Malt Modification and Mashing Conditions as Factors Influencing the Minerals of Wort[1]

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ABSTRACT

The influence of mashing temperature, pH, mash concentration, and mashing time on potassium, sodium, calcium, magnesium, copper, iron, manganese, and zinc contents of wort was investigated. The metals were determined by atomic absorption spectrophotometry. Variations in pH and mashing temperature affect the solubility of the metals more than do mash concentration and mashing time. By means of the analysis of variance, the relative importance of mashing conditions and malt modification was calculated. Potassium, sodium, calcium, and copper are mainly influenced by malt modification; iron is more affected by mashing conditions, whereas magnesium, manganese, and zinc depend on both variables. As a consequence, the brewer must carefully consider both factors in order to achieve a desired metal level in the wort.

Key words: *Biometrical analysis, Malt quality, Mashing parameters, Metals.*

In addition to carbohydrates and amino acids, the minerals of wort play an important role in fermentation and beer quality (Fig. 1).

Metals (*e.g.*, magnesium) are components of DNA and RNA as well as of coenzymes and cosubstrates. Minerals activate or inhibit enzymes and influence the transport of carbohydrates and amino acids into the cell. Phosphorus is involved in the formation of metabolic energy (ATP). Zinc promotes the fermentation rate, calcium improves the flocculation. Small amounts of iron, copper, and zinc are required to support yeast growth. Gushing is attributable to heavy metals. Zinc, copper, and iron increase the head retention of beer. Copper and iron contents in the haze material are 5000 to 50,000 times as high as in the bulk of beer. As enzyme activators, metals affect the by-product formation, whereas the anions have a direct or indirect influence on beer flavor. Chloride seems to impart fullness and sweetness to beer. Sulfate is said to give a dry flavor. Trace metals, such as copper and iron, act as oxidation catalysts and impair the flavor stability. High levels of phosphorus, magnesium, and potassium are of importance for the dietetic properties of beer.

Raw materials and brewing processes exert an influence on wort salts. With barley, these influences are variety, environment, and plant production techniques. Steeping, germination, and kilning are significant malting conditions. In mashing, temperature, time, pH, concentration, and grist composition have an effect. Brewing water can contain high levels of nitrate and fluoride. Wort boiling diminishes the mineral concentration due to binding metals to the precipitated material. With the addition of hops, metals are also added. The use of adjuncts and syrups normally dilutes the metal level of an all-malt wort. Adjunct worts are less buffered, which results in a greater decrease of the pH value during fermentation. On the other hand, syrups may contain heavy metals and chlorides in abundance.

For further details, see the review papers "Role of trace metals in brewing" (3), "Mineral matter, trace elements, organic and inorganic acids in hopped wort" (10), and "Wort salts in beers brewed using adjuncts" (13).

An all-malt pale lager wort (12°P) should contain about 550 mg/l. potassium, 30 mg/l. sodium, 35 mg/l. calcium, 100 mg/l. magnesium, 0.10 mg/l. copper, 0.10 mg/l. iron, 0.15 mg/l. manganese, and 0.15 mg/l. zinc (9,10).

In an earlier paper (2) the effects of barley and malting technology on the wort minerals were presented. In the same connection, the current report presents a detailed study of the influence of mashing conditions, using malts of varied modification.

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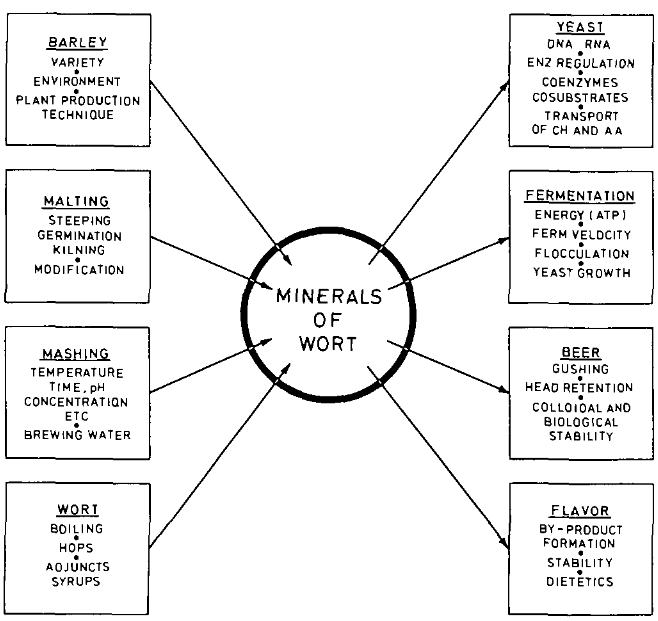

Fig. 1. Minerals of wort: influences from barley, malting and mashing, and effects on yeast, fermentation, and beer.

TABLE I
Properties of Malts

	Under-modified Malt 1	Normally Modified Malt 2	Normally Modified Malt 3	Over-modified Malt 4
Fine grind extract, g/100 g dry wt	80.3	80.8	81.4	82.5
Coarse grind extract, g/100 g dry wt	73.7	78.7	79.4	81.9
Fine-coarse grind extract difference, %	6.6	2.1	2.0	0.6
Conversion time, min	20	10–15	10–15	5–10
Color, EBC	2.5	4.0	3.3	4.2
Protein, g/100 g dry wt	11.5	11.4	11.2	9.9
Soluble nitrogen, mg/100 g dry wt	580	725	693	730
Protein modification, %	31.5	39.8	38.7	46.2
pH, EBC	5.90	5.81	5.87	5.84
Viscosity, cP	2.00	1.62	1.58	1.49
Hardness, BU	650	365	330	220
Extract at 45°C, Hartong-Kretschmer	28.5	38.6	38.1	46.5

EXPERIMENTAL

The investigations were carried out with four malts of varying modification degrees (Table I). Malt 1 is undermodified; the values for fine-coarse grind extract difference, viscosity, and hardness are high, and the values of soluble nitrogen, protein modification, and extract at 45° C are low. Malts 2 and 3 are normally modified. They reflect normal cytolytic, amylolytic, and proteolytic activities. Malt 4 is overmodified; the values for fine-coarse grind extract difference, viscosity, and hardness are low, whereas those for soluble nitrogen, protein modification, and extract at 45° C are high.

The malts were coarsely ground and 50-g grist samples were mashed with varying amounts of distilled water. Glass beakers and glass stirrers were used for mashing. At the end, the mash was filled up to a weight of 450 g. The worts were centrifuged (not filtered) for 30 min at 4000 rpm. The metals were determined in the unboiled worts by atomic absorption spectrophotometry (12).

