

# A Homebrewing Perspective on Mash pH III: Distilled-Water pH and Buffering Capacity of the Grist\*

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*We have determined the distilled-water mash pH ( $pH_i$ ) and buffering capacity ( $B_i$ ) of a number of different specialty grains used in beer brewing; our measurements have focused on flaked grains and 19 to 130 °L noncrystal malts. Our simple technique, which any homebrewer with a pH meter and temperature controller (plus some common kitchen equipment) can replicate, is to measure the pH of precise mixtures of each test grain with a fiducial grain (for which  $B_i$  is assumed to be known). Owing to a variety of processes used in the manufacture of noncrystal specialty malts, the pH and (especially) the buffering capacity of these malts exhibit much less correlation with malt color than is observed with similarly colored crystal malts. Flaked grain pH and buffering capacity varies quite dramatically among the different grain types. In addition to results specific to flaked and specialty grains, we have obtained two other general results: for a given grain (i)  $pH_i$  and relative values of  $B_i$  are largely independent of mash thickness (in the range of 2.5 to 8 L/kg), and (ii) batch to batch variability of  $pH_i$  can vary upwards of  $\pm 0.05$ .*

## 1. INTRODUCTION

The pH of a brewer’s mash depends upon three broad inputs: (i) the composition of the grist, (ii) the ions pre-dissolved in or added to the brewing liquor, and (iii) the concentration of strong acids or bases added by the brewer [1].<sup>1</sup> Factors that tend to make the mash more acidic – driving the pH down – are darker grains, the divalent ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , and acids. Conversely, factors that tend to make the mash less acidic – driving the pH up – include lighter colored malts, carbonates ( $\text{H}_2\text{CO}_3$  in one of its ionic states), and bases.

Each type of grain that composes the grist affects the pH through two properties. The first is the pH that results when the grain is mashed in distilled water. This is known as the **distilled-water pH** ( $pH_i$ ) for that particular grain [1].<sup>2</sup> The second property is the resistance that each type of grain has to other influences that effect changes in the pH. This quality can be characterized by a quantity known as the **buffering capacity** ( $B_i$ ) of the grain [2, 3]. If one knows both  $pH_i$  and  $B_i$  for each component of the grist ( $i = 1$  to  $N$ , where  $N$  is the number of components), then one can readily estimate the **grist pH** ( $pH_G$ ), which is the pH when the entire grain bill is mashed using distilled water. Knowing these quantities also allows one to predict the pH shift from any other pH changing ions that may already be present in a typical water supply or added by the brewer. The bad news is that malts do not arrive from the malting company with

$pH_i$  or  $B_i$  printed on the bag.

The good news is that a number of experimental studies have been carried out that inform us about  $pH_i$  and  $B_i$  for a variety of brewing grains. The most extensive work to date is that of Kai Troester (KT), who has made measurements on no fewer than 22 grains [1, 4]. A. J. deLange (AJdL), another brewer with a keen interest in mash pH, has carried out careful measurements on 10 different grist components [3, 5, 6]. The maltsters at Briess have gotten into the act: experimental results on a variety of Briess products have been obtained by Bies (8 grains) [7] and Geurts (18 grains) [8]. Fairly recently, Joe Walts, a professional brewer with an analytical bent, has made  $pH_i$  and  $B_i$  measurements on 17 different grains [9]. All of these studies have focused on base malts, caramel (crystal) malts, and dark roasted grains.

Here we build upon this previous experimental work in several ways. First, we have developed a simple experimental technique for determining  $pH_i$  and  $B_i$  values. Briefly, our technique consists of measuring pH values of a set of precise mixtures of a test grain and a fiducial grain (for which  $B_i$  is already assumed to be known). For a typical homebrewer this technique is much simpler than the standard acid/base titration experiment typically used to determine  $B_i$ . Second, we have measured a variety of brewing grains from two categories that have so far been largely neglected: (i) noncrystal (but not dark roasted) specialty malts and (ii) flaked grains. Third, we discuss the relationship of various aspects of the malting process to trends in pH and buffering capacity.

Our paper proceeds as follows. In Section 2 our experimental technique is described. In Section 3 we present a precise definition of  $B_i$  and discuss how  $pH_i$  and  $B_i$  determine  $pH_G$ . This theory provides the basis for the analysis of our experimental data. In Section 4 we discuss our data and its subsequent analysis before looking at the larger context of our work in Section 5. A brief summary concludes the paper.

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<sup>1</sup> OK, so strong acids and bases do simply alter the ionic composition of the water, but most brewers typically think about acids and bases as distinct from other ions important to brewing; hence, our distinction.

<sup>2</sup> Here  $i$  is an index that generically labels a particular grain.

## 2. EXPERIMENTAL DETAILS

In order to obtain reasonable accuracy with our technique, the test grain must have a  $pH_i$  value that is not too close to that of the fiducial grain. To ensure this condition is met with all of our test grains, we had to find two fiducial grains with disparate  $pH_i$  values. Owing to extensive prior data on Briess Caramel malts, we chose Briess Caramel L10 ( $pH_i \approx 5.3$ ) and Briess Caramel L120 ( $pH_i \approx 4.6$ ) as the fiducial grains. As is evident in the following discussion, in each experiment the test grain is mixed with one of these fiducial grains.

Each individual mash comprises a total of 12.5 g of grain and 31.25, 50.0, or 100.0 g of water, which results in mash thicknesses  $R = 2.5, 4,$  and  $8$  L/kg, respectively. In any given experiment each specific mash condition is carried out in three independent mashes.

Grains are pulverized by processing 1/4 cup at a time for 12 seconds in a Braun Type 4041 Coffee Grinder. Pulverized grain samples are then weighed using a Jscale JS-100xV scale.

A warm water bath is used to both pre-heat the jars and to maintain samples at 145 F. The warm water bath consists of a Corningware Electrics Model SC0-150 slow cooker (crock pot) and a braising rack to keep the jars from making contact with the crock pot bottom, filled with water to a depth of approximately 2 inches (just low enough that jars do not float). The steeping temperature is pre-set and maintained with a Johnson A490 controller with its temperature probe placed in a thermowell in the bath. The crock pot lid is in place on top at all times, except when transferring jars in/out.

Distilled water is heated on a stove to the required strike temperature. In order to achieve a consistent mash temperature, the strike water temperature for each mash is varied with  $R$ : 158, 153, and 150 F for  $R$  values of 2.5, 4, and 8 L/kg, respectively. Water for each steep sample is weighed on a Sunbeam Model SP5 scale and added to a preheated Mason jar, to which the pulverized preweighed grain sample is immediately added and stirred. Each jar is then immediately lidded and placed in the warm water bath for 10 minutes. After 10 minutes in the warm water bath, each jar is removed and a liquid sample is poured off from the steeping jar through a strainer into a clean jar. The liquid-sample jar is immediately lidded and placed in an ice water bath until cooled to 77 F. Once cooled, pH measurements are performed with a calibrated Milwaukee MW101 pH meter.

Over time our protocol evolved. In the early trials all three value of  $R$  were used with fiducial-grain fractions of 0, 0.5, and 1. These experiments led to the discovery that  $pH_i$  and (relative)  $B_i$  values are largely independent of  $R$ . Later trials were thus modified to emphasize the determination of  $B_i$ : we fixed  $R$  at 4 L/kg, but increased the number of mixtures to six, with fiducial-grain fractions of 0, 0.2, 0.4, 0.6, 0.8, and 1.0. In the later trials with flaked grains  $R = 8$  L/kg was instead utilized, owing to excessive water absorption by the flaked component in

$R = 4$  L/kg mashes.

## 3. HOW $pH_i$ AND $B_i$ DETERMINE $pH_G$

In this section we discuss a theory that allows us to calculate the expected pH when a mixture of grains is mashed in distilled water. The underlying principle is the conservation of charge associated with the absorption and release of  $H^+$  ions by constituents in the mash. We begin with an in-depth discussion of the meaning of the buffering capacity  $B_i$  of a single malt. From there we are able to discern the pH when two or more malts are mashed together.

When a single grain type is mixed with distilled water the resulting mash pH is invariably acidic, typically in the range between 4.5 and 6. This acidity can be attributed to malt-derived acidic buffers comprising phosphates and organic acids [10, 11]. In addition to setting the pH, this buffer system resists the ability of other added acids or bases to change the pH of the mash. This resistance to changes in pH occurs because the malt buffer system is quite efficient at (i) absorbing  $H^+$  when an acid is added and (ii) releasing  $H^+$  (which neutralizes  $OH^-$ ) if a base is added. In fact, without too much error we may assume all the  $H^+$  ions provided by an acid are consumed by the buffering system. Likewise, we may also assume all  $OH^-$  provided by a base are neutralized by the buffer-system donated  $H^+$ . This assumption is, of course, not quite true as the number of free  $H^+$  in solution (as indicated by pH) does change when an acid or base is added.<sup>3</sup> However, this change in the number dissolved  $H^+$  ions is typically far smaller than the number of  $H^+$  either consumed or donated by the buffer.

In Fig. 1, using data from AJdL [5, 6], we illustrate these the two key properties of any given grain. First, notice when each grain is mashed in distilled water (indicated by zero acidity on the vertical axis), a particular  $pH_i$  results. As the figure shows, the Maris Otter and Pils malts both have  $pH_i$  values close to 5.85, while  $pH_i$  for Roasted Barley is close to 4.70.<sup>4</sup> Figure 1 also illustrates what happens if a strong acid or base is added to the strike water: the amount of acid or base added [which is quantified in terms of mEq of  $H^+$  (positive acidity) or  $OH^-$  (positive alkalinity = negative acidity) per kg of grain] vs the resulting change in pH is often well described by a linear function. For the grains in Fig. 1 a linear least-squares fit of the each data set yields the straight lines shown in the figure. Under some circumstances deviations from linearity are noticeable (as is the case for the roasted barley data in Fig. 1). Even in these

<sup>3</sup> Of course, any buffer system can be overwhelmed if too much acid or base is added.

