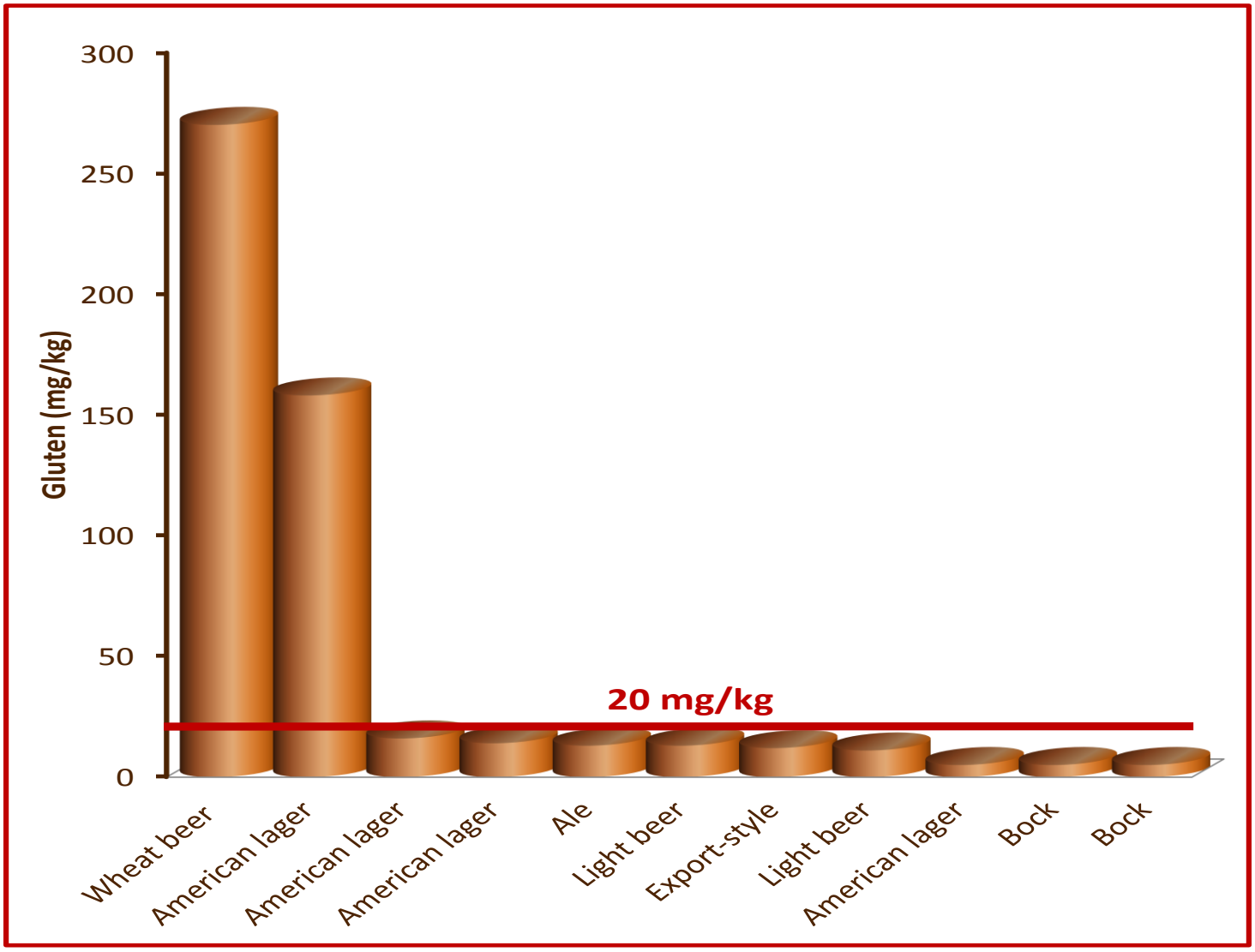
Experimental:

Measurement of Colloidal Stability: Forcing values were not used because last year's work showed that forcing introduced chemistries beyond the presence of protein and tannin that were difficult to control or explain. Instead, Chapon Chill Haze (-4^{o}C, 30 minutes, with 4% ethanol added) collected on unforced beer by a Pfeuffer Tannometer was used. It has been previously shown to correlate well with forced haze.

