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Reactivity of Vegetables Towards Sulphur Dioxide

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ABSTRACT

When Brussels sprouts, cabbage, carrot, peas and potato are dried in air at 80°C in the presence of sulphur(IV) oxospecies, S(IV), 51 ± 6% of the additive is lost, irrespective of the vegetable or the amount of S(IV) in the final product when present in the following amounts: Brussels sprouts, 800–2000 mg SO_2/kg; cabbage, 260–1900 mg SO_2/kg; carrot, 270–1300 mg SO_2/kg; peas, 250 mg SO_2/kg; potato, 32–220 mg SO_2/kg.

The reactivity, towards S(IV), of aqueous extracts of different vegetables is compared and assessed in relation to the total solids, glucose, fructose, amino-nitrogen and Kjeldahl-nitrogen contents of the extracts. It is suggested that the rate-limiting process in the loss of S(IV) during vegetable dehydration is not the reaction of reducing sugars with amines but is possibly some physical process.

INTRODUCTION

An interesting demonstration of the reactivity of sulphur(IV) oxospecies, S(IV), during the dehydration of vegetables is that of Gilbert & McWeeny (1976) who reported that 55–65% of the additive is converted to stable organic products during the dehydration of cabbage, carrot and potato. It is surprising that this loss seems to be independent of the vegetable used. It is

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evident that an important contributor to the loss of S(IV) during vegetable dehydration is its reactions with intermediates in non-enzymic browning (Wedzicha, 1984). The compositions of these vegetables differ considerably with respect to reducing sugar and nitrogen content (Paul & Southgate, 1978; Souci *et al.*, 1981). It is possible, therefore, that the rate-limiting process is similar in each vegetable and may be unrelated to composition with respect to components capable of reacting irreversibly with S(IV).

In many countries, for example, Canada, Denmark, Norway, Sweden and the UK, the legislation concerning the use of S(IV) for the dehydration of different fruits and vegetables is, to a large extent, independent of the chemical nature of the food being dehydrated. In the UK a uniform limit of 2000–2500 mg SO_2/kg is stated for dehydrated vegetables with the exception of potato powder for which the limit is 550 mg SO_2/kg. It is important to assess whether any chemical criteria should be taken into account and different levels of additive be stipulated for individual vegetables. The purpose of this investigation is to examine the reactivity of S(IV) with components of different vegetables.

EXPERIMENTAL

The vegetables used in this study were Brussels sprouts, white cabbage, carrot, peas, potato and swede. All were obtained locally. Cabbage, carrot, potato and swede were cut into slices (2 mm × 10 mm × 10 mm) whilst Brussels sprouts were cut in half and peas were used whole. Wherever possible, reagents were of AnalaR grade and, unless otherwise stated, were obtained from BDH Chemicals Ltd.

Preparation of dehydrated vegetables

Blanching liquor contained 0·1–6·0 g sodium disulphite in 2 litres of solution. Vegetables (100–400 g) were blanched in boiling liquor until they showed a negative test for peroxidase as described by Greensmith (1971). Actual blanching times were 2 min for cabbage, 4 min for carrot, peas and potato and 6 min for Brussels sprouts. The vegetables were drained and their moisture contents determined by oven drying to constant weight at 103 ± 1°C. Their S(IV) contents were determined by the method of Wedzicha & Bindra (1980).

Dehydration of vegetables was carried out to constant weight in aluminium wire mesh trays in a laboratory scale air-dryer at an air temperature of 80°C. Typical drying times were 5–8 h and the moisture and the S(IV) contents of the products were determined as before.

For some experiments, powdered freeze-dried vegetables containing no S(IV) were required and these were prepared by steam blanching the vegetables, until the peroxidase test was negative, followed by freeze-drying. The products were ground to powders and their moisture contents determined as before.

Preparation of vegetable extracts

Freeze-dried vegetable powder (12·5 g) was mixed with water (300 ml) in a centrifuge bottle. The suspension was shaken for 30 min and centrifuged at 23 000 × *g* for 45 min. The supernatant was filtered using Whatman No. 5 paper and the extraction of the residue repeated twice. The combined extracts were immediately freeze-dried. The solids from four such extractions were dissolved in water and made up to 250 ml. The residue from the extractions was also freeze-dried.