<sup>4</sup> As we discuss in more detail below,  $pH_i$  for a particular grain is largely independent of the mash thickness  $R$ .

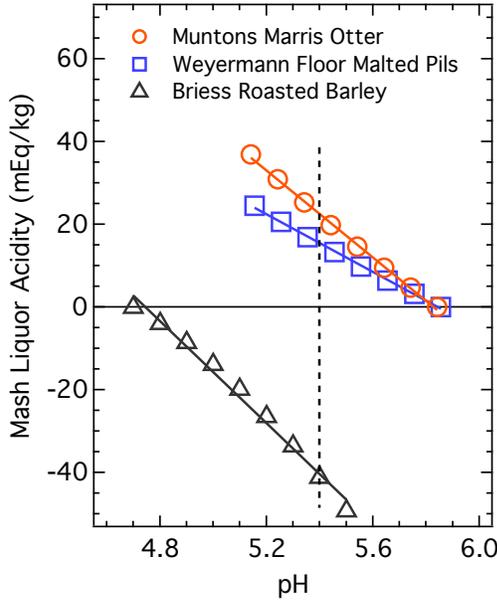


FIG. 1: Single-malt mash pH values vs mash liquor acidity, obtained from AJdL titration data on three different grains [5]. The data points (open symbols) are obtained from AJdL’s cubic fits to his experimental data. The straight lines through the symbols are our linear fits to the cubic-fit derived data points. The vertical dashed line indicates a typical mash-pH target of 5.4.

cases, though, the linear function is usually a reasonable approximation to the data.

This observation of near linearity leads to the definition of the buffering capacity  $B_i$  of a malt: the buffering capacity is simply the slope of the straight line that best fits the added acidity  $A^-$  vs resulting pH. Based on the fits to the three grains in Fig. 1, the buffering capacities are  $-51$ ,  $-34$  and  $-59$  mEq/kg for the Maris Otter, Pils, and Roasted Barley grains, respectively.<sup>5</sup>

With this property of a given malt we can estimate the pH for any given amount of acid added using

$$pH = pH_i + \frac{A^-}{B_i}. \quad (1)$$

For example, if we mash the Maris Otter malt of Fig. 1 using water with  $A^- = 20$  mEq/kg, then Eq. (1) tells us the resulting pH should be

$$pH = 5.85 - \frac{20}{51} = 5.46.$$

Notice this value is quite close to the pH indicated in Fig. 1 for Maris Otter when  $A^- = 20$  mEq/kg.

We are now ready to consider what happens when two different malts are mashed in distilled water. As we now describe,  $pH_G$  is determined by the condition of charge conservation. For the sake of this discussion we (i) imagine we initially have two individual distilled water mashes, one with malt 1 at  $pH_1$  and one with malt 2 at  $pH_2$ , and (ii) assume  $pH_1 < pH_2$ . Let’s say we now mix the two individual mashes, which produces a mash comprising both malts. As far as malt 1 is concerned malt 2 is a base, and as far as malt 2 is concerned malt 1 is an acid. Therefore malt 1 releases  $H^+$  ions which are then absorbed by malt 2. There is only one pH value where the number of  $H^+$  released by malt 1 equals the number of  $H^+$  absorbed by malt 2; this pH is  $pH_G$ . Of course, as  $pH_G$  reflects an equilibrium condition, this same  $pH_G$  will result if we simply start out with the grains mixed together before any water is added.

Using this idea of the conservation of charge, we can derive an equation that determines  $pH_G$  when any number of malts are mixed together. As  $B_i$  is the amount of charge  $Q_i$  per mass  $m_i$  of malt per pH change,<sup>6</sup> the total amount of charge taken up or released by a given malt as the pH changes from  $pH_i$  to  $pH_G$  is simply

$$Q_i = (pH_G - pH_i) B_i m_i.$$

In passing, we note  $Q_i > 0$  indicates a particular malt has taken up positive charge (in the form of  $H^+$ ). Conversely,  $Q_i < 0$  indicates the release of positive charge.<sup>7</sup> Because the sum of all charge released and consumed by all malts in a given mash must equal zero, we have

$$\sum_i (pH_G - pH_i) B_i m_i = 0, \quad (2)$$

which is readily solved for  $pH_G$  as

$$pH_G = \frac{\sum_i pH_i B_i m_i}{\sum_i B_i m_i}. \quad (3)$$

A slightly friendlier version of this equation is obtained by recognizing the fraction  $f_i$  of a given grain in any particular mash is simply

$$f_i = \frac{m_i}{\sum_i m_i},$$

which allows us to rewrite Eq. (3) as

$$pH_G = \frac{\sum_i pH_i B_i f_i}{\sum_i B_i f_i}. \quad (4)$$

With this equation we can readily predict  $pH_G$  when any number of malts (with given  $pH_i$  and  $B_i$  values) are mashed together in distilled water.

<sup>5</sup> In some sources the units utilized for  $B_i$  are mEq/(kg pH). However, as pH is not really a unit, we feel it is better to simply use mEq/kg for the units of buffering capacity.

<sup>6</sup> Mathematically,  $B_i = Q_i / (m_i \Delta pH)$ , where  $\Delta pH$  is the change in pH.

<sup>7</sup> Because  $Q_i$  and  $pH_G - pH_i$  have opposite signs,  $B_i$  is always a negative number.

Equation (4) is the basis for our experimental determination of  $B_i$  values. Let's say we have a mash made up of just two malts, malt 1 (a test malt, say) with fraction  $f_1$  and malt 2 (perhaps a fiducial malt) with fraction  $f_2$ . Then Eq. (4) can be written (using  $f_1 = 1 - f_2$ ) as

$$pH_G = \frac{pH_1 r (1 - f_2) + pH_2 f_2}{r (1 - f_2) + f_2}, \quad (5)$$

where

$$r = \frac{B_1}{B_2} \quad (6)$$

is the ratio of the buffering capacity of malt 1 to that of malt 2. If a set of measurements of  $pH_G$  as a function of  $f_2$  is made, then the data can be least-squares analyzed in order to determine best-fit values of  $pH_1$ ,  $pH_2$ , and  $r$ . If one has knowledge of the fiducial-grain buffering capacity  $B_2$ , then the unknown buffering capacity  $B_1$  can be inferred from  $B_2$  and the value of  $r$  determined from the data. As there are three unknown parameters in Eq. 5, at least three data points are required to determine values for all of them. As mentioned above, our first protocol is distinguished by the minimum of three  $f_2$  values, while our second protocol increases the number of  $f_2$  values to six.

## 4. RESULTS AND ANALYSIS

### 4.1. $pH_i$ and relative $B_i$ values

The data obtained using our first protocol are summarized in Fig. 2. Each panel plots  $pH_i$  for a test grain,  $pH_i$  for a fiducial grain, and the  $pH_G$  for a 50/50 mixture of the two grains. For most experiments data were obtained at mash thicknesses of 2.5, 4.0, and 8.0 L/kg. Data at 2.5 L/kg for 100% Briess Victory and Crisp Amber were unobtainable, as both of these grains absorbed nearly all of the mash liquor, turning these two attempted mashes into solid bricks.

Our very first data set is shown in the bottom-left panel, which is a comparison of the two fiducial grains used in all subsequent experiments, Briess Caramel L10 and L120. Even without any analysis, these data are quite revealing. First, we see that pH is rather independent of mash thickness (which is more-or-less true for all malts we have measured). Second, because the 50/50-mixture mashes have pH values closer to the L120 pH values, we immediately know that the buffering capacity of Briess L120 malt is larger than that of Briess L10.

As we have used both L10 and L120 malts as fiducial malts, we require a reliable value for the buffering-capacity ratio  $B_{L120}/B_{L10}$  for these two malts. From our initial data shown in Fig. 2 we initially inferred a buffering-capacity ratio  $B_{L120}/B_{L10} = 1.97$ . However, data later collected on several malts using our second protocol suggest this ratio is a bit high. We therefore made

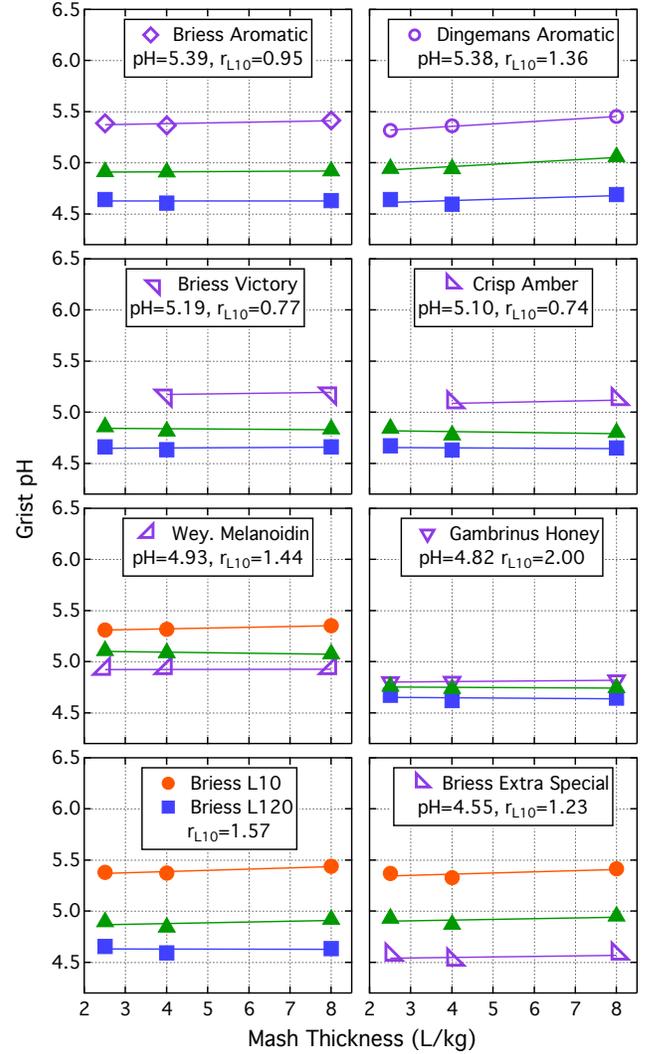


FIG. 2: Grist pH vs mash thickness for fiducial-grain fractions of 0, 0.5, and 1.0. Data were obtained for mash thicknesses of 2.5, 4.0, and 8.0 L/kg. The green triangles are the data for 50/50 mixed mashes. The pH values reported in the legends are averages from all data obtained on a given grain (including any data obtained using our second protocol). Here  $r_{L10} = B_i/B_{L10}$ , where  $B_i$  and  $B_{L10}$  are the test-grain and Briess-Caramel-L10 buffering capacities, respectively.