Measurement of other Beer Properties: Sensitive Protein and Tannoids were measured on unforced beer using a Tannometer. Alcohol was measured by distillation and density using ASBC Method Beer-4B. pH and conductivity were measured at 21^{o}C using standard methods.

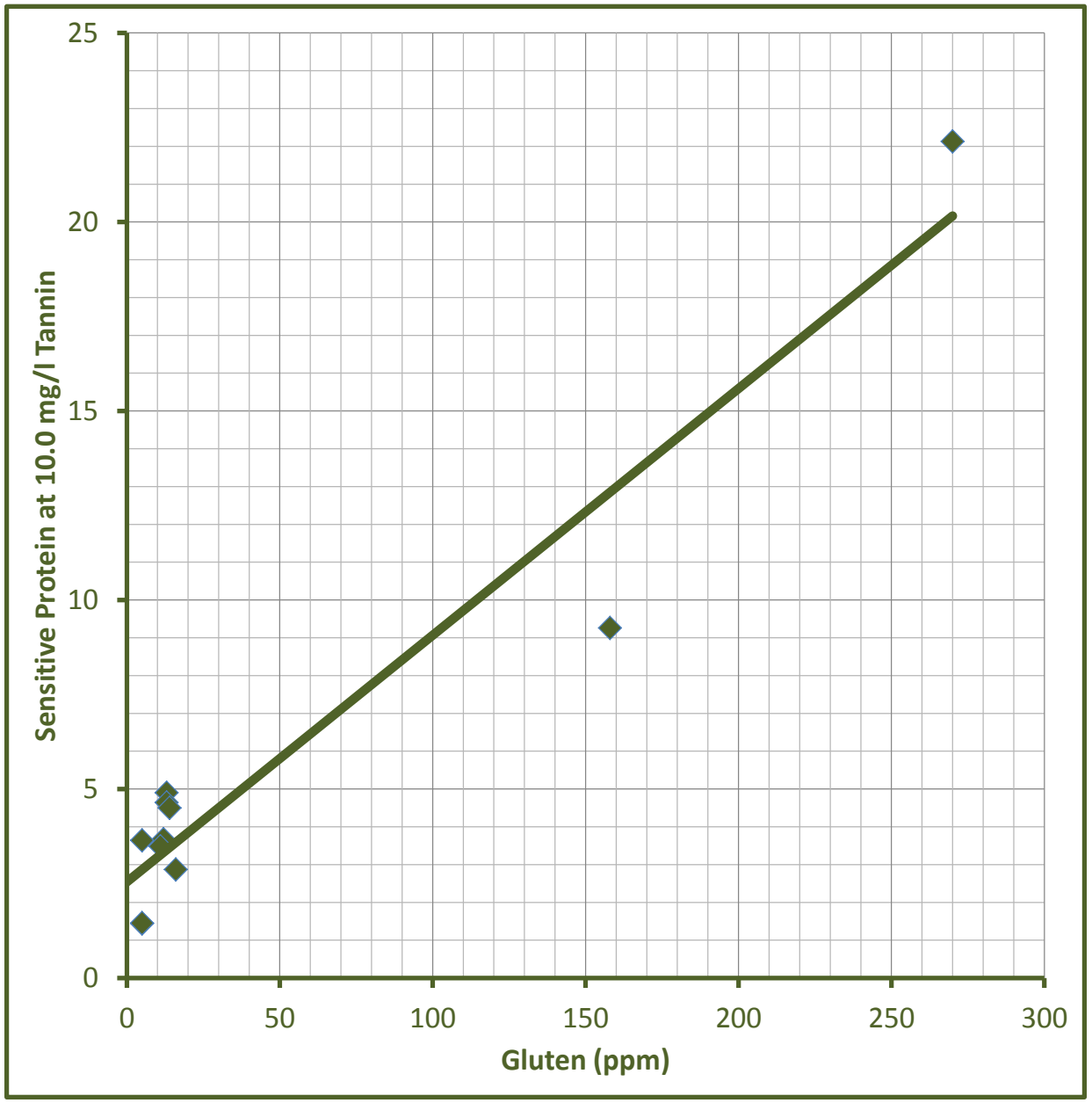
Measurement of Gluten: The gluten content of each beer sample was measured by Eurofins GeneScan (New Orleans, LA) using the R5 competitive ELISA test.