Reactivity of S(IV) in vegetable slurries

A constant weight (0·2–0·8 g) of each freeze-dried vegetable powder was placed into several 5-ml glass ampoules and S(IV) solution (1·0 ml, 5 mM) added, followed by water (4 ml). Air in the headspace was displaced with a stream of nitrogen and the ampoules sealed. For reaction, ampoules were heated in a water bath at 80·0 ± 0·1°C, samples withdrawn at timed intervals and their S(IV) contents determined by the method of Wedzicha & Bindra (1980).

Reactivity of S(IV) towards vegetable extracts

Each vegetable extract was diluted as required and aliquots (4 ml) placed in several 5-ml glass ampoules. Air in the extract and headspace was removed by passing nitrogen and a solution of S(IV) (1·0 ml, 0·05M) added. For reaction, ampoules were heated in a water bath at 80·0 ± 0·1°C and removed at timed intervals for analysis of S(IV). Preliminary studies involved the use of the method of Wedzicha & Bindra (1980) whilst, for the majority of experiments, analysis was carried out by mixing an aliquot (1–5 ml) of an appropriately diluted reaction mixture with a solution of 5,5′-dithiobis(2-nitrobenzoic acid) (DTNB) (50 ml, 1·6 mM) in phosphate buffer (16 mM Na_2HPO_4 + 1·8 mM KH_2PO_4, pH 8·0) and making the volume up to 100 ml with the phosphate buffer. The absorbance of the resulting mixture was measured at 412 nm and concentrations calculated from a standard curve obtained using iodimetrically standardised solutions of S(IV).

Determination of total solids content of extracts

The solids contents of extracts were determined by oven drying and by means of a refractometer. In oven drying the extract was first concentrated to a thick paste on a steam bath in a stainless steel dish and drying to constant weight was then carried out in a vacuum oven (50°C, 100 mm Hg) for 24 h. The refractometer was calibrated using glucose solutions.

Determination of glucose and fructose in vegetable extracts

An enzyme assay kit supplied by Boehringer Mannheim based on hexokinase, glucose-6-phosphate dehydrogenase and phosphoglucoisomerase was used. In order to test for the possible presence of enzyme inhibitors or other unexpected interfering substances in the vegetable extracts a recovery test was carried out after extracts had been spiked with known amounts of glucose and fructose.

Determination of amino groups and nitrogen in vegetable extracts

The amino-nitrogen content of extracts was determined by the method of Satake *et al.* (1960) based on the reaction of amino groups with 2,4,6-trinitrobenzene-1-sulphonic acid (TNBS). Prior to analysis, extracts were diluted so as to contain $<0{\cdot}8\,\mu$mol NH_2 groups per millilitre and the analysis was standardised using glycine. The total nitrogen content of extracts was determined by means of the Kjeldahl method.

Selective removal of components from vegetable extracts

In order to assess the importance of amino and protein nitrogen and of sugar content on the reactivity of extracts towards S(IV), extracts were fractionated as follows: the extract (10–100 ml) was acidified to pH 2 with H_2SO_4 and applied to a column (bed volume 60 ml) of Dowex 50W-X8 anion exchange resin in the H^+ form. Neutral components were eluted with water (2 bed volumes) whilst amino compounds were eluted with varying volumes (1–7 bed volumes) of ammonia solution (1M and 2M). In each case column effluent was evaporated to dryness under reduced pressure at 40°C. In the case of the amino fractions the residue was redissolved in water and evaporated, three times, to ensure removal of ammonia. Extracts were analysed for glucose, fructose and amino groups as described above. In order to assess the importance of macromolecules to the reactivity of S(IV) with extracts, solutions of extracts (10–50 ml) were dialysed against water using visking tubing for 3 days. The total volume of dialysate was 9 litres

(3 × 3 litres) which was concentrated under reduced pressure at 40°C and finally subjected to the separation described above.