another direct comparison of Briess L10 and L120 using our second protocol. These data (discussed in detail below) yield  $B_{L120}/B_{L10} = 1.57$ . Owing to (i) the L10-L120 comparison in Fig 2 being the first data we collected (thus likely making those data relatively less precise) and (ii) our belief that our second protocol is generally a more reliable method for determining buffering-capacity ratios, we have used  $B_{L120}/B_{L10} = 1.57$  in order to determine the buffering capacity ratio  $r_{L10} = B_i/B_{L10}$  of all test malts with respect to Briess Caramel L10.

There are other observations of the data in Fig. 2 worth noting. First, Briess and Dingemans Aromatic malts have fairly similar properties: their pH values are nearly

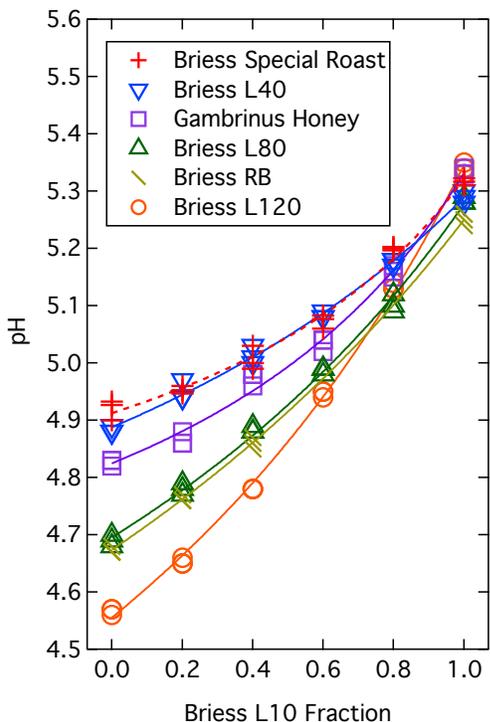


FIG. 3: Grist pH of various grains vs Briess Caramel L10 fraction. All malts labeled Briess LX are Briess Caramel malts, where X represents the color of the malt in °L.

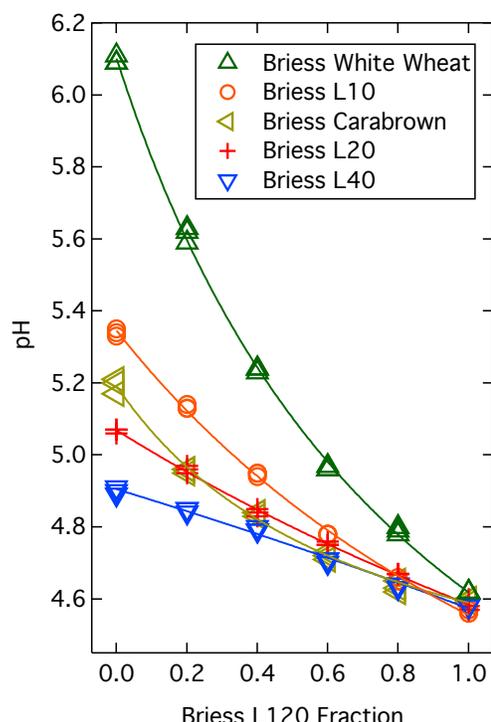


FIG. 4: Grist pH of various grains vs Briess Caramel L120 fraction. All malts labeled Briess LX are Briess Caramel malts, where X represents the color of the malt in °L.

identical, and their buffering capacities are not wildly different. Second, Briess Victory and Crisp Amber – two examples of biscuit malt – have very close values of  $pH_i$  and essentially identical values of  $B_i$ . Finally, we point out our comparison of Gambrinus Honey malt with L120 was ill advised, due to their similar values of pH when mashed in distilled water.<sup>8</sup> Using our second protocol we compared Gambrinus Honey malt with L10, which produced the value of  $r_{L10}$  shown in the legend.

Figures 3 through 5 present data collected using our second protocol. Figure 3 plots pH data for mashes consisting of test grains mixed with Briess Caramel L10, while Figs. 4 and 5 plot pH values mixtures with Caramel L120. The curve through each data set is a least-squares fit of the data to Eq. 5, from which we deduce  $pH_i$  for each test and fiducial grain, as well as the buffering-capacity ratio  $r_{L10}$  or  $r_{L120}$ . The orange circles in Figs. 3 and 4 represent the same data set obtained from mixtures of Briess Caramel L10 and L120. As discussed above, these data yield the buffering capacity ratio  $B_{L120}/B_{L10} = 1.57$ , from which we have deduced  $r_{L10}$  for test grains that have been mashed with Briess L120. The results for  $pH_i$  and  $r_{L10}$  for all grains are presented in Table I.

We point out a few features regarding the data in these

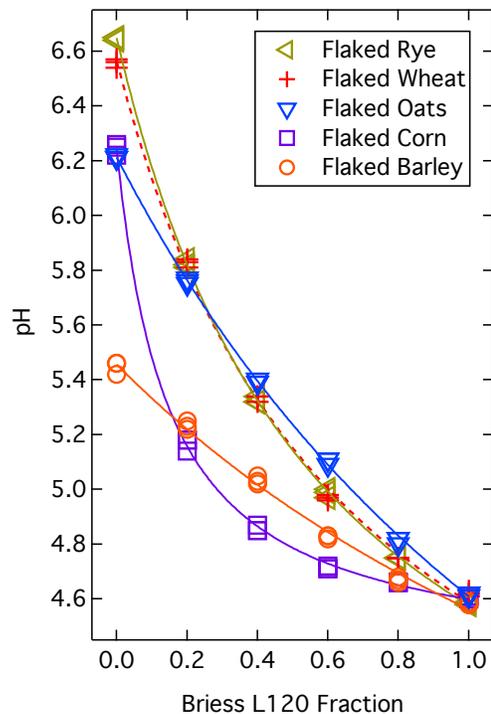


FIG. 5: Grist pH of flaked grains vs Briess Caramel L120 fraction.

<sup>8</sup> Based on its color, Honey malt has an unexpectedly low pH; why this is the case is discussed in detail below.

TABLE I: Experimental results for  $pH_i$ ,  $r_{L10}$ , and  $B_i$  of grains measured in this study. As indicated,  $r_{L10}$  and (hence)  $B_i$  of Crisp Brown malt were not determined.

Grain	Color (°L)	$pH_i$	$r_{L10}$	$-B_i$ (mEq/kg)
Flaked Rye	3	6.65	0.59	29.8
Flaked Wheat	2	6.57	0.63	28.2
Flaked Corn	1	6.24	0.20	9.6
Flaked Oats	2	6.21	1.01	48.2
Flaked Barley	1	5.46	1.09	51.8
Briess White Wheat	2	6.10	0.48	36.4
Dingemans Aromatic	19	5.38	1.36	64.7
Briess Aromatic	20	5.39	0.95	45.5
Briess Victory	28	5.19	0.77	36.8
Crisp Amber	29	5.10	0.74	35.5
Briess Carabrown	55	5.19	0.66	31.4
Crisp Brown <sup>a</sup>	65	4.97		
Gambrinus Honey	25	4.82	2.00	95.4
Weyermann Melanoidin	27	4.93	1.44	68.9
Briess Special Roast	40	4.91	2.08	99.1
Briess Extra Special	130	4.55	1.23	58.8
Briess Caramel L10	10	5.34	1.00	47.7
Briess Caramel L20	20	5.07	1.20	59.7
Briess Caramel L40	40	4.90	1.51	72.2
Briess Caramel L80	80	4.70	1.52	72.3
Briess Caramel L120	120	4.63	1.57	75.0
Briess Roasted Barley	300	4.67	1.41	67.5

<sup>a</sup>We measured the pH of this malt before embarking on our buffering-capacity experiments.

three figures and the results in Table I. First, that nearly all of the the curves are concave up is a result of the grain with the lower pH having a relatively higher buffering capacity. The only exception to this is the slightly concave downward data from mixtures of Briess L40 and Briess L120, which indicates the buffering capacity of L40 is slightly larger than that of L120 ( $r_{L120} = 1.10$ ). This result is slightly at odds with the data from mixtures of Briess L10 and Briess L40, which suggest the buffering capacity of L40 is ever so slightly smaller than that of L120 ( $r_{L120} = 0.96$ ). We also note only four data points are shown for mixtures of Briess Roasted Barley and Briess L10; data at L10 fractions of 0.6 and 0.8 were collected, but were judged to be outliers, and so are not shown. Perhaps most surprising are the results for flaked rye, wheat, and corn, all of which have remarkably high values of  $pH_i$  and low values of  $B_i$  (see Table I). These data suggest the hot-roller mill processing of rye and wheat does not develop the acidity that occurs when these grains undergoes traditional malting. The spectacular curvature of pH vs L120 fraction for flaked corn is due to its extremely low buffering capacity, which is  $\sim 14\%$  of the buffering capacity of the L120 malt.

