The Effect of pH on Stem-end Blackening of Potato

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Potatoes of certain stocks when heated for a sufficient length of time and then exposed to air develop a greyish black discoloration. This occurs mainly at the stem or basal end of the tuber and is known as stem-end blackening. The minimum time of heating is said to be 2 min. (Robison, 1941); this is sufficient to cause slight greyness only and a longer period of heating leads to a greater amount of blackening. The usual method of inducing formation of the pigment for estimation of its quantity is to cook the potato tissue in boiling water (Cowie, 1942; Rieman, Tottingham & McFarlane, 1944; Smith, Nash & Dittman, 1942); this method has been used in the present investigation.

The chemical nature of the pigment and of its precursors is unknown. It seems fairly certain that it is not melanin (Robison, 1941; Nutting, 1942); the pigment does not develop in acid solutions (Tinkler, 1931; Robison, 1941; Smith *et al.* 1942; Nutting & Pfund, 1942), but no quantitative data are available nor is the cause of this effect clear. Strong reducing agents are reported to decrease the extent of development of the colour (Smith *et al.* 1942)—it does not develop in the absence of oxygen (Tinkler, 1931; Nutting and Pfund, 1942; Robison, 1941)—and from this aspect the addition of sodium sulphite to the potato was tried but it was found ineffective in reducing discoloration (Wager, Tomkins, Brightwell, Allen & Mapson, 1946). Variety and agricultural conditions influence the liability of tubers to blacken (Wallace, 1921; Findlay, 1928; Cowie, 1941, 1942; Smith *et al.* 1942; Rieman *et al.* 1944, etc.); this has also been studied and the results will be reported elsewhere.

METHODS

Strips of dried potato were utilized in most of this work. They were prepared by cutting the raw tuber into strips $\frac{1}{4} \times \frac{1}{4}$ in. in cross-section, washing them, 'scalding' them in boiling water long enough to inactivate the enzymes and drying in a current of hot air at 60° (see Wager *et al.* 1945). The behaviour of such material with regard to colour and pH is similar to that of strips of raw potato. It can be stored for long periods with no detectable change and the use of 10–20 g. of strips per test eliminates most sampling variation, which is relatively large as between different batches of raw tubers taken from the same stock.

The short period of boiling (1½–2 min.) necessary to inactivate the enzymes before drying causes only a partial

development of stem-end blackening pigment. To complete this development the strips were soaked for 1 hr. at room temperature in a phosphate-citrate buffer, boiled until cooked (5–10 min.), drained and left for not less than 30 min. to allow maximum development of pigment.

The greyness of the cooked samples was estimated by a group of experienced 'judges' and their individual estimates averaged. Colorimeters were not used because of difficulty in reducing different samples of potato tissue to a homogeneous mash in a comparable physical state, especially with regard to the content of air and water. Samples were awarded marks on a scale of 4 (very grey) to 0 (not grey).

The pH of a sludge of cooked strips in distilled water was found to differ little from that of the solution in which they were cooked and therefore the pH of this solution has been used as an estimate of that of the cooked tissue.

RESULTS

The effect of pH on the colour of cooked potato. The relationship between the greyness of cooked strips of potatoes from different stocks and varieties and their pH is shown in Fig. 1. The curves all show a similar increase in mark for greyness with increase in pH from the point at which the greyness mark attains a value of 0.4–0.5, but the pH at which this occurs differs markedly in different stocks. Below this level the marks for greyness are a less reliable estimate of stem-end blackening since other minor discolorations (such as traces of melanin, etc.) unaffected by pH in this range contribute to the greyness mark. For this reason the shape of the curves below a greyness mark of 0.4–0.5 is disregarded. At pH values greater than 7.5–8.0 the grey colour of the strips changes to a brown and this tendency increases as the pH is increased.

The greyness of strips cooked in buffer solutions is independent of their colour before cooking, e.g. potato scalded in an acid solution made pale yellow dried strips but when scalded in a slightly alkaline

Table 1. *Greyness of potato strips scalded at pH 7.6 (Sample A) and pH 5.7 (Sample B) and cooked at varying pH's*

pH of solution used for cooking	Greyness	
	Sample A	Sample B
4.8	0.0	0.2
5.8	0.2	0.2
6.8	1.7	1.4
7.5	2.2	2.2

solution the dried strips were of a grey colour; both batches were, however, equally grey when cooked in buffer solutions (Table 1).