The reactivity of S(IV) towards fractions was assessed by dissolving the solid products in an appropriate amount of water, adjusting the pH and adding any other reagent, and measuring the rate of reaction with S(IV) as described for whole extracts above.

RESULTS

Loss of S(IV) on dehydration of vegetables

The distillation method used for the analysis of S(IV) in dehydrated sulphited vegetables and some extracts involves a small-scale distillation followed by trapping of sulphur dioxide in the distillate, in a solution of DTNB reagent at pH 8·0. The analysis is based on the quantitative cleavage of the disulphide bond in the reagent to form a highly absorbing thiol (E_{max} at 412 nm = 15 500 M^{-1} cm^{-1}). The technique was validated in the present work using standardised solutions of S(IV) (total amount of S(IV) analysed of the order of 10^{-6} mol) when the recovery was 96 ± 2% (mean ± standard deviation of six measurements). Repeated analysis of commercial dehydrated cabbage (0·2 g samples) gave 1534 ± 44 mg SO_2/kg (mean ± standard deviation of six measurements). The coefficient of variation of 3% is considered excellent for an analysis of this type. According to Wedzicha & Bindra (1980) the results obtained when dehydrated vegetables are analysed are very similar to those obtained by the conventional Monier–Williams distillation procedure and the technique therefore measures total S(IV).

The amounts of S(IV) present in Brussels sprouts, cabbage, carrot, peas and potato before and after dehydration are summarised in Table 1. In the cases of Brussels sprouts, cabbage and carrot, the extent of browning in the final product increased as the final S(IV) content fell below 1000 mg SO_2/kg. The amounts of S(IV) reported have been calculated after taking into account the measured moisture contents of the vegetables and the experimental error associated with this value includes any variation in measured water content as well as S(IV) content. Typically, five identical measurements on cabbage gave an S(IV) content of 2938 ± 370 mg SO_2/kg before dehydration and 1555 ± 68 mg SO_2/kg after dehydration. In the case of peas the values from four identical measurements were, respectively, 4170 ± 527 mg SO_2/kg and 2500 ± 57 mg SO_2/kg. Whilst the coefficients of variation for the measurements on the dehydrated product are, respectively, 4·4% and 2·3%, those for the measurements on the vegetables

TABLE 1
Uptake of S(IV) on Blanching Vegetables in Sulphite Liquor and Loss of S(IV) on Dehydration in Air at 80°C

	Before dehydration			*After dehydration*		
	Weight $Na_2S_2O_5$ (g) in 2 litres of blanching liquor	*Moisture content* (%)	*SO_2 content* (*mg kg^{-1}*)	*Moisture content* (%)	*SO_2 content* (*mg kg^{-1}*)	*Loss of S(IV)* (%)
Cabbage	0·3	90·2	493	4·8	256	48
Cabbage	0·4	93·5	672	12·4	371	45
Cabbage	0·6	91·8	1 683	10·6	787	53
Cabbage	1·0	95·8	3 859	10·3	1 888	51
Cabbage	2·0	91·6	2 938	5·5	1 555	47
Cabbage	6·0	95·4	1 587	14·9	749	53
Carrot	0·3	93·3	569	8·4	269	53
Carrot	0·5	92·2	486	8·7	256	48
Carrot	6·0	92·9	2 931	10·9	1 338	54
Peas	1·0	82·5	461	8·2	250	46
Potato	0·2	78·9	70	8·5	32	55
Potato	0·6	83·0	371	6·1	218	41
Sprouts	2·0	88·5	1 907	8·5	800	58
Sprouts	4·0	89·0	5 395	7·7	1 971	63

before dehydration are somewhat larger (12·6%) and reflect a much greater uncertainty in the measurement of water content and, perhaps, the variability in draining excess blanching liquor. It is surprising that the uptake of S(IV) by the vegetable on blanching is not always correlated with the concentration of S(IV) in the blanching liquor but it is very striking that the fractional loss of S(IV) on dehydration is approximately constant despite a 77-fold range of initial S(IV) content, the use of five different vegetables, the different degrees of browning and the variable moisture content of the final product.