An ancillary bonus of our study is an extensive set of measurements of  $pH_i$  for Briess Caramel L10 and L120, which are displayed in Fig. 6. As these data illustrate, the mash thickness is rather inconsequential as far as  $pH_i$  is concerned. The data do suggest a slightly lower

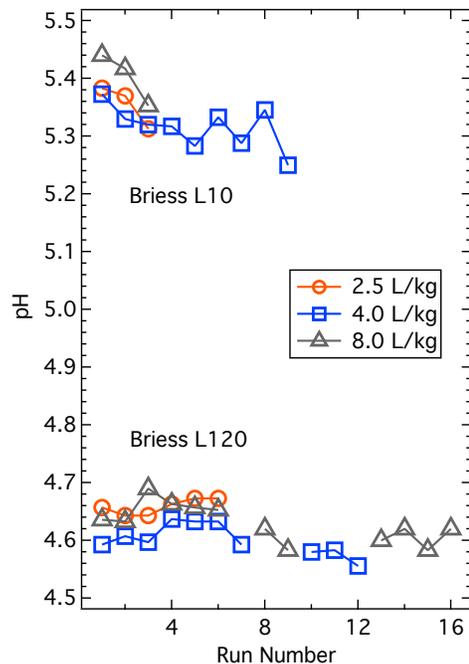


FIG. 6: Measured  $pH_i$  values for Briess Caramel L10 and L120. Lines between data points are guides to the eye.

$pH_i$  value at 4.0 L/kg compared to the other two mash thicknesses, but even if this is true, the pH difference is well under 0.1, and the difference is approximately of the same size as typical fluctuations in the measurements. From these data we extract  $pH_{L10} = 5.34 \pm 0.05$  and  $pH_{L120} = 4.63 \pm 0.03$ . Our observed variations in pH are similar to those in measurements of Briess caramel malts made by Geurts [8].

#### 4.2. Absolute $B_i$ Values

While values of  $pH_i$  and  $r_{L10}$  are sufficient for predicting the distilled water pH for any mixture of grains, the  $r_{L10}$  values are insufficient for predicting pH changes induced by acid (or mineral) additions. This is because the average buffering capacity  $\sum_i f_i B_i$  of the grist is required to know exactly how a given acid addition will change the pH of the mash. To this end we made measurements on a spectrum of Briess Caramel malts, as this was the most widely measured group of malts in prior studies [1, 3, 5, 7–9]. Our initial thinking was that these prior data would allow us to straightforwardly determine the value of  $B_i$  for Briess Caramel L10, which would in turn allow us to determine  $B_i$  values for all of our measured malts.

As it turns out, the final gameplan was not as simple as we initially envisioned. This is because there are systematic differences among the sets of  $B_i$  values derived

from the data of the various researchers.<sup>9</sup> This is evident when groups of  $B_i$  values from different researchers are compared. Such data are displayed in Fig. 7(b) and parts (b), (e) and (h) of Fig. 8. From the data displayed in these graphs we can conclude the  $B_i$  values of Troester are systematically the lowest, followed in order by values determined from the data of Bies, deLange, and Walts. The data of Geurts, while appearing to be self consistent within a given malt group, do not have a clear systematic relationship with the data from other researchers.

To what can we attribute these systematic differences? There are three possibilities, all of which may have some contribution. First, a systematic error in the strength of the acid/base solution used in titrating the mash would necessarily lead to a systematic multiplicative error in the assessed values of  $B_i$ . Second, it is possible that differences in malt grinding might lead to variation in the measured buffering capacity. Indeed, a dependence on malt preparation was observed by KT, who made measurements on mashes with not only pulverized grains but also roller-mill crushed grains [1]. KT's data indicate pulverized grains have a buffering capacity that is  $\sim 1.4$  times that of crushed grains. As the grains in all the experiments discussed here appear to have been at least finely ground, the contribution from this effect is likely minimal, but is perhaps worthy of future experimental investigation. Third, it is possible that mash thickness might affect the buffering capacity of a given grain. Again, KT's measurements indicate buffering capacity increases by a factor of  $\sim 1.25$  as the mash thickness increases from 2 L/kg to 5 L/kg. This effect might account for some of the systematic differences among researchers.

As nearly all researchers have measured at least two different Caramel malts manufactured by Briess, we chose to use these data to normalize  $B_i$  values among all researchers. This, of course, requires a choice of a particular researcher's data as the standard. Impressed by deLange's careful, sophisticated approach to his titration protocol [6], we have chosen his measurements as this standard. We determined the multiplicative factor to apply to each other researcher's  $B_i$  values (as well as our  $r_{L10}$  values) by adjusting each researcher's Briess Caramel malt  $B_i$  values by a single multiplier until the minimum average standard deviation was achieved across all Briess Caramel malt data. The multiplicative factors that resulted from this process are 1.62, 1.42, and 0.86 for the data of Troester, Bies, and Walts, respectively.<sup>10</sup> For our data this process sets the value  $B_i = -47.7$  mEq/kg for Briess L10, from which we determine  $B_i$  for all of our

measured malts.

When we apply these multiplicative factors to all other data by each researcher, the  $B_i$  values are found to align nicely for all malts types, as we show in parts (c), (f), and (i) of Fig. 8. Quite clearly,  $B_i$  values for all grain types are much better aligned after our normalization process. Perhaps most striking is the much smaller variation in  $B_i$  values for Briess Roasted Barley (RB), which has been measured by all researchers. Before the normalization the standard deviation of the RB data of Bies, KT, Walts, and deLange was 19.9 mEq/kg; after normalization the standard deviation dropped dramatically to 6.3 mEq/kg. We emphasize only Briess Caramel malts were used to determine the normalization factors. The good agreement across all grain types confirms the validity of our procedure.

## 5. DISCUSSION

### 5.1. Comparison of Measured $pH_i$ Values

Our measured values of  $pH_i$  are completely in line with values from other researchers. This result is illustrated in Figs. 7 and 8. Perhaps the best quantitative comparison is provided by the data in Fig. 7(a), which shows  $pH_i$  for Briess crystal malts measured by us and others.<sup>11</sup> As shown there, versus the logarithm of the malt color we find a decrease in  $pH_i$  that is quite quite linear, as is also observed by Geurts [8]. All other researchers observe a general decrease in pH with increasing color, even if their data are not monotonic.

A second quantitative comparison is afforded by measurements of 300 °L Briess RB. Data from all researchers for this grain are plotted in Fig. 8(g).<sup>12</sup> All measured pH values for this grain fall between 4.62 and 4.75; our value is 4.67. Taken together, the six measurements on Briess RB can be summarized by a pH value of  $4.69 \pm 0.05$ .

### 5.2. Trends in $pH_i$ and $B_i$ Values

So what can we learn from the totality of  $pH_i$  and  $B_i$  values? Here we discuss trends in both of these quantities for each distinct category of grain. As we shall see, the behavior of (i)  $pH_i$  and  $B_i$  vs malt color and (ii)  $B_i$  vs  $pH_i$  provide insight into the properties of different types of malt.

As is well known, different malt products largely result from differences in the processing steps used in their manufacture; we thus naturally focus on these differences in our discussion. All barley seed that eventually ends up

<sup>9</sup> Where titration data have been reported as the amount of acid/base added vs pH change, we have derived  $B_i$  by assuming a linear relationship between pH and amount of acid/base added (as discussed above).

<sup>10</sup> For the data of Geurts we have determined multiplicative factors of 1.08 for wheat and crystal malts, 1.33 for dark roasted malts, and 1.90 for base and noncrystal specialty malts.

<sup>11</sup> All values were either measured near room temperature or corrected to reflect room-temperature values.

<sup>12</sup> Briess RB is the only 300 °L grain represented in this graph.

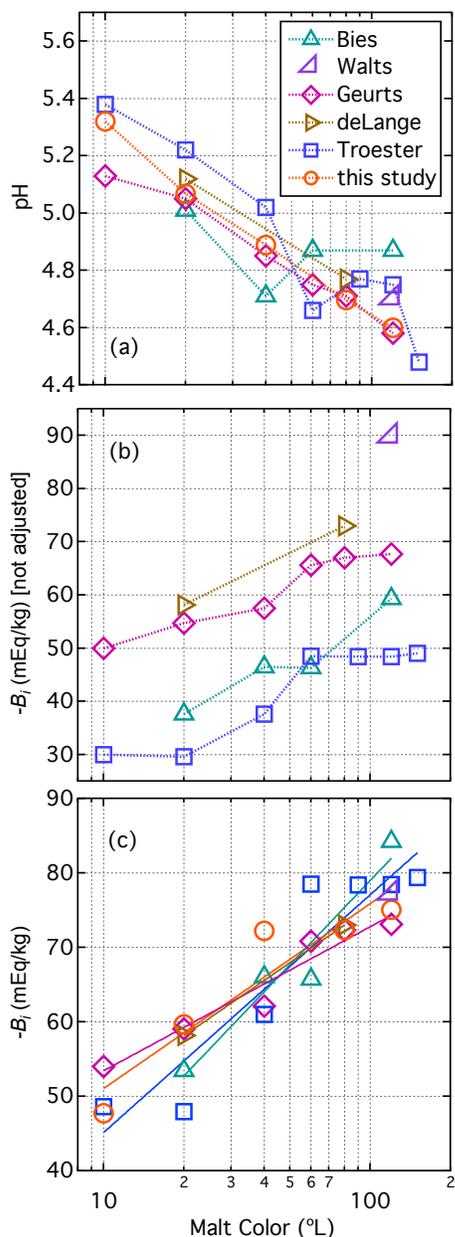


FIG. 7: Briess Caramel malt  $pH_i$  and  $B_i$  values from our data as well as measurements reported in the literature. Dotted lines in (a) and (b) are guides to the eye. Straight lines in (c) are least-squares fits. See text for further details.

as malt undergoes two initial processing steps. First, the grain is steeped in water to increase its moisture content. It then undergoes a germination phase in which the seed begins to grow. Malt at this stage is known as green malt. After hydration and germination all malt undergoes further processing at elevated temperatures in either a kiln or roaster, with the path through parameter space defined by time, temperature, and moisture content (largely) determining the state of the final product. The myriad of possible paths allow the maltster to produce

the large variety of products available to the brewer.