The results were calculated biometrically. A program was used from Reiner of the Technical University Munich/Germany (2-4V), for the analysis of variance. An analysis of variance was made, and the components of variance were estimated on the basis of mean squares (SQ × DF). The total of the components of variance was 100%. For example, the sum of the components of variance, mashing temperature, and malt modification, and the interaction of both factors will be 100%. This type of biometrical calculation shows which component of variance (*e.g.*, mashing temperature or malt modification, or the interaction of both factors) is—relatively—the most important.

The significance of the biometrical results for each sample was examined on the basis of the F-test. A single asterisk (*) and double asterisks (**) denote "significant" and "highly significant" values, respectively. The term "malt modification" (in Figs. 3, 5, 7, 9, and 11) includes the four malt qualities. The terms "mashing temperature" (Fig. 2), "pH in mashing" (Fig. 4), "mash concentration" (Fig. 6), and "mashing time" (Figs. 8 and 10) include a varying number of cases; the number of calculated cases is set in parentheses behind the corresponding mashing factor in Figs. 3, 5, 7, 9, and 11.

RESULTS

Mashing Temperature

For this study, 50-g grist samples were mashed with 350 ml distilled water for 30 min at the following temperatures: 20°, 25°, 30°, 35°, 40°, 45°, 50°, 55°, 60°, 65°, 70°, 75°, and 80°C.

An increase in the mashing temperature from 20° to 80° C shows the following effects (Fig. 2): a stepwise increase in potassium until 55° C; a slight increase in sodium until 55° C; a decrease in calcium, especially above 70° C; a strong increase in magnesium until 60° C, and a decrease above 65° C; a slight increase in copper, especially in the mashes at higher temperatures (70° to 80°C); and a stepwise decrease in iron, manganese, and zinc.

For the calculation of the components of variance, only the values for mashing temperatures between 45° and 75° C were considered. A comparison of the relative importance of mashing temperature and malt modification shows that the former factor has a greater effect on copper, iron, manganese, and zinc, while the latter is more important for potassium, sodium, calcium, and magnesium (Fig. 3).

pH in Mashing

For the hydrogen ion concentration study, 50-g grist samples

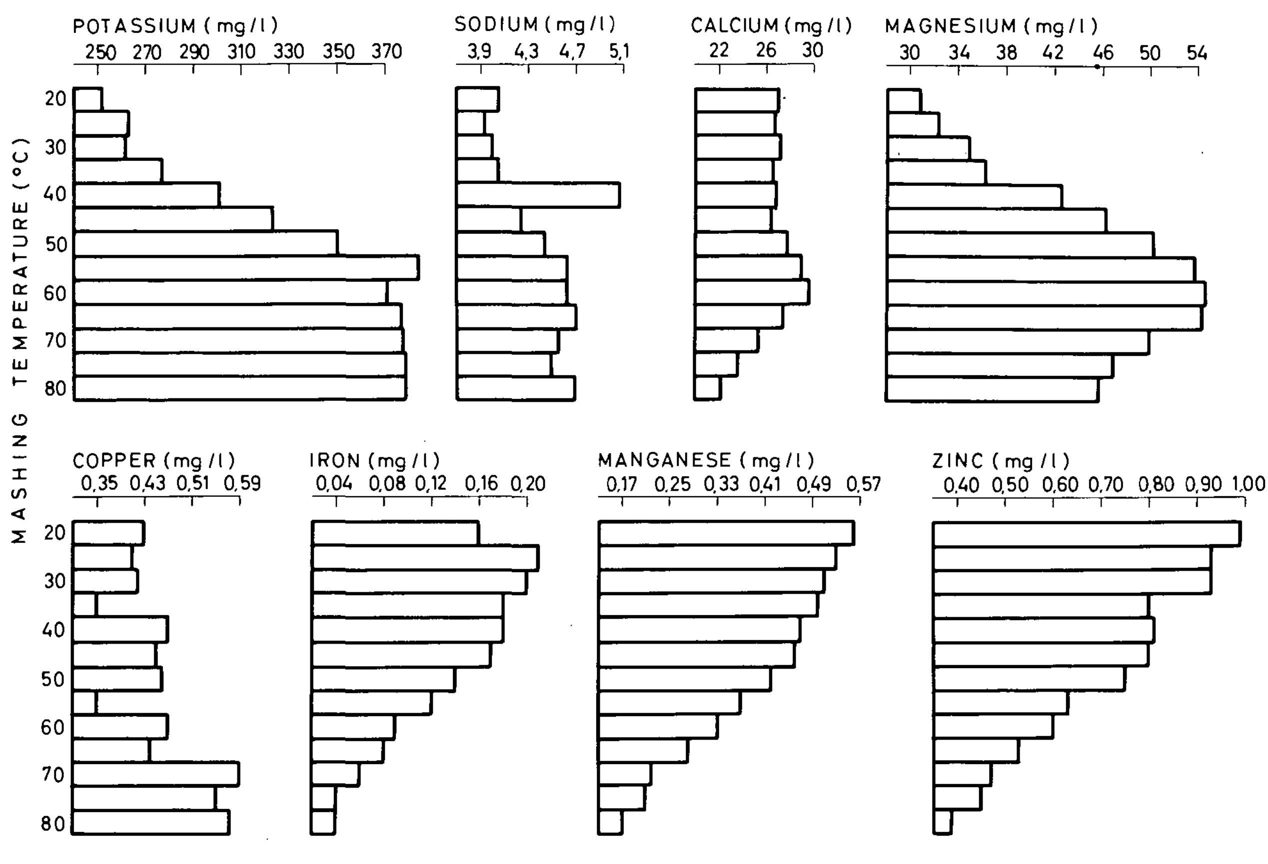

Fig. 2. Mashing temperature and mineral content of wort (average values of four differently modified malts).

were mashed with 350 ml liquid for 30 min at 45°C, 20 min at 62°C, and 40 min at 70°C. In the final worts, the pH values and the metals were determined. The amounts of acids and alkalis used and the resulting pH values are given in Table II.

A lowering of pH leads to a higher solubilization of potassium, calcium, magnesium, iron, manganese, and zinc (Fig. 4). High amounts of sodium and copper are obtained in a pH range from 5.5 to 5.7.