A: Some silica-treated beers are already gluten-acceptable



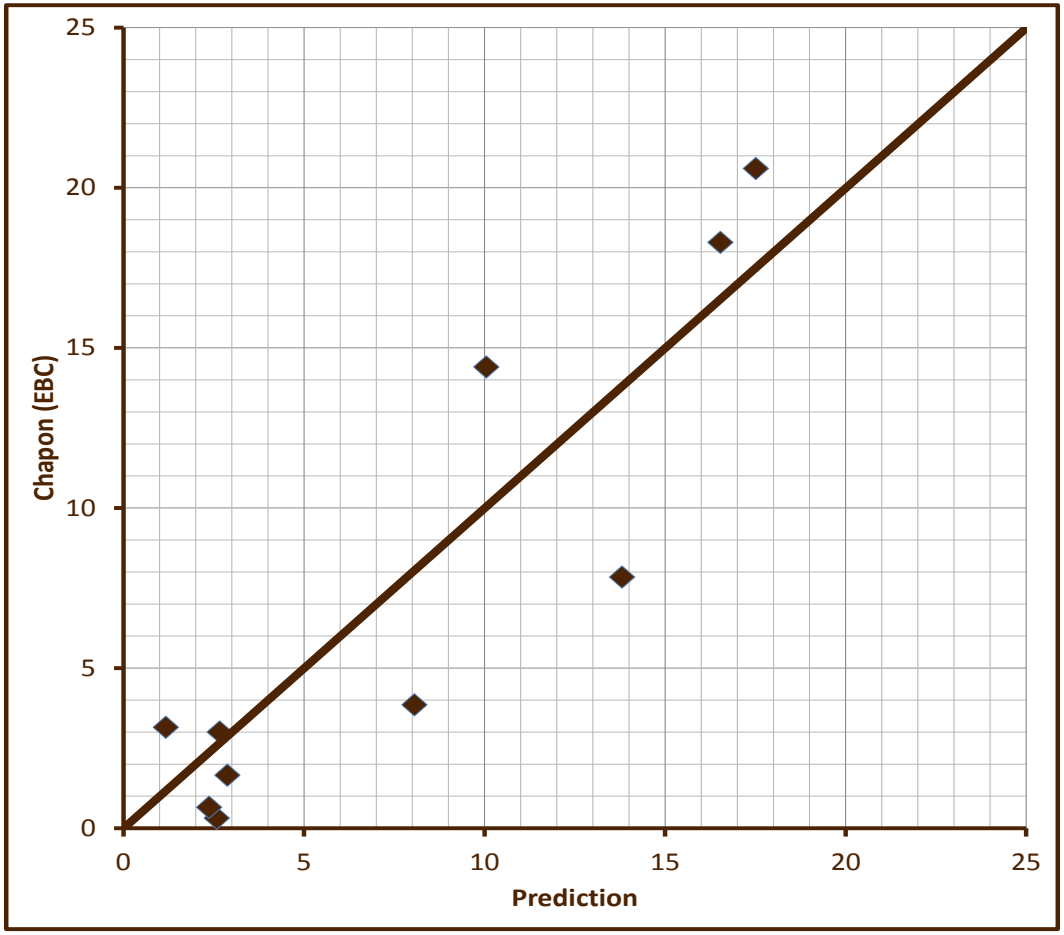
This figure shows that many, but not all silica-stabilized beers are already below the 20 mg/kg limit. Although all of the beers were treated with silica, two were considerably higher in gluten than the others. The likely explanation is that the dose of silica used was too low for the amount of gluten present. Silica titrates out the gluten, but has only a certain number of binding sites per gram. If the initial gluten level is high or the haze active polyphenol level is low, it may take much more silica to remove all the gluten than is needed to stabilize the beer.