As will become obvious from the  $pH_i$  and  $B_i$  data, malted barley naturally fall into four distinct categories: (i) dark roasted grains, (ii) caramel/crystal/dextrin malts, (iii) base malts, and (iv) noncrystal specialty malts. We now discuss in turn the  $pH_i$  and  $B_i$  properties of grains in each of these categories. We also discuss the properties of wheat malt and flaked grains.

### 5.2.1. Dark Roasted Grains

We start with dark roasted grains as the results for this category are the simplest: both the  $pH_i$  and  $B_i$  values are rather independent of the color of the grain (see Fig. 8). With only two exceptions (Briess Dark Chocolate and Briess Black Malt [8]), all  $pH_i$  values lie between 4.5 and 4.8. Overall, these malts are among those with the lowest  $pH_i$  values. Similarly,  $B_i$  values exhibit a fairly narrow range, between  $-60$  and  $-80$  mEq/kg. These values are towards the high end of the range of all malts. The data can be characterized by  $pH_i = 4.64 \pm 0.13$  and  $B_i = -68.7 \pm 6.6$  mEq/kg [as indicated in Fig. 9(b)]. The data from Geurts for the two darkest Briess malts weakly suggest some dependence of  $pH_i$  on malt color, although this observation is unique to this particular study [8].

A plot of  $B_i$  vs  $pH_i$  for these malts [see Fig. 9(a)] exhibits a clear lack of correlation between these two quantities, especially if the two darkest grains measured by Geurts are ignored.

Dark roasted malt is produced from green malt by processing in a roaster: the temperature is slowly increased, typically reaching a final temperature in the range of 350 to 450 °F [12]. Roasting time is typically between 2 and 4 hours [13]. Higher temperatures and/or longer processing times result in darker grains. Because roasted barley (which is not malted before being roasted) exhibits the same  $pH_i$  and  $B_i$  values as dark roasted malt, we can infer the initial malting stages are not crucial to properties of the end product. Evidently, the acidity of dark roasted grains is largely developed in the roaster by the time a color of 300 °L is reached.<sup>13</sup>

### 5.2.2. Caramel/Crystal/Dextrin Malts

We have grouped caramel, crystal, and dextrin (CCD) malts together owing to their properties being characterized by common trends. While the case can be made for the distinctness of these three malt types, there is definite overlap among them, especially insofar as all provide unfermentable dextrins and fermentable sugars to the wort without the need for an enzymatic mash. The

<sup>13</sup> An excellent review of the chemistry involved in the production of dark roasted malts is provided by [14].

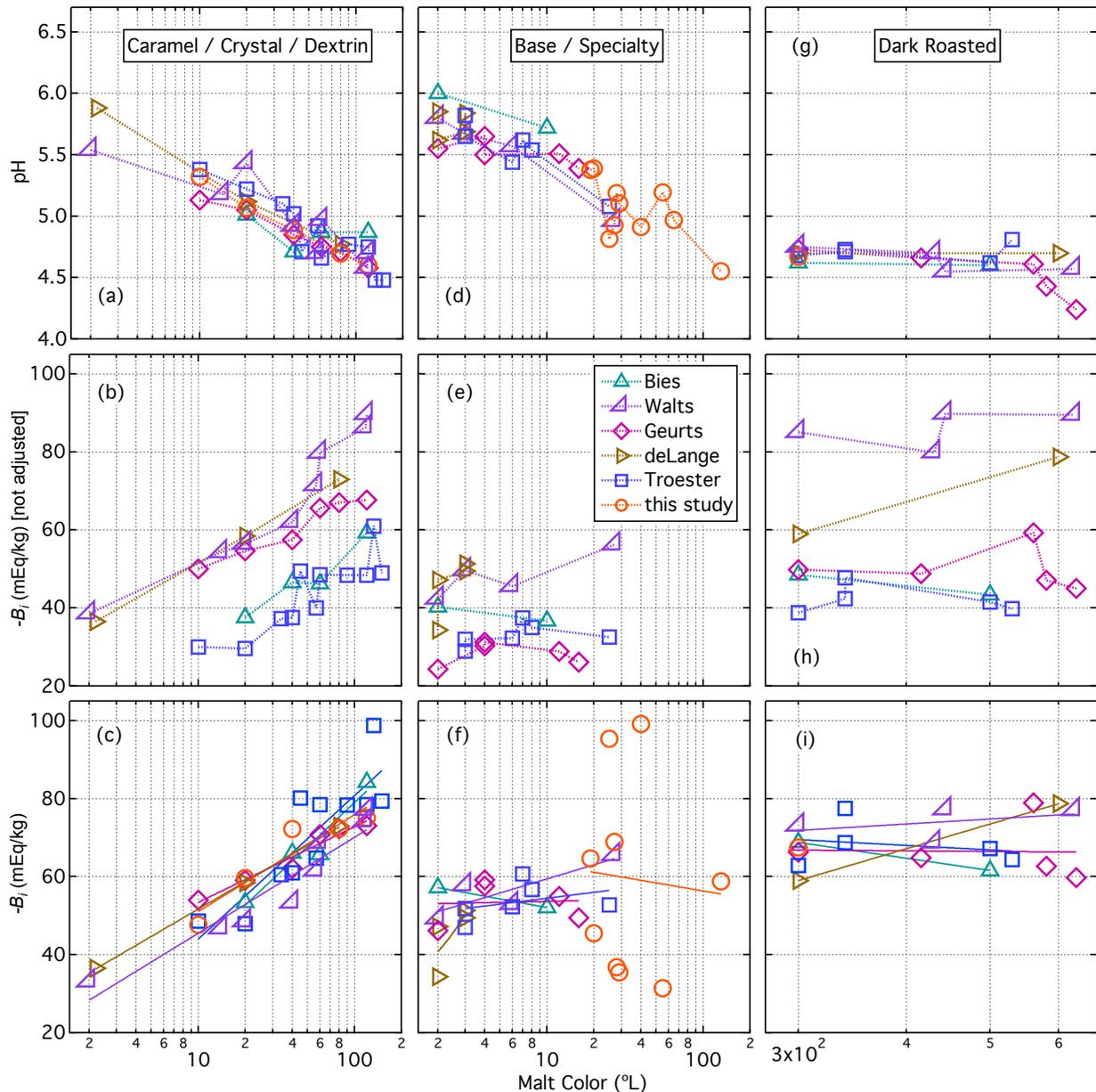


FIG. 8:  $pH_i$  and  $B_i$  values from our data as well as measurements reported in the literature. Dotted lines are guides to the eye. Straight lines are least-squares fits. See text for further details.

lightest of the group are known as dextrin malts, which are touted as providing body and head retention, but very little in the way of flavor. Some dextrin malts have glassy interiors (Briess Carapils is one such example), while others have interiors that are quite mealy (Weyermann Carafoam, for example). Some examples (such as Dingemans Cara 8) appear to be no more than lightly colored crystal malt.<sup>14</sup> The term caramel malt encompasses

malts that provide not only body but also caramel-like character. Some have a glassy interior (the true crystal malts, such as those from Briess), while others have a mealy interior (caramel malts from Cargill, for example).<sup>15</sup>

<sup>14</sup> Dingemans Cara 8 was previously marketed as dextrine malt.

<sup>15</sup> Curiously, Briess is careful to point out that Carapils is not a crystal malt, even though it has a glassy interior. The reason for Briess' distinction is not readily apparent, as the maltster does not share the exact steps in the processing of any of their specialty malts.