The amount of S(IV) which has undergone reaction at the end of dehydration is the integral, over the change in concentration, water activity and temperature, of the rate equation for the loss of S(IV), as dehydration proceeds. The observation that the fractional loss of S(IV) is independent of S(IV) concentration suggests that this process must be of overall first order since the fractional conversion, f, of reactants to products in a first order process after a time, t_f, is given by:

$$f = 1 - \exp(-kt_f)$$

where k is a rate constant. For the case considered here, k would need to be replaced by $\int k\,dt$ but the fractional loss after a given time remains independent of concentration.

Reaction of S(IV) with vegetable extracts

It is possible that the rate of loss of S(IV) during vegetable dehydration is controlled by physical factors such as diffusion of reactants which could well give rise to observed first order behaviour. In order to test this possibility an attempt was made to measure the rate of loss of S(IV) in slurries of the vegetables so that the physical barriers may be modified. The variation in results of repeated identical determinations proved to be of the same magnitude as the changes in S(IV) concentration and an alternative approach of using vegetable extracts was therefore adopted.

The concentration of S(IV) in mixtures of vegetable extract and S(IV) was determined by direct addition of the diluted extract to DTNB reagent. In all cases the extract caused some formation of absorbing thiol in the absence of S(IV), and was attributed to the presence, in vegetables, of naturally occurring thiols which are capable of cleaving the disulphide bonds of the reagent. A blank for the analysis was, therefore, prepared using appropriate amounts of extract and DTNB reagent. The highest blank absorbance was found in the case of cabbage extract. When a reaction mixture consisting of 4 volumes of cabbage extract (equivalent to 20 g freeze-dried cabbage) + 1 volume of 0·05M S(IV) solution was allowed to react at 80°C for 9 h, the amount of residual S(IV) measured by distillation was 96% of that found by direct addition, with coefficients of variation of 9% and 2·5% (six experiments in each case) for distillation and direct addition analysis, respectively. This result also demonstrates that the direct addition method gives the total S(IV) concentration.

A typical set of concentration–time graphs is shown in Fig. 1 for the reaction of S(IV) with cabbage extract. For all vegetable extracts, plots were sufficiently linear to measure rates of reaction. Concentrations of extracts used were specified in terms of the amount of freeze-dried vegetable equivalent to 100 ml extract and Fig. 2 shows the relationship between rate of loss of S(IV) and concentration of extract used. The data fit the rate equation:

$$\text{rate} = k_1 + k_2\,[\text{extract}]$$

where k_1 and k_2 are rate constants. The results for potato extract are not included as no significant correlation between rate and extract concentration was found. In the cases of Brussels sprouts and cabbage extracts, the large intercept suggests a large value of k_1, indicating that some of the

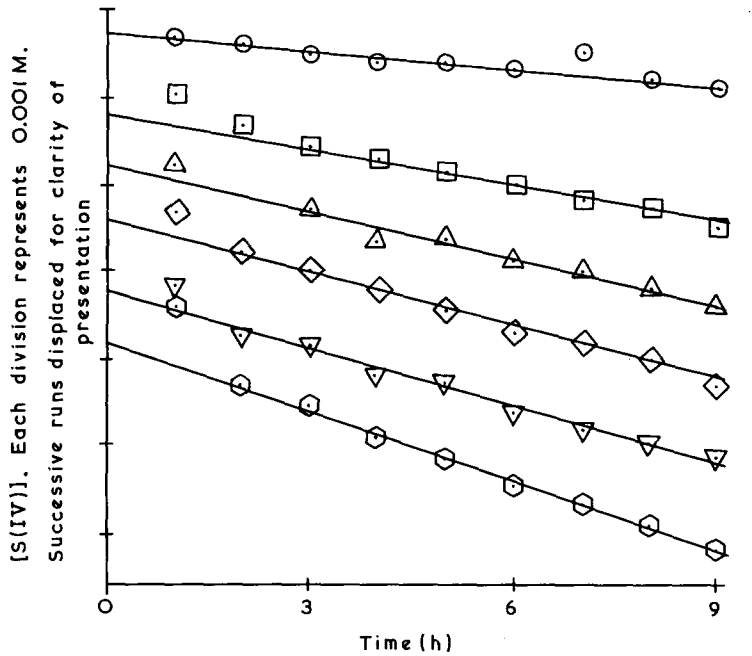

Fig. 1. Typical concentration–time plots for reaction of vegetable extracts with S(IV) illustrated for cabbage extract. Concentrations of extract, expressed as weight of dry cabbage (g) equivalent to 100 ml are as follows: ⊙ 4 g; ⊡ 8 g; △ 10 g; ◈ 12 g; ▽ 16 g; ⊙ 20 g.