B: Gluten correlates with Sensitive Protein.



The correlation between gluten and Sensitive Protein is not surprising, as it has been shown that the two classes of proteins have identical properties and should therefore be the same protein group: high proline and high glutamic acid.

C: Gluten remaining after stabilization correlates with chill haze.

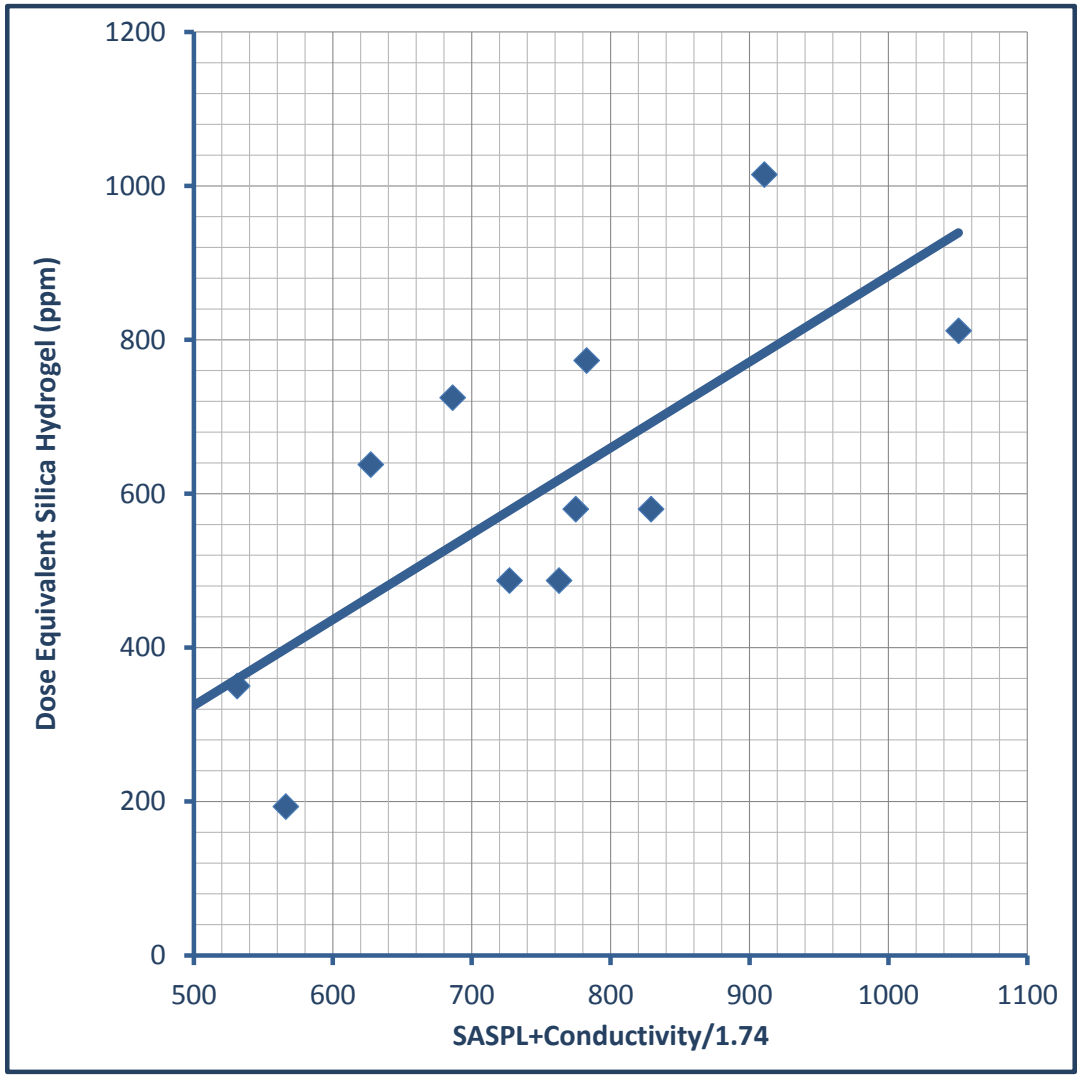


Chill haze is an extremely complex phenomenon affected by many properties, as clearly shown by the model work of Karl Siebert(5). In the present work all that was known about the manufacture of the beer was silica type and silica dose: we simply took what we found in the market made some measurements on it. One would expect these interactions: pH on the solubility of protein-polyphenol complexes, probably curved with an optimum; higher alcohol content making smaller haze particles; higher salt (conductivity) decreasing solubility and increasing haze; Tannoids indicating some aspect of the concentration of the protein-polyphenol complexes; Gluten (sensitive protein) indicating a different aspect of the concentration of the complexes. These factors were used by JMP statistical software to predict the Chapon Chill Haze by the following equation:

Chapon Chill Haze (EBC) = 15.065 – 0.0624*Tannoids (mg/L) – 5.43*pH
+ 0.01847*Conductivity (µmho) – 1.849*Alcohol (% v/v) + 0.0299*Gluten (ppm)

All the factors have the positive or negative influence expected. The most significant factors were conductivity and gluten. $R^2 = 0.789$.

D: The Dose of silica gel used correlates with assumed initial gluten content



Beers were produced using three different silica gels: two xerogels and one hydrogel. The doses were converted to equivalent hydrogel doses using conversion factors based on our unpublished experience.