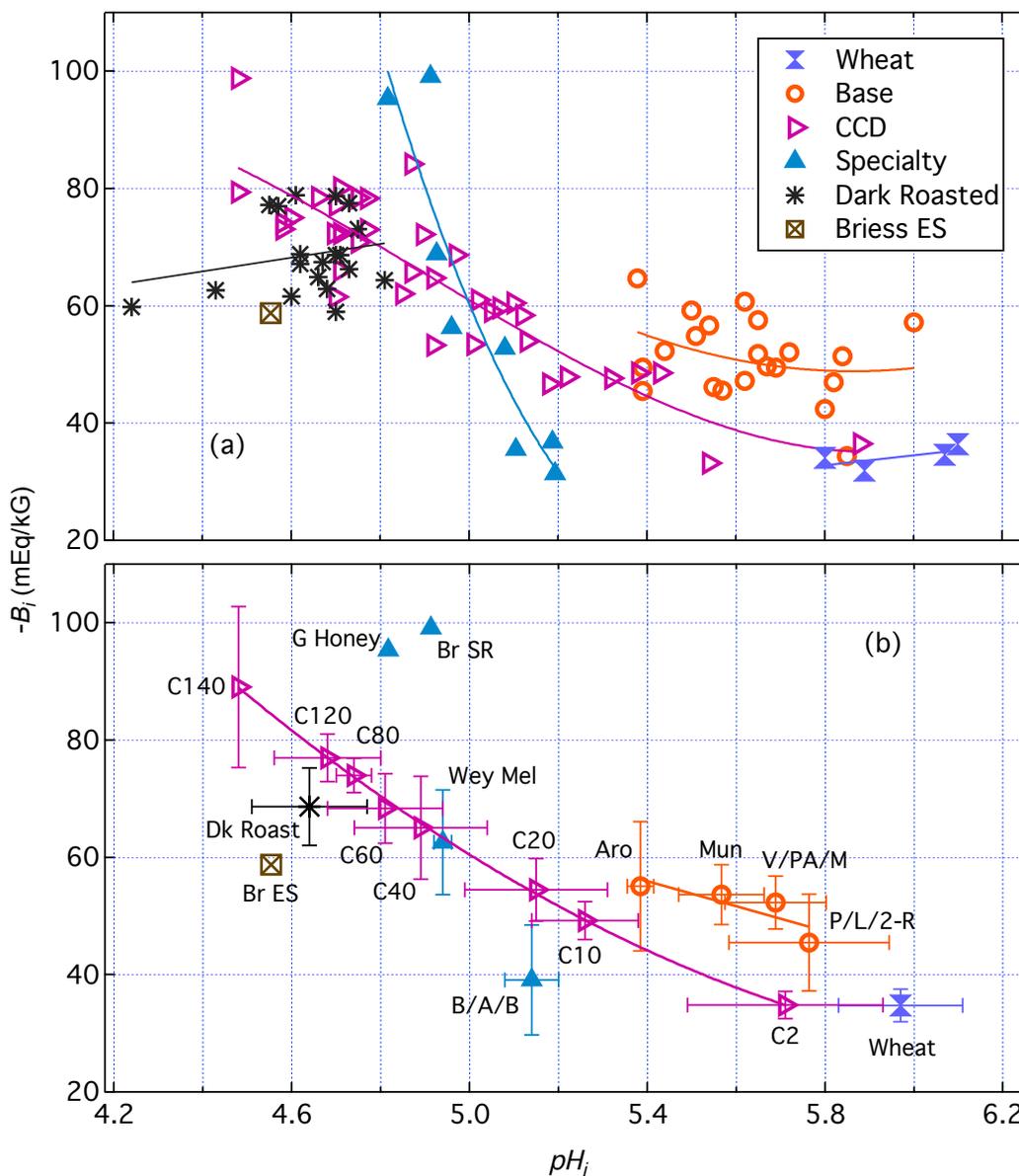


FIG. 9:  $B_i$  vs  $pH_i$  values from our data as well as measurements reported in the literature. In (a) individual data points are plotted. In (b) average and standard deviations of values from malts in particular categories are indicated, as well as individual data points for several malts (Gambrinus Honey, Briess Special Roast, and Briess Extra Special). Solid lines are guides to the eye. See text for further details.

In contrast to dark roasted malts, the properties of malts in the CCD group are highly correlated with malt color. As is clearly illustrated in Fig. 8, these malts exhibit (i) a striking decrease in  $pH_i$  and (ii) an equally striking increase in  $-B_i$  with increasing malt color. The lightest malts (Weyermann Carafoam [5] and Crisp Dextrin [9]) have  $pH_i$  values in the range of 5.5 to 5.9, while the darkest malts typically exhibit values as low as 4.5. With increasing malt color the values of  $B_i$  trend from  $\sim -35$  to  $-80$  mEq/kg, with Weyermann Caraaroma [1] coming in at an exceptional  $-100$  mEq/kg.

A plot of  $B_i$  vs  $pH_i$  for these malts [see Fig. 9(a)]

directly shows the inverse correlation of  $-B_i$  and  $pH_i$ : the buffering capacity magnitude  $-B_i$  decreases as  $pH_i$  increases. As Fig. 9(b) demonstrates, if the CCD malts are grouped by color,<sup>16</sup> then the average values of  $B_i$  vs average values of  $pH_i$  follow a smooth curve with a clear decrease (increase) in  $pH_i$  ( $-B_i$ ) as the color increases.

<sup>16</sup> The designation C40 (for example) includes all crystal malt that are closer to 40 °L than any of the other color designations on the graph.

As is the case for dark roasted malts, CCD malts are usually produced in a roaster.<sup>17</sup> The essential character of true crystal malts – the hard, glassy, candy-like interior – arises from a combination of (i) internal starch saccharification during a prolonged rest near 150 °F while the malt is still moisture laden and (ii) roasting at a finishing temperature in the range of 250 - 320 °F [15]. As the color of a particular caramel malt is developed during roasting, it is clear that compounds responsible for the  $pH_i$  and  $B_i$  values of these malts are also developed during this stage of processing. The darkest crystal malts have  $pH_i$  and  $B_i$  values that overlap significantly with dark roasted malts, even though crystal-malt color tops out at  $\sim 150$  °L. For example (as is evident in Fig. 3 and Table I) the  $pH_i$  and  $B_i$  values for Briess Caramel 80 and Briess Roasted Barley are nearly identical. The uniformity of the  $pH_i$  and  $B_i$  results across the spectrum of maltsters represented (Briess, Weyermann, Simpsons, Crisp, and Cargill) is likely due to the utilization of rather similar steps in CCD production [16].

### 5.2.3. Base Malts

There is not a sharp demarcation between base malts and noncrystal specialty malts (discussed in the next section). This is partially due to the fact that one cannot readily identify a single distinguishing factor that determines whether a particular malt belongs in one category or the other. One might argue that diastatic power is the distinguishing parameter, with base grains being able to at least convert their own starches in the mashing process. In this case Gambrinus Honey malt would qualify as a base malt even though it is predominately (if not exclusively) used as a specialty grain [17]. In addition, there are some malted grains that are sometimes used as a base malt and sometimes used as a specialty malt. For example, in some beers Munich is a true base grain (when it provides substantial gravity and drives the character of the beer), while in other beers it can justifiably be considered a specialty malt (when it is used in quantities typical of a specialty grain to provided nuance to the beer’s flavor). In our discussion to follow we do offer a distinction; perhaps not surprisingly, our distinction is partially based on a combination of  $pH_i$  and  $B_i$ .

In order to make sense of pH and buffering capacity values of both base and noncrystal specialty malts, it is helpful to consider both the germination and kilning/roasting processes [10, 12, 15, 18–27]. Differences in these processes among major groups of malt types are indicated in Table II. The lightest (in color) of the base malts are pils/lager/2-row malts. Grains that become

these malts endure processing that is as minimal as is possible: (i) germination occurs at the lowest temperatures with the least amount of water uptake, (ii) kilning is characterized by relatively low humidity in the drying phases, and (iii) curing occurs at the lowest possible temperatures.<sup>18</sup> The second lightest malts – Vienna/pale ale/mild malts – differ in their processing (compared to the lightest malts) by having a higher curing temperature, which results in the development of slightly more melanoidins and other Maillard-reaction products, and thus slightly more color and malt character. The intense malt character of Munich and aromatic malts is due to a combination of processing differences: (i) germination occurs at relatively higher temperature and moisture content (which enhance the development of melanoidin precursors), (ii) during the drying phases the grains are kept at relatively high moisture content (which further promotes melanoidin precursor development), and (iii) curing takes place at higher temperatures yet. The difference between aromatic and Munich malts largely lies in the curing phase; as Table II indicates, aromatic malts are typically cured at temperatures 10 to 15 °F higher than Munich malts.

The values of  $pH_i$  and  $B_i$  for malts ranging from pils/lager/2-row to aromatic, which are indicated by the orange circles in Fig. 9(a), lead us to classify all of these types as base malts. The one potentially questionable type is aromatic malt.<sup>19</sup> Although aromatic malt rarely composes a large fraction of a beer’s grist, the  $pH_i$  and  $B_i$  values are fairly close to values for Munich malts. In addition, aromatic malts typically have just enough diastatic power to be able to convert themselves.<sup>20</sup> As Fig. 9(a) shows, for the base malts  $pH_i$  values range from just under 5.4 to just above 5.8, (with one outlier at 6.0), while  $B_i$  values are typically between 40 and 60 mEq/kg. The solid-line fit to these data show a slight correlation of  $pH_i$  and  $B_i$ .

Further insight into the properties of these four base-malt categories is provided by the average values of  $pH_i$  and  $B_i$  that are plotted as orange circles in Fig. 9(b).

<sup>17</sup> Some caramel malts are produced in kilns rather than roasters. Differences that arise due to kilning vs roasting are discussed in [15] and [16].

<sup>18</sup> Malt kilning is typically characterized by three distinct phases: (i) The first stage is free drying (also known as withering) in which moisture is driven from the grain at relatively low temperature. The moisture content of the grain typically drops from  $\sim 45\%$  to  $\sim 24\%$  during this stage. (ii) The second stage is known as forced drying, in which the grain temperature rises as the moisture further drops to  $\sim 10\%$ . (iii) The third stage is known as the curing stage, in which the higher temperatures develop melanoidins and other Maillard-reaction products from precursors that are formed during germination and earlier stages of kilning [15, 18].

<sup>19</sup> In Fig. 9 the three orange-circle data points with pH values slightly less than 5.4 are from aromatic malts (from Briess and Dingemans).

<sup>20</sup> Briess and Dingemans Aromatic malts are reported to have diastatic powers of 20 and 30 °Linter, respectively. The rule-of-thumb minimum for self-conversion is often taken to be 30 °Linter.

TABLE II: Typical processing details of base and noncrystal specialty malts. Here T represents temperature, and H represents humidity.