The relative effects of pH in mashing and malt modification were evaluated (taking into account only the values between pH 6.0 and pH 5.2). Calcium, magnesium, iron, manganese, and zinc are more affected by hydrogen ion concentration, and potassium and sodium

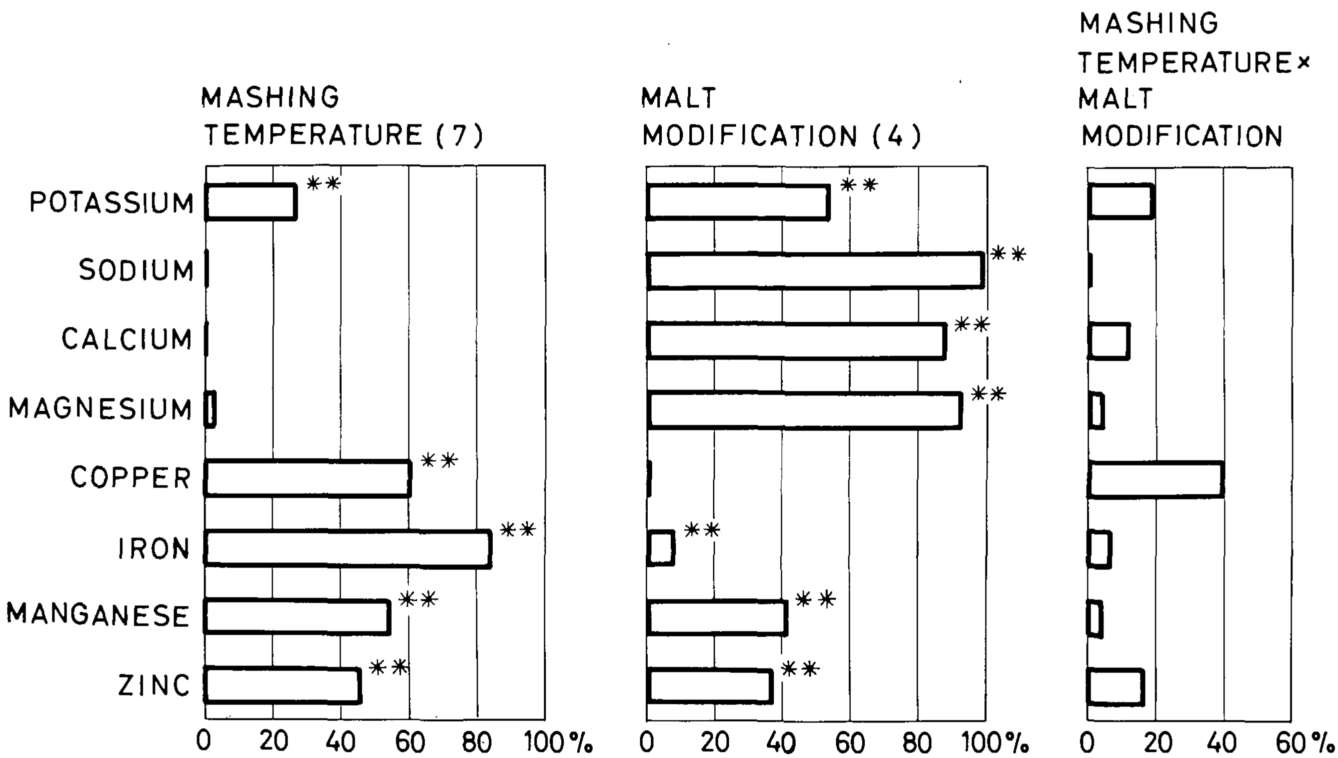

Fig. 3. Relative effects of mashing temperature and malt modification on the minerals of wort.

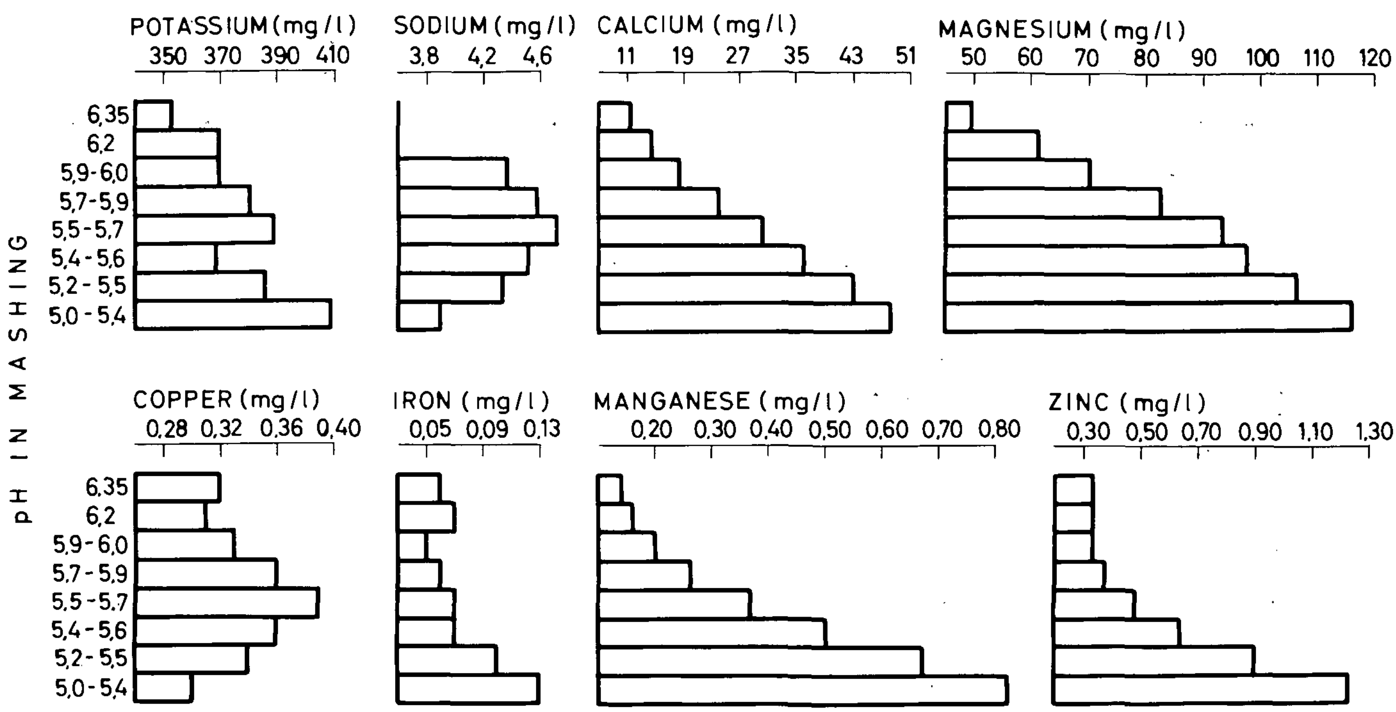

Fig. 4. pH in mashing and mineral content of wort (average values of four differently modified malts).