Since we don't have access to the pre-stabilized beer, an assumption can be made from the SASPL test on what the initial gluten load was. It has already been shown that SASPL measures all the proteins left in the beer, not just the chill-haze causing ones(6). Since SASPL measures the salt level needed to begin protein precipitation, it makes sense to combine the "saltiness" of the beer (measured as conductivity) with the SASPL measurement. The relationship was optimized to reduce scatter, and the factor of 1.74 was identified: the most linear correlation between dose of silica gel used (as equivalent mg/kg of hydrogel) was found vs. SASPL + Conductivity/1.74.

The R^2 of this relationship is 0.54. That there is any relationship at all is almost surprising, since normal beer processing removes 98% of the barley gluten(1).

Conclusions:

1. Barley-based beers labelled “gluten-free” cannot yet be shipped across state lines, regardless of the gluten level.
2. Colloidal stabilization of beer by silica does seem to bring many beers below the target level of 20 mg/kg.
3. Based on the present results and the TTB ruling of February 11, 2014(4), it seems to us that many silica-stabilized beers may already be ready to be labelled:

GLUTEN DECLARATION

- Product fermented from grains containing gluten and treated to remove gluten.
- The gluten content of this product cannot be verified, and this product may contain gluten.
- Treatment steps include protein reduction steps in the brewing process, and adsorption of gluten by silica gel.
- Less than 20 mg/kg gluten was measured in this beer by the R5 Mendez competitive ELISA assay, which the FDA does not consider accurate for beer.

Possible language for a gluten label!

References:

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2. *Gluten-Reduced Beers Made with Barley*. S. Van Zandycke, The New Brewer Nov/Dec: 78-84, 2013.
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4. *Revised Interim Policy on Gluten Content Statements in the Labeling and Advertising of Wines, Distilled Spirits, and Malt Beverages*. Department of the Treasury Alcohol and Tobacco Tax and Trade Bureau, TTB Ruling Number 2014-2, Feb 11, 2014.
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