The greyness is due, therefore, to a pigment (or to a group of several pigments) whose colour is reversibly affected by pH and the quantity of the pigment (or pigments) formed in any given stock appears to be independent of pH.

If different pigments or different proportions of the same group of pigments were present in different varieties of potato, the curves in Fig. 1 would be

Table 2. *Effect of initial melanin on greyness of cooked potato strips*

pH of cooked strips	Greyness	
	Strips containing melanin	Control
3.5	2.1	0.0
5.2	2.5	0.1
6.1	2.8	0.2
7.0	2.9	0.7
7.6	3.2	1.2

Fig. 1. The relation of the pH of the cooking liquor to the greyness of cooked dried potato strips from stocks of Golden Wonder, Doon Star, King Edward and Kerr's Pink potatoes.

likely to diverge. Since they are as nearly parallel above a greyness mark of 0.4–0.5 as could be expected from visual estimates, they offer no evidence for the existence of more than one pigment either in different stocks or varieties.

Stem-end blackening pigment and melanin. Strips of potato were allowed to discolour by enzymic oxidation before scalding so that grey-coloured dried strips were obtained. A control batch of dried strips was also made. Both batches were cooked in solutions with a range of pH. The results are shown in Table 2.

The approximately constant difference between the marks awarded to the two sets of strips is to be attributed to melanin which is unaffected by changes of pH in this range. This is direct evidence that the stem-end blackening pigment is not of the melanin

type; indeed the proportion of both present may be readily estimated by alteration of the pH of the tissue.

The effect of pH on an extract of stem-end blackening pigment. The same degree of discoloration, due to stem-end blackening, may occur at pH values ranging from 4 to 7 in different stocks. If this discoloration is due to varying amounts of one pigment in different stocks, then this pigment must (a) be grey in colour when at pH values of from 4 to 7 and (b) increase progressively in intensity of greyness over the same range of pH. This would result in strips from a stock with a low content of pigment being graded as nearly white until they attained a high pH value and conversely.

To test this an aqueous extract of cooked dried strips from a blackening stock of potatoes was

partially purified by repeated precipitation of impurities with ethanol and concentration at 40° under reduced pressure. A solution was thus obtained which was pale brown-yellow when acid, brownish blue in the pH range of about 4-7.5 and bright yellow-brown when alkaline (pH 11-12). Portions of this were adjusted to pH values ranging from 1.5-9.5 by the addition of HCl or NaOH. The absorption of light by these solutions was estimated with a Zeiss Pulfrich photometer using a range of colour filters. The curves in Fig. 2 show the values

Fig. 2. The relation between the pH of a solution of stem-end blackening pigment and the absorption coefficient for three wave-bands. Wave-bands of violet filter <460 m μ maximum (approx.) 420 m μ . Wave-bands of green filter 507-555 m μ maximum (approx.) 540 m μ . Wave-bands of red filter >640 m μ maximum (approx.) 680 m μ .

of the absorption coefficient for three wave-bands (violet, yellow-green and red) as related to the pH of the solution. The graph shows that the composition of the transmitted light varied little over the pH range of 1.5-7.5, while at pH values above this the solutions became relatively redder. The intensity of coloration, shown by the magnitude of the absorption coefficient, decreased rapidly from pH 9.5 to 6.5 and thereafter more slowly.

As a further check on the relative effects of change of pH of the solution and of concentration of the pigment on the composition of the transmitted light, a solution was diluted five times at a pH of 8.5 and

compared with an undiluted solution at a lower pH. The results are shown in Table 3. The discrepancies in the two sets of readings are well within the experimental error.

Table 3. *Relative effects of change of pH and concentration on composition of transmitted light*

Filter used	Absorption coefficient	
	Diluted solution pH 8.5	Undiluted solution pH 3.7
Violet	0.42	0.42
Blue	0.30	0.31
Blue-green	0.23	0.24
Green-blue	0.19	0.18
Yellow	0.17	0.16
Light red	0.16	0.15
Dark red	0.11	0.12

Extracts were prepared from cooked strips of a blackening stock of Golden Wonder and of Kerr's Pink potatoes. The absorption of light by solutions of these at pH values from 6.5-12.0 was determined. Over the whole of this range and for seven wave-bands of light the differences in absorption were small, such as could well have been produced by traces of other pigments (melanin, etc.). Thus, again, there is no evidence that more than one pigment is concerned in stem-end blackening.