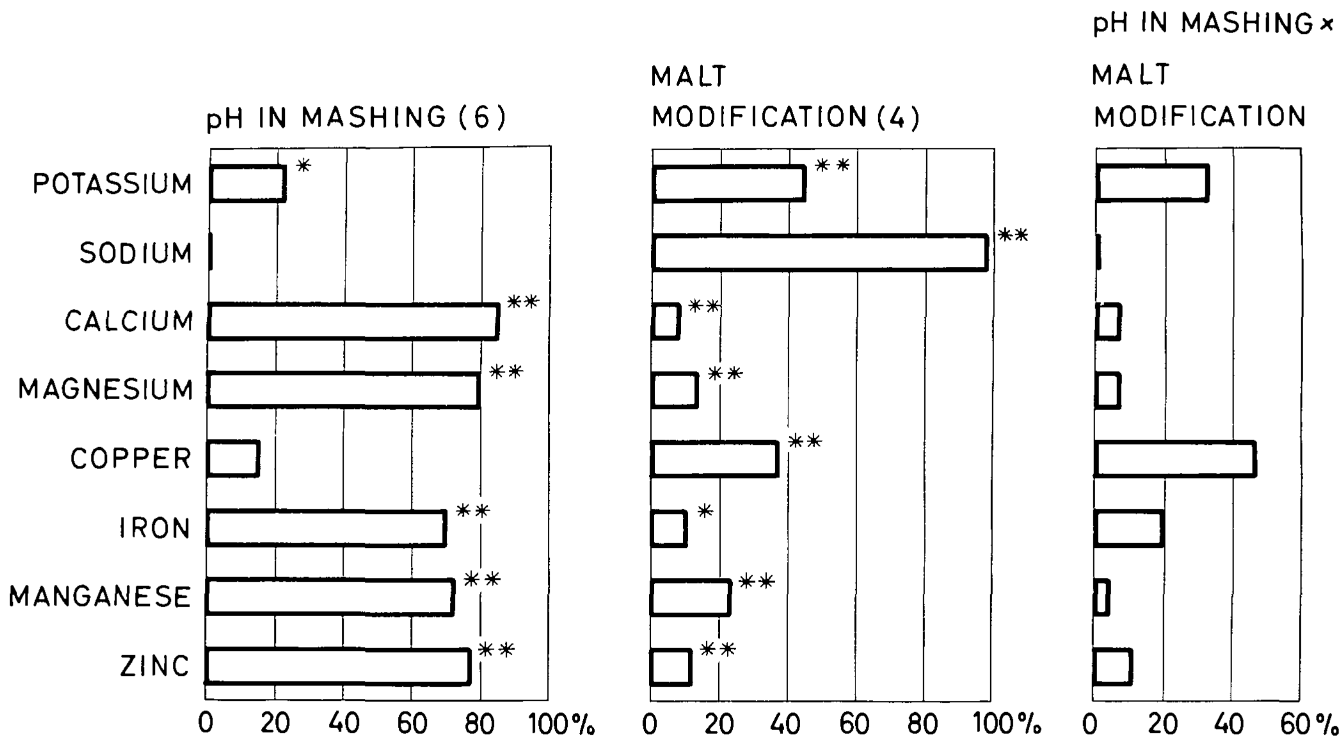

Fig. 5. Relative effects of pH in mashing and malt modification on the minerals of wort.