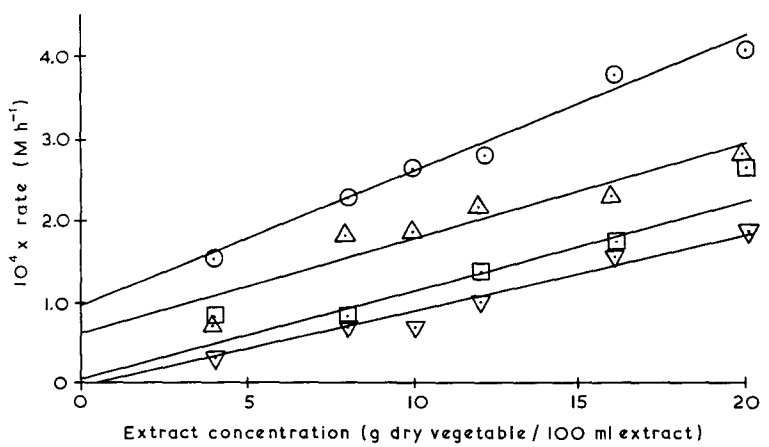

Fig. 2. Relationship between rate of loss of S(IV) and concentration of extract, expressed as weight of dry vegetable (g) equivalent to 100 ml extract for: ⊙ Brussels sprouts, △ cabbage, ⊡ swede, ▽ carrot.

S(IV) is lost through a mechanism which is independent of extract concentration. It is difficult to imagine such a process since no significant loss of S(IV) was observed in control experiments containing no extract. A possible explanation is, therefore, that the kinetics of the reaction at low extract concentration (<4 g dry vegetable/100 ml extract) are different from those at the concentrations studied. The concentration–time data also show that the loss of S(IV) is a biphasic process, particularly for Brussels sprouts and cabbage extracts. When graphs are extrapolated to zero time it is evident that the intercept is always less than the expected initial S(IV) concentration. This discrepancy could be due to a rapid initial reaction, between extract and S(IV), which is essentially over by the time of the first measurement, and is most marked in the case of the Brussels sprouts extract. The dependence of the shortfall of initial S(IV) concentration on the concentration of extract is illustrated for this extract in Fig. 3. The effect is clearly of first order with respect to the concentration of extract and can only be explained by the presence of a highly reactive component in the extract. Measurements of the reactivity of the residue remaining after extraction of vegetables showed the extraction to have been exhaustive.

The units of the rate constant k_2 are unconventional but since its absolute values are of limited significance, the units should best be regarded as arbitrary. The values of k_2 are, however, proportional to the rate of loss of S(IV) per unit weight of freeze-dried vegetable. Values of k_2, alongside the compositions of the extracts with respect to total solids, glucose, fructose,