Malt	Typical Color (°L)	Germination features	Moisture content while drying	Curing T (°F)
Pils/Lager/2-Row	1.4 - 1.8	low T, low H	low	176 - 185
Vienna/Pale Ale/Mild	2 - 5	low T, low H	low	195 - 215
Munich	6 - 12	high T, high H	high	212 - 221
Aromatic	17 - 21	high T, high H	high	220 - 239
Biscuit/Amber/Brown	20 - 75	low T, low H	low	280 - 350
Melanoidin/Honey/Brumalt	20 - 30	high T, high H, O <sub>2</sub> restricted	high	195 - 221

For these malts increased melanoidin development is correlated with both  $pH_i$  and  $B_i$ ; the correlation with  $pH_i$  appears to be the stronger of the two.

#### 5.2.4. Noncrystal Specialty Malts

We now move on to noncrystal specialty malts. Many of these malts fall into one of two categories: (i) Biscuit/Amber/Brown or (ii) Melanoidin/Honey/Brumalt. There are, however, a number of noncrystal specialty malts made by various manufacturers that do not clearly fall into either of these categories. An example is Briess Extra Special, which we have measured (see Fig. 2) and discuss below.

Malts designated biscuit, amber (Briess Victory is perhaps the most ubiquitous example), and brown are processed exactly like the lowest color base malts aside from one crucial difference: as indicated in Table II, curing temperatures typically range from 280 to 350 °F, well above the maximum curing temperatures of *any* base malts [12, 23]. Several manufacturers (Crisp, Fawcett, and Bairds, e.g.) produce both amber and brown malts; the brown malt is invariably the darker malt, and so is cured at higher temperatures or for longer times than the corresponding amber malt. It should be no surprise that the high-temperature curing stage is responsible for the well known toasty/bread-crust notes of these malts.<sup>21,22</sup>

So what is the impact of the high curing temperatures on  $pH_i$  and  $B_i$ ? As the point labeled B/A/B in Fig. 9(b) shows, these malts have a significantly lower  $pH_i$  than any of the base malts.<sup>23</sup> The buffering capacity  $B_i$  of these malts also tends to be lower than the base malts:

Briess Victory and Crisp Amber have  $B_i$  values close to  $-36$  mEq/kg (see Table I). Our results of  $pH_i = 5.19$  and  $B_i = -31.4$  mEq/kg for Briess Carabrown malt clearly place it in this category, despite the presence of “Cara” in its name. Consistent with our assessment, Briess states “Carabrown malt was developed on the light side of the brown malt style in order to retain some residual sweetness while still delivering an assortment of lightly toasted flavors.” [28] Biscuit malt measured by KT has  $pH_i = 5.08$  and  $B_i = -52.8$  mEq/kg [1]. While this value of  $pH_i$  is consistent with other malts in this category, the  $B_i$  value is significantly larger in magnitude than these other three malts. Unfortunately KT did not know the manufacturer of this malt, and so further assessment of this difference is not possible.

Malts referred to as Melanoidin (Weyermann’s product is perhaps the most common), Honey (a Gambrinus Malting product), and Brumalt (a generic German term for these malts) have the most extensive processing of any noncrystal malts [12, 19]. They are produced much like Munich and aromatic malts, but with one additional step: near the end of germination the malt is oxygen deprived at temperatures close to 120 °F. This step encourages the development of even more melanoidin precursors. These conditions are also prime for encouraging lactobacillus bacteria that is naturally present on the grains to produce lactic acid.

The results of this extra germination step are evident in Fig. 9(b), which displays results for both Weyermann Melanoidin and Gambrinus Honey malts. Both of these malts exhibit  $pH_i$  values in the range of 4.8 to 5.0, well below the values for any of the Munich or aromatic malts. It seems likely this sharp drop in pH is at least partially due to the action of lactobacillus bacteria during the last stage of germination.

Although Briess does not advertise their Special Roast malt as a Melanoidin type of malt, its  $pH_i$  and  $B_i$  values place it very close to Gambrinus Honey malt. Briess characterizes this malt with the statement “Proprietary malting process intensifies toasty and biscuity flavors, develops noticeable bran flake notes, and creates its distinguishing bold sourdough/tangy flavor.” [28] The sourdough/tangy flavor is not inconsistent with the low  $pH_i$  value for this malt. However, Special Roast has a dry-toast character that both Melanoidin and Honey malt

<sup>21</sup> Apparently the high curing temperature is also responsible for the ability of these malts to absorb more water than other malt, as discussed above.

<sup>22</sup> In addition, the high curing temperatures destroy alpha and beta amylase enzymes, so these malts cannot convert themselves in the mash.

<sup>23</sup> This point in Fig. 9(b) is the average of the four lowest-buffering-capacity specialty-malt points in (a) of Fig. 9. These malts are Crisp Amber, Briess Victory, Briess Carabrown, and biscuit malt of unknown origin.

lack. We note the buffering capacities of Honey and Special Roast malts are among the highest of all malts that have been measured.

As can be ascertained from Fig. 9, our results for Briess Extra Special (ES) malt are not consistent with any malt category we have so far discussed. While it is closest to malts in the dark-roasted category, its color is only 130 °L, much less than any of the dark-roasted grains. Briess gives some insight into this malt. They state “A proprietary drum roasting process develops both caramel and dry roasted flavors.” [28] Additionally, in a presentation at the Pacific Northwest Homebrewers Conference 2017, Aaron Hyde of Briess states “ES has a shorter starch conversion in roaster prior to roasting. This yields its unique flavor profile, with some biscuity notes, but also fig/prunes/dates compared with Caramel malts.” [29] It seems this malt is designed to compete with Dingemans Special B. We note Patagonia malting makes a malt designated Especial with a color of 140 °L. We judge all three of these malts to have very similar flavor profiles. It would thus be interesting to make measurements on both Special B and the Patagonia Especial.

#### 5.2.5. Wheat

The malting process for pale wheat malt does not substantially differ from that for the palest barley malts [12, 26, 30]. It is thus no surprise that  $pH_i$  and  $B_i$  values are close to those for pilsner/lager/2-row malts, as can be seen in Fig. 9. The slightly higher  $pH_i$  and slightly lower  $-B_i$  values are likely attributable to inherent differences in the wheat as compared to barley. The four measurements shown in Fig. 9(a) are characterized by  $pH_i = 5.97 \pm 0.14$  and  $B_i = -34.2 \pm 1.9$  mEq/kg.

#### 5.2.6. Flaked Grains

There are four basic steps in the production of flaked grains: (i) infusion of moisture, (ii) cooking, (iii) rolling, and (iv) cooling [31]. For some grains (corn and rice are examples) the grains are degermed before the flaking process begins. Moisture infusion and cooking take place simultaneously when the cooking agent is steam. If infrared radiation is used to cook the grains, then they are steeped beforehand to raise their moisture content.

Our results for flaked grains are shown in Table I. Aside from flaked barley,  $pH_i$  values are all well above

6.0. The variations in  $B_i$  are quite large, ranging from  $-9.6$  mEq/kg for flaked corn to  $-51.8$  mEq/kg for flaked barley. As can be ascertained from the results in Table I, there is clearly no correlation between color and pH or buffering capacity for these grains. Hence, color cannot be used as a surrogate for either  $pH_i$  or  $B_i$  for these flaked products. Owing to the minimal processing – as compared to malted grains – it seems likely the differences in  $pH_i$  and  $B_i$  among the different grains are due to the inherent nature of the unprocessed grains.

## 6. SUMMARY AND CONCLUSIONS

We have presented distilled-water mash pH ( $pH_i$ ) and buffering capacity ( $B_i$ ) measurements on two classes of grains that heretofore have been largely neglected: non-crystal specialty malts and flaked grains. As opposed to crystal malts, simple correlations between grain color and these two measured quantities does not exist. For the specialty malts this result is not terribly surprising, as processing of these malts is rather varied. For the flaked grains, the variations in  $pH_i$  and  $B_i$  are large even though all products are relatively light in color.

We have also considered previously acquired data on a number of malted grains (and roasted barley). Interestingly, there are study-dependent systematic differences in  $B_i$  values extracted from these data. Nonetheless, we have been able to normalize all of the data and thus present a coherent picture of  $pH_i$  and  $B_i$  trends across the various categories of malted barley.

On the theoretical side, we have discussed how  $pH_i$  and  $B_i$  values can be used to predict the distilled-water pH ( $pH_G$ ) of a mixture of grains. Simple put,  $pH_G$  is the average of the  $pH_i$  values weighted by the product of the grain fraction  $f_i$  and buffering capacity  $B_i$ .

Unfortunately, the data presented here are not sufficient to reliably predict the pH of a mash made with other than distilled water. This is because we do not know whether the  $B_i$  values presented here are valid in a typical homebrewer mash setting. In fact, as the  $B_i$  values were all normalized to the experimental conditions of AJdL, it is highly unlikely they are valid for a typical homebrewer’s mash. It is thus likely that a multiplicative correction factor to our normalized  $B_i$  values is required in order for our result to be applicable to a homebrewer’s mash. More experimental data are required to ascertain what this factor might be. Something for the future!

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## APPENDIX

In the following tables we tabulate all  $pH_i$  and  $B_i$  data from this study and the previously published studies of KT [1, 4], AJdL [3, 5, 6], Bies [7], Geurts [8], and Walts [9]. All  $B_i$  values are normalized to the data of AJdL, as discussed above.

TABLE III: Values of  $pH_i$  and  $B_i$  for **flaked grains** and **wheat malts** from previous studies and this study (TS). Malt-color values are generally taken to be the midpoint of published values, although the value in parenthesis is that reported by Geurts for his sample. Where appropriate for a given malt or group of malts the average value (Ave)  $\pm$  1 standard deviation (SD) is indicated.