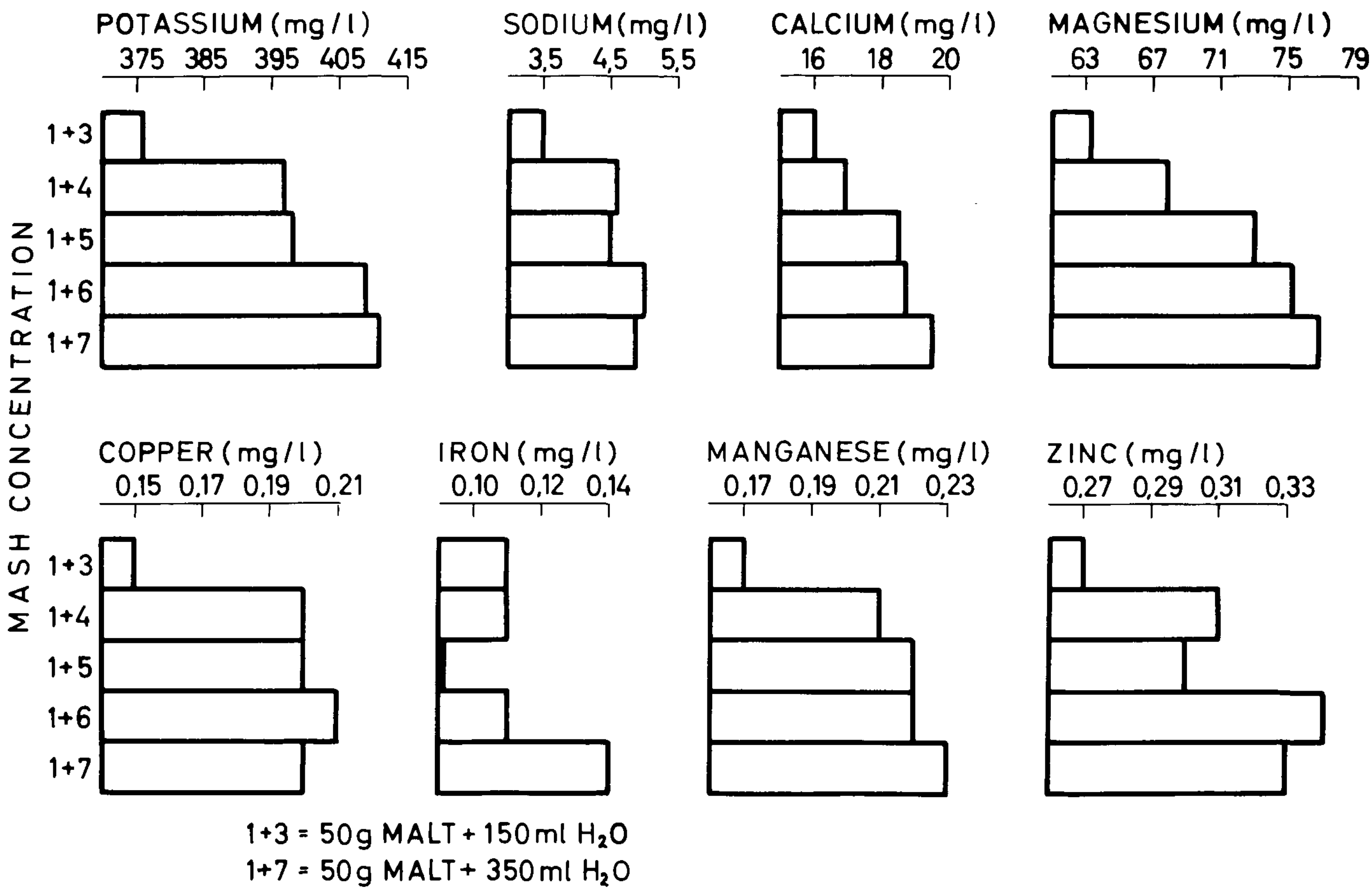

Fig. 6. Mash concentration and mineral content of wort (average values of four differently modified malts).

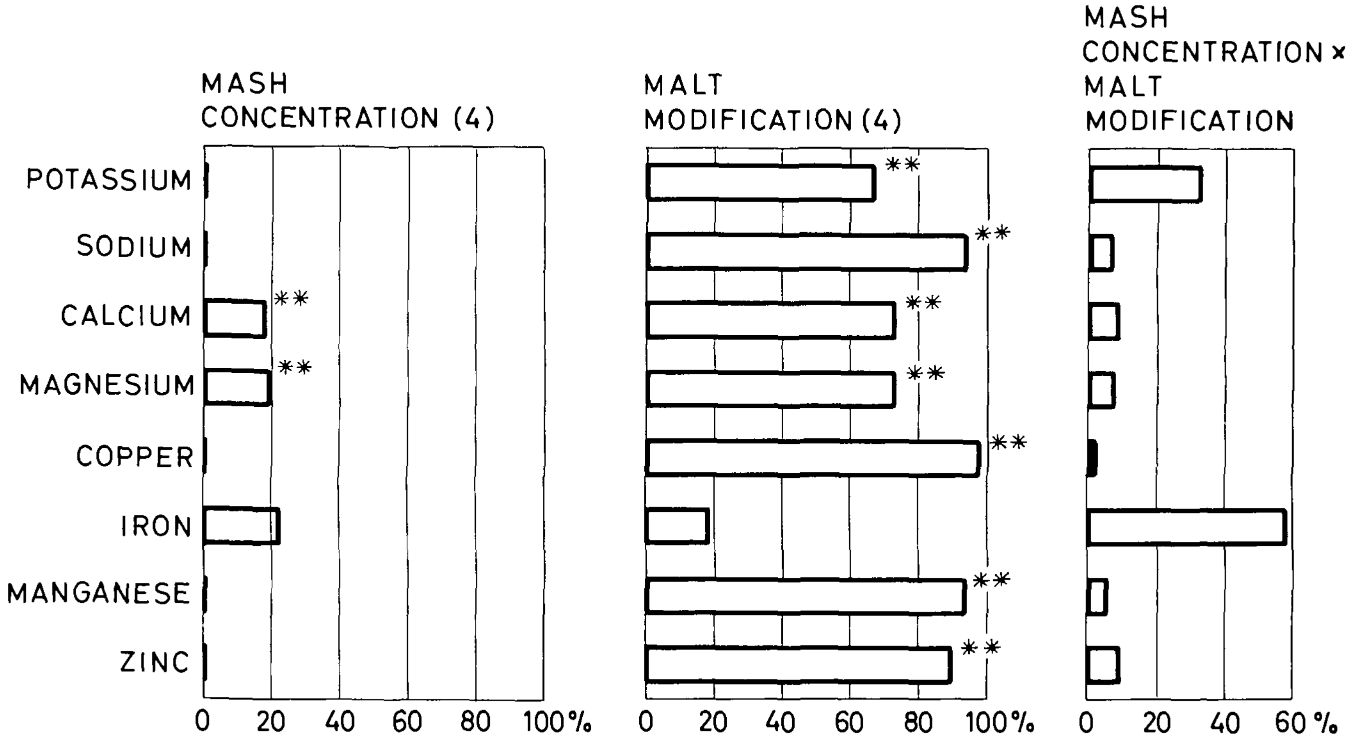

Fig. 7. Relative effects of mash concentration and malt modification on the minerals of wort.