The behaviour, therefore, of relatively pure extracts of the pigment accords with the assumption that greyiness of cooked potato is due to the presence of one pigment in different amounts in different stocks. This view is further supported by the similarity in shape of the curves in Fig. 1 and of those in Fig. 2.

SUMMARY

1. The greyiness of cooked potato has been estimated at a range of pH values. A rapid increase in greyiness with pH above a certain value, characteristic of each stock, was observed. The absorption of light by a water extract of stem-end blackening pigment at a range of pH values has been measured.

2. It is concluded that stem-end blackening is caused by a single pigment whose colour is reversibly affected by pH and that variation in the degree of blackening between different stocks is due to the presence of different amounts of this pigment.

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Chromatography in Aqueous Solution with Mineral Precipitates Insoluble in Water

1. APPLICATION TO THE SEPARATION OF AMINO-ACIDS BY ADSORPTION ON Ag_2S

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The application of chromatography in aqueous solution has not yet been fully explored, owing to the novelty of the technique and to the empirical character of the work to which it has given rise. Experimental considerations have so far limited its use to a fairly miscellaneous choice of adsorbents, the composition and chemical properties of most of which are not well known (silicates, activated carbons, synthetic resins, etc.). The only exception is alumina. Silica gel, which also is a chemically well-defined adsorbent, in most cases functions only as a support (Martin & Synge, 1941). The time has now come to free this technique from its present empiricism and to define its sphere of application. We hope that this work will be a contribution in this direction.

At first sight, the utilization of the mineral precipitates commonly available in the laboratory, in chromatography, does not seem to be of particular interest. Alumina appears to constitute a special case; its adsorbent properties with respect to cations, and perhaps to anions, are due to the impurities which it contains. The impurities can accentuate corrosion during activation of the adsorbent by an acid and thus considerably increase the surface. The fact that the use of the mineral precipitates has so far been systematically avoided is equally significant. According to Schwab (Böttger, 1939), they are not suitable, on account of their lack of selectivity and of their too weak adsorbing power.

To assess the interest of the question, however, it suffices to compare the adsorbent properties of the usual adsorbents and of mineral precipitates. The latter, prepared in presence of an excess of one

of the ions of the lattice, show a heterogeneous surface structure entirely similar to that of an 'acid' column of alumina (Fajans & von Beckerath, 1921; Kolthoff, 1934); their adsorbent properties are very well known, thanks to studies in adsorption (Fajans, 1941; Fajans & Erdey-Gruz, 1931; Kolthoff & MacNevin, 1936; Kolthoff & Rosenblum, 1933 *a, b*; Kolthoff, Von Fischer & Rosenblum, 1934), in analytical chemistry (Fajans & Wolff, 1924; Burnstein, 1927; Kolthoff & Lingane, 1936), in colloidal chemistry (Verwey, 1933; Verwey & Kruyt, 1934), to studies utilizing radio-active elements (Hahn, 1926, 1930; Paneth, 1914), and studies on photographic sensitivity (Sheppard, Lambert & Walker, 1939; Trillat & Aubry, 1941; Trillat & Merigoux, 1941). It must be remembered that the determining factor of the adsorption is the insolubility of the adsorption compound which the adsorbed ion forms with an ion of the opposite sign, which is part of the lattice or is itself adsorbed on it (Fajans & von Beckerath, 1921). After the precipitate is washed, the amount of excess ion of the lattice adsorbed is very slight, even in the case of substances which are sparingly soluble; the adsorption phenomena to which they give rise are only observable with solutions of radio-active elements (Kolthoff, 1934, 1936). We shall show, nevertheless, that their adsorptive power is still sufficient to allow of their utilization in chromatography in aqueous solutions.

We have attempted to separate mixtures of natural amino-acids by chromatography on a precipitate of silver sulphide.* Various chromato-

* A preliminary note on this subject has already been published (Hamoir, 1943).