Grain	Color (°L)	$pH_i$	$-B_i$ (mEq/kg)	Study
<b>Flaked Grains</b>				
Flaked Rye	3	6.65	29.8	TS
Flaked Wheat	2	6.57	28.2	TS
Flaked Corn	1	6.24	9.6	TS
Flaked Oats	2	6.21	48.2	TS
Flaked Barley	2	5.65	39.5	AJdL
	1	5.46	51.8	TS
		<b>5.55<math>\pm</math>0.13</b>	<b>47.2<math>\pm</math>10.9</b>	<b>Ave <math>\pm</math> SD</b>
<b>Wheat Malts</b>				
Briess White Wheat	3	5.89	31.9	Geurts
		6.10	38.5	TS
Briess Red Wheat	(3)	5.80	34.1	Geurts
Weyermann Wheat	2	6.07	34.6	Walts
		<b>5.97<math>\pm</math>0.14</b>	<b>34.8<math>\pm</math>2.8</b>	<b>Ave <math>\pm</math> SD</b>

TABLE IV: Values of  $pH_i$  and  $B_i$  for **dark roasted grains** from previous studies and this study (TS). Malt-color values are generally taken to be the midpoint of published values, although values in parenthesis are those reported by Geurts for his samples. Where appropriate for a given malt the average value (Ave)  $\pm$  1 standard deviation (SD) is indicated. The overall Ave  $\pm$  SD for the whole group of malts is also indicated.

Grain	Color (°L)	$pH_i$	$-B_i$ (mEq/kg)	Study
Briess Roasted Barley	300	4.62	68.6	Bies
		4.75	73.1	Walts
	(292)	4.73	66.3	Geurts
		4.70	59.0	AJdL
		4.68	62.9	KT
		4.67	67.5	TS
		<b>4.69<math>\pm</math>0.05</b>	<b>66.0<math>\pm</math>6.3</b>	<b>Ave <math>\pm</math> SD</b>
Briess Black Barley	500	4.60	61.6	Bies
	(561)	4.61	78.9	Geurts
		4.62	67.2	KT
		<b>4.61<math>\pm</math>0.01</b>	<b>69.2<math>\pm</math>8.8</b>	<b>Ave <math>\pm</math> SD</b>
Briess Chocolate	(416)	4.66	64.9	Geurts
Briess Dark Chocolate	(581)	4.43	62.7	Geurts
Briess Black	(629)	4.24	59.8	Geurts
Crisp Chocolate	600	4.70	78.7	AJdL
Simpsons Chocolate	444	4.55	77.2	Walts
Simpsons Black	625	4.57	77.0	Walts
Weyermann Carafa I	340	4.71	68.7	KT
Weyermann Carafa I Special	340	4.73	77.5	KT
Weyermann Carafa II Special	431	4.70	68.7	Walts
Weyermann Carafa III	525	4.81	64.4	KT
<b>Overall Ave <math>\pm</math> SD</b>		<b>4.64<math>\pm</math>0.13</b>	<b>68.7<math>\pm</math>6.6</b>	

TABLE V: Values of  $pH_i$  and  $B_i$  for **base malts** and **noncrystal specialty malts** from this study (TS) and previous studies. Malt-color values are generally taken to be the midpoint of published values, although values in parenthesis are those reported by Geurts for his samples. Where appropriate for a given malt or groups of malts, the average value (Ave)  $\pm$  1 standard deviation (SD) is indicated.

Grain	Color (°L)	$pH_i$	$-B_i$ (mEq/kg)	Study
<b>Pils/Lager/2-Row</b>				
Briess 2-Row	2	6.00	57.2	Bies
		5.55	46.2	Geurts
Rahr Pils	2	5.80	42.4	Walts
Weyermann Pneumatic Pils	2	5.62	47.2	AJdL
Weyermann Floor Malted Pils	2	5.85	34.4	AJdL
		<b>5.76<math>\pm</math>0.18</b>	<b>45.5<math>\pm</math>8.3</b>	<b>Ave <math>\pm</math> SD</b>
<b>Pale Ale/ Vienna/ Mild</b>				
Rahr Pale Ale	3	5.67	49.7	Walts
Crisp Maris Otter	3	5.69	49.5	AJdL
Muntons Maris Otter	3	5.84	51.4	AJdL
(unspecified) Maris Otter	3	5.82	47.0	KT (2010)
Weyermann Vienna	3	5.65	51.8	KT
Briess Goldpils Vienna	(4)	5.65	57.6	Geurts
Briess Ashburne Mild	(4)	5.50	59.2	Geurts
		<b>5.69<math>\pm</math>0.11</b>	<b>52.3<math>\pm</math>4.5</b>	<b>Ave <math>\pm</math> SD</b>
<b>Munich</b>				
Weyermann Munich I	6	5.57	45.6	Walts
		5.44	52.3	KT
Franco Belges Munich Light	7	5.62	60.7	KT
Weyermann Munich II	8	5.54	56.7	KT
Briess Munich 10L	10	5.72	52.1	Bies
	(12)	5.51	54.9	Geurts
		<b>5.57<math>\pm</math>0.10</b>	<b>53.7<math>\pm</math>5.1</b>	<b>Ave <math>\pm</math> SD</b>
<b>Aromatic</b>				
Briess Aromatic	(16)	5.39	49.5	Geurts
	20	5.39	45.5	TS
Dingemans Aromatic	19	5.38	64.7	TS
		<b>5.39<math>\pm</math>0.01</b>	<b>55.1<math>\pm</math>13.5</b>	<b>Ave <math>\pm</math> SD</b>
<b>Biscuit / Amber / Brown</b>				
(unspecified) Biscuit	25	5.08	52.8	KT
Briess Victory	28	5.19	36.8	TS
Crisp Amber	29	5.10	35.5	TS
Briess Carabrown	55	5.19	31.4	TS
		<b>5.14<math>\pm</math>0.06</b>	<b>39.1<math>\pm</math>9.4</b>	<b>Ave <math>\pm</math> SD</b>
Crisp Brown	65	4.97		TS
<b>Melanoidin / Honey / Brumalt</b>				
Weyermann Melanoidin	27	4.96	56.3	Walts
		4.93	68.9	TS
		<b>4.94<math>\pm</math>0.02</b>	<b>62.6<math>\pm</math>8.9</b>	<b>Ave <math>\pm</math> SD</b>
Gambrinus Honey	25	4.82	95.4	TS
Briess Special Roast	40	4.91	99.1	TS
<b>Other</b>				
Briess Extra Special	130	4.55	58.8	TS

TABLE VI: Values of  $pH_i$  and  $B_i$  for **crystal, caramel, and dextrine malts** from this study (TS) and previous studies. Malt-color values are generally the midpoint of published values. For each group of malts the average value (Ave)  $\pm$  1 standard deviation (SD) is indicated.

Grain	Color (°L)	$pH_i$	$-B_i$ (mEq/kg)	Study
<b>C 2</b>				
Crisp Dextrin	2	5.54	33.2	Walts
Weyermann Carafoam	2	5.88	36.5	AJdL
		<b>5.71<math>\pm</math>0.24</b>	<b>34.8<math>\pm</math>2.4</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 10</b>				
Briess Caramel L10	10	5.13	54.0	Geurts
		5.38	48.6	KT
		5.34	47.7	TS
Simpsons Caramalt	14	5.18	46.7	Walts
		<b>5.26<math>\pm</math>0.12</b>	<b>49.3<math>\pm</math>3.25</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 20</b>				
Briess Caramel L20	20	5.12	58.4	AJdL
		5.01	53.4	Bies
		5.05	59.1	Geurts
		5.22	47.9	KT
		5.07	59.7	TS
Cargill Caramel 20	20	5.43	48.6	Walts
		<b>5.15<math>\pm</math>0.016</b>	<b>54.5<math>\pm</math>5.3</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 40</b>				
Briess Caramel 40L	40	4.71	66.1	Bies
		4.85	62.1	Geurts
		5.02	61.0	KT
		4.90	72.2	TS
Simpsons Crystal Light	40	4.92	53.3	Walts
Weyermann CaraMunich I	34	5.10	60.5	KT
Weyermann CaraMunich II	45	4.71	80.182	KT
		<b>4.89<math>\pm</math>0.15</b>	<b>65.0<math>\pm</math>8.8</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 60</b>				
Briess Caramel 60L	60	4.87	65.7	Bies
		4.75	70.8	Geurts
		4.66	78.5	KT
Cargill Caramel 60	60	4.97	68.6	Walts
Weyermann CaraMunich III	57	4.7	61.5	Walts
		4.92	64.8	KT
		<b>4.81<math>\pm</math>0.13</b>	<b>68.3<math>\pm</math>5.9</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 80</b>				
Briess Caramel 80L	80	4.71	72.4	Geurts
		4.77	73.0	AJdL
		4.70	72.3	TS
Briess Caramel 90L	90	4.77	78.4	KT
		<b>4.74<math>\pm</math>0.04</b>	<b>74.0<math>\pm</math>2.9</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 120</b>				
Briess Caramel 120L	120	4.87	84.2	Bies
		4.58	73.1	Geurts
		4.75	78.4	KT
		4.70	77.2	Walts
		4.63	75.0	TS
Simpson's DRC	113	4.58	74.2	Walts
		<b>4.68<math>\pm</math>0.11</b>	<b>77.0<math>\pm</math>4.0</b>	<b>Ave <math>\pm</math> SD</b>
<b>C 140</b>				
Briess Caramel 150L	150	4.48	79.4	KT
Weyermann Caraaroma	133	4.48	98.8	KT
		<b>4.48<math>\pm</math>0.00</b>	<b>89.1<math>\pm</math>13.7</b>	<b>Ave <math>\pm</math> SD</b>