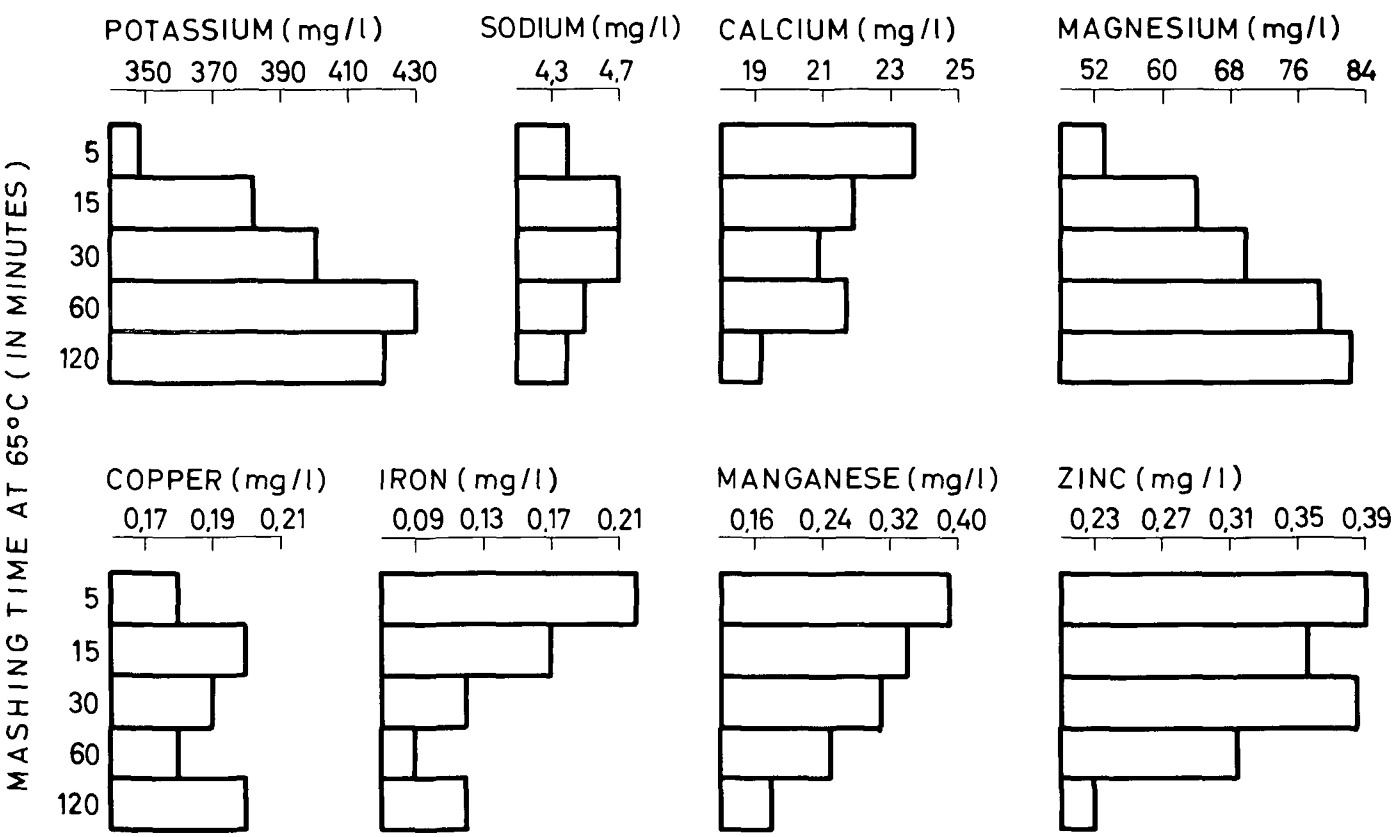

Fig. 8. Mashing time (at 65°C) and mineral content of wort (average values of four differently modified malts).

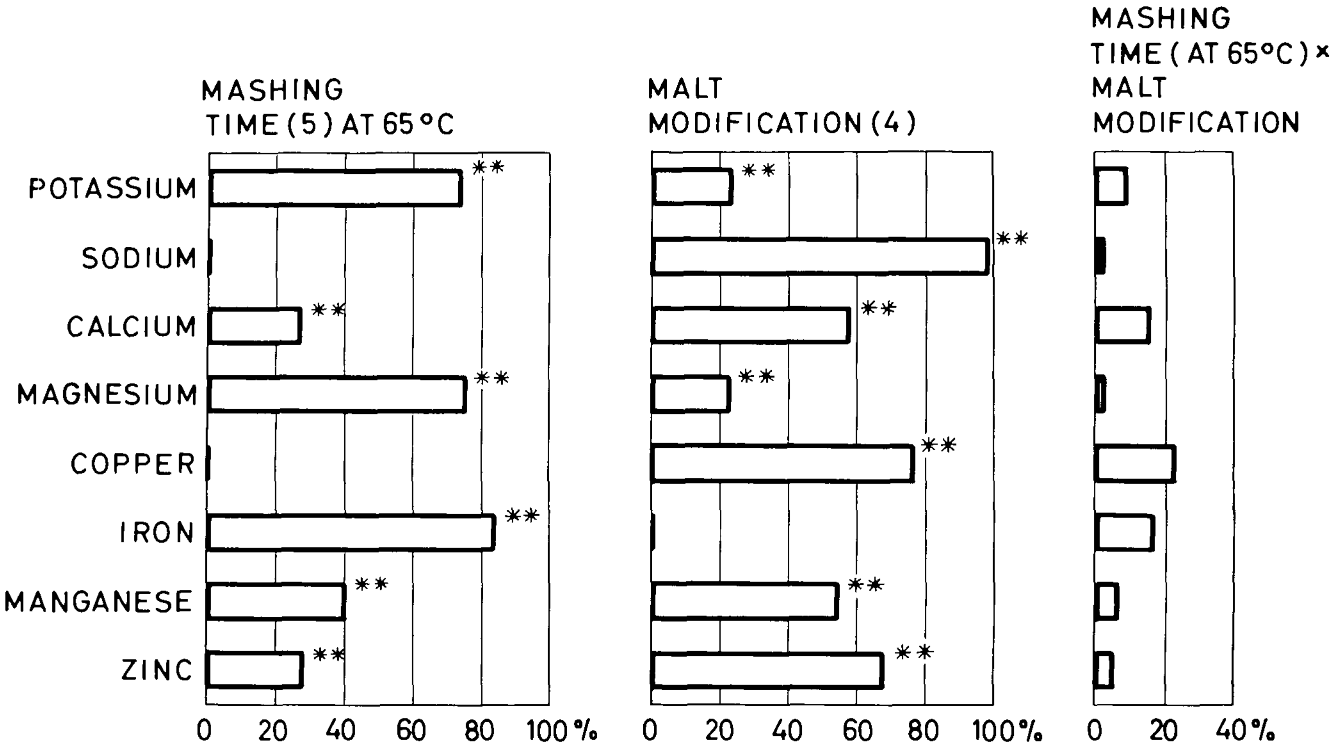

Fig. 9. Relative effects of mashing time (at 65°C) and malt modification on the minerals of wort.

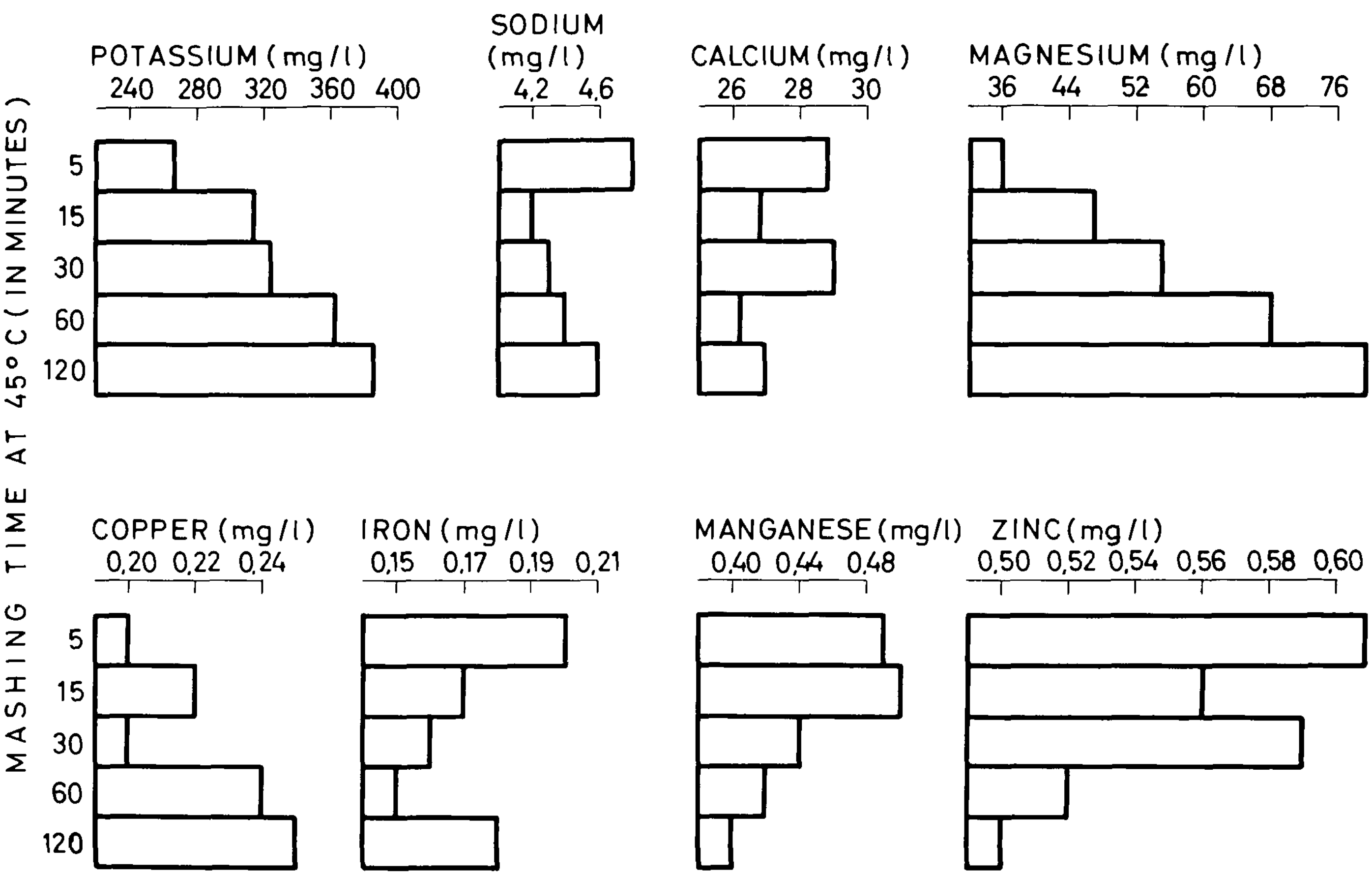

Fig. 10. Mashing time (at 45°C) and mineral content of wort (average values of four differently modified malts).

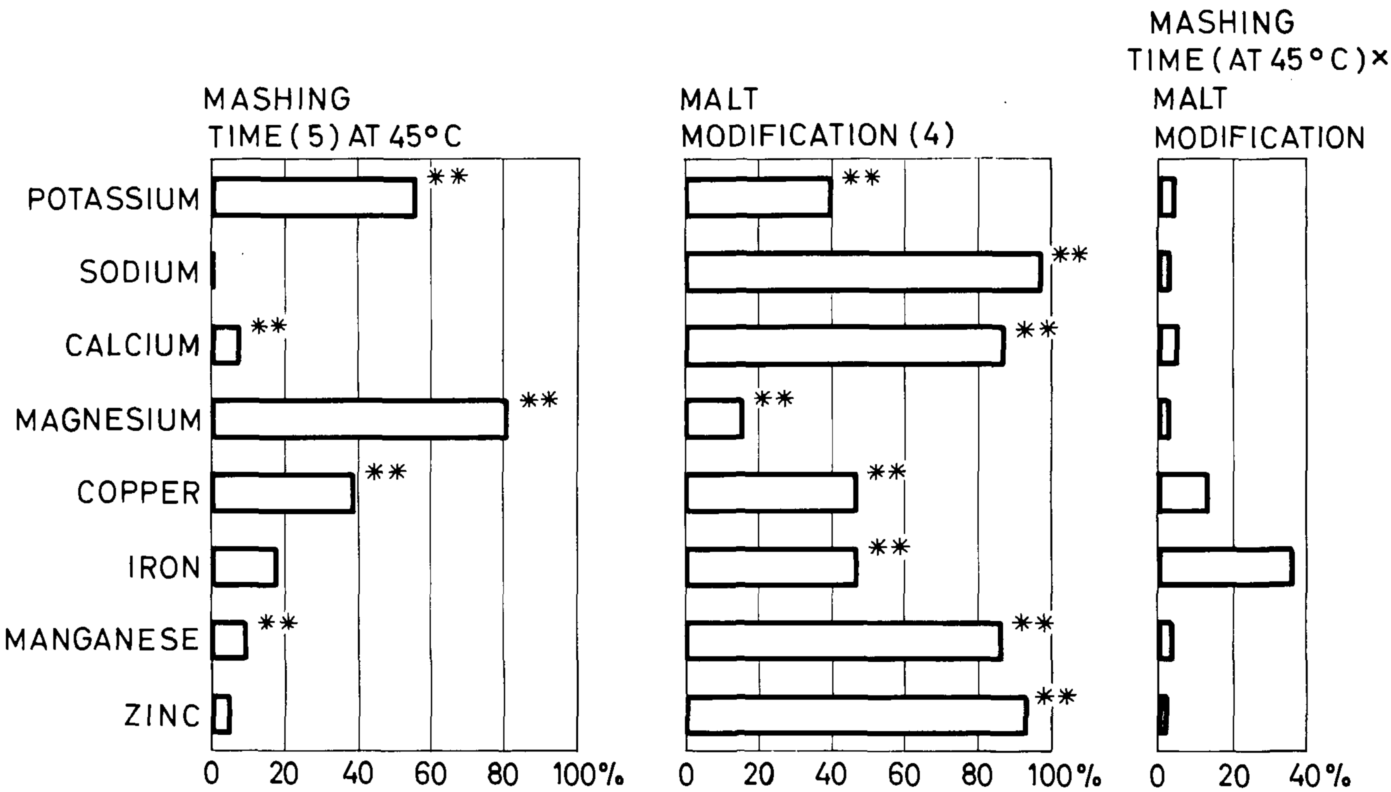

Fig. 11. Relative effects of mashing time (at 45°C) and malt modification on the minerals of wort.

TABLE II
pH in Mashing

Step	Distilled Water ml	+ Addition	pH Value of Wort
1	340	+ 10 ml n/10 NaOH	6.35
2	345	+ 5 ml n/10 NaOH	6.2
3	350	...	5.9 – 6.0
4	345	+ 5 ml n/10 HCl	5.7 – 5.9
5	340	+ 10 ml n/10 HCl	5.5 – 5.7
6	335	+ 15 ml n/10 HCl	5.4 – 5.6
7	330	+ 20 ml n/10 HCl	5.2 – 5.5
8	325	+ 25 ml n/10 HCl	5.0 – 5.4

more by malt modification (Fig. 5).

Mash Concentration

Mash concentration varied between 1+3 (*i.e.*, 50 g grist and 150 ml distilled water) and 1+7 (*i.e.*, 50 g grist and 350 ml water). The malts were mashed at 45°, 62°, and 70°C.

A dilution of the mash concentration leads to a higher solubilization of potassium, sodium, calcium, magnesium, manganese, and zinc. Much copper is already solubilized in steps 1+4, and most of the iron in steps 1+7 (Fig. 6).

For the calculation of the components of variance, only the data for the mash concentrations 1+4 through 1+7 were used. The biometrical evaluation shows that seven of eight metals are more influenced by malt modification, whereas iron depends neither on mash concentration nor on malt modification (Fig. 7).

Mashing Time

In the last experiment, mashing time was determined. For this purpose, two model systems were chosen: one experiment was carried out with a temperature of 65°C, and one with a temperature of 45°C. The mashing time varied between 5, 15, 30, 60, and 120 min.

An extension of the mashing time (at 65°C) from 5 to 120 min leads to an increase in potassium, magnesium, and (partly) copper, and a stepwise decrease in sodium, calcium, iron, manganese, and zinc (Fig. 8).

Potassium, magnesium, and iron are more influenced by mashing time (at 65°C), whereas sodium, calcium, copper, manganese, and zinc depend more on malt modification (Fig. 9).

The experiment with mashing time at 45°C yielded—with the exception of sodium—similar results (Fig. 10): a stepwise increase in potassium, magnesium, and copper, and a stepwise decrease in calcium, iron, manganese, and zinc.

The analysis of variance shows that mashing time (at 45°C) has a greater effect on potassium and magnesium; whereas malt modification has more influence on sodium, calcium, copper, iron, manganese, and zinc (Fig. 11).

Finally, the relative importance of malt modification and mashing conditions was assessed. The term "malt modification" included undermodified malt, overmodified malt, and the two normally modified samples. The term "mashing conditions" included mashing temperature, pH in mashing, mashing concentration, and mashing time at 65°C and at 45°C. From this evaluation, it can be seen that potassium, sodium, calcium, and copper are mainly influenced by malt modification, and iron is more affected by mashing conditions; whereas magnesium, manganese, and zinc depend on both variables (Fig. 12).

DISCUSSION

Variations in the pH and in mashing temperature have more effect on the solubility of the metals than do mash concentration and mashing time.

Potassium is more solubilized in a range in which α-amylase activity is optimal. The sodium level shows a certain correlation with the formation of lower nitrogen compounds. Calcium and

MINERALS OF WORT	MAINLY INFLUENCED BY	
	MALT MODIFICATION	MASHING CONDITIONS
POTASSIUM	●	
SODIUM	●	
CALCIUM	●	
MAGNESIUM	●	●
COPPER	●	
IRON		●
MANGANESE	●	●
ZINC	●	●

Fig. 12. Malt modification and mashing conditions as main factors influencing minerals in wort—a statistical summary.

magnesium are more solubilized in a range in which β-amylase activity is optimal and in which amino acids are formed. Copper, iron, manganese, and zinc levels exhibit a relationship with the formation of soluble nitrogen.

The decrease in metal concentration during mashing is due to the formation of insoluble phosphates (*e.g.*, with calcium and magnesium), the formation of salts with the acidic groups of proteins, and the mechanical adsorption on spent grains and trub (1,11,14). The insoluble material is precipitated and thus prevented from getting into the wort.

The brewhouse yield of minerals is about 100% for potassium and sodium (11), about 95% for chloride, 84% for sulfuric acid, and 63% for phosphoric acid (5). More than 50% of other minerals is lost, and the loss is particularly high for trace elements (5,11).

The metal content of wort is mainly governed by a partition between the sequestering agents in wort and the metal binders in the insoluble matter of the mash (6). Amino acids (such as histidine and cysteine), polyphenols (tannins), and phytic acid are strong metal binders. Naturally occurring chelators in wort are sulfur-, nitrogen- or oxygen-compounds, containing reactive groups such as carboxyl, sulfhydryl, *o*-diphenyl, and amine (4).

The binding capacity of a metal chelator is highly pH-dependent, due to competition between the hydrogen and metal ions in solution (6). Usually, a decrease in pH leads to an increase in free metal ions, since the stability constant of the metal binder decreases. The precipitation of nitrogenous components at elevated temperatures removes sequestering agents from the wort (6), leading to a greater loss of minerals.

The amount of metals extracted from malt varies with the mashing conditions as well as with the chemical and physical properties of the malt.

A short germinated and undermodified malt has a different grist composition in husks, grits, and flour than a longer germinated and overmodified malt. In a cereal grain, there is a general transfer of mineral elements from the storage tissues to the developing seedling. Minerals are more concentrated in the germ end than in the central section, whereas the distal section has intermediate amounts (7). Rootlets and shoots contain substantially more potassium, phosphorus, iron, zinc, manganese, and copper than kilned malt. Calcium is transported to rootlets but not to shoots (7), and it is more uniformly distributed throughout the kernel than is magnesium (8). High-protein fractions are substantially richer in minerals than low-protein fractions.

In differently modified malts, the development of rootlets and acrospires and the extent of metal transport from the central and distal sections to the germ end are variable. It can thus be expected that worts derived from such malts will vary in their metal concentrations. The metal distribution is also highly dependent on the protein modification (6), a characteristic in which the analyzed malts greatly varied (Table I). As a consequence, the brewer must carefully consider both malt modification and mashing conditions in order to achieve a desired metal level in the wort.

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