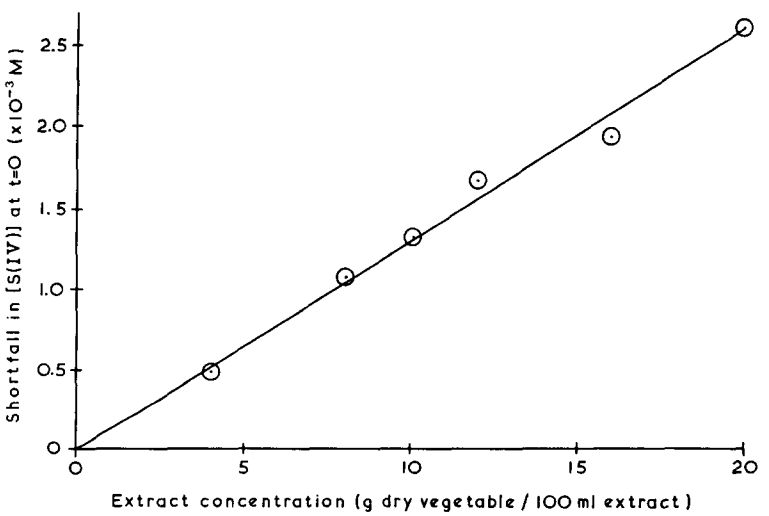

Fig. 3. Relationship between shortfall in [S(IV)] when concentration–time graphs are extrapolated to $t = 0$, and concentration of Brussels sprouts extract, expressed as weight of dry Brussels sprouts (g) equivalent to 100 ml extract.

amino groups and total nitrogen contents, are shown in Table 2. The actual solids contents given are values obtained using the vacuum oven method. The values obtained by refractometry were, respectively, 10·5, 12·0, 12·5, 3·5 and 12·5% for Brussels sprouts, cabbage, carrot, potato and swede extracts, in excellent agreement with those shown in Table 2. In the case of the analyses of glucose and fructose, the recoveries when vegetable extracts were spiked with pure glucose and fructose were greater than 98% and 94%, respectively. In the case of fructose the 94% yield was obtained using the extract of swede; in all other cases the yield was better than 98%. Consequently, there was no evidence of substantial interference to the analysis from components of the extracts. When the results are expressed in terms of the amounts of glucose and fructose in the original vegetable, assuming complete extraction, they are found to be of similar magnitude to published values (Souci *et al.*, 1981).

With the exception of potato, the rate constants are very similar and demonstrate the similar intrinsic reactivities of the components extracted from the different vegetables. There is, however, no significant correlation between the rate constant and any of the concentrations measured. When the rates of loss of S(IV) were plotted as a function of the weight of the solid

TABLE 2

Measured Compositions of Vegetable Extracts (equivalent to 20 g dry vegetable/100 ml extract) and Values of Rate Constants determined from Lines plotted in Fig. 2

	Solids content (%)	*pH*	*Concentration* (*g/100 ml*)	
			Glucose	*Fructose*
Sprouts	10·15 ± 0·03	6·35	1·2 ± 0·3	1·0 ± 0·1
Cabbage	11·63 ± 0·08	6·08	4·5 ± 0·2	3·5 ± 0·2
Carrot	12·99 ± 0·08	6·09	2·6 ± 0·2	2·3 ± 0·1
Potato	3·44 ± 0·02	6·00	0·16 ± 0·01	0·12 ± 0·08
Swede	12·35 ± 0·06	5·82	6·0 ± 0·4	3·8 ± 0·1

	Kjeldahl nitrogen (*matom/100 ml*)	*NH_2 groups content* (*mmol/100 ml*)	*k_2* (*arbitrary units*)	*Correlation coefficient*[a]
Sprouts	47·4 ± 0·9	14·9 ± 1·4	6·13	0·912
Cabbage	14·3 ± 2·7	6·1 ± 0·3	5·68	0·964
Carrot	7·4 ± 0·0	4·4 ± 0·8	5·22	0·940
Potato	16·6 ± 0·4	7·5 ± 1·4	0·10	0·108
Swede	12·6 ± 0·4	7·2 ± 1·1	5·32	0·909

[a] Correlation coefficient of line used to find rate constant.

in each extract used to obtain the results shown in Fig. 2, the rate constants per unit weight of extract showed the same behaviour as those given in Table 2.

Despite the similarity of values of k_2 for all vegetables except potato, the actual reactivities of given concentrations of extracts differ as a result of differing k_1 values. Thus, for the most concentrated extracts, the order of reactivities is:

Brussels sprouts > cabbage > swede > carrot ≫ potato.

It is interesting to note that the total nitrogen content of extracts ranks as follows:

Brussels sprouts > potato > cabbage > swede > carrot

and if the low reactivity of potato is the result of a limiting concentration of reducing sugar then the reactivity of the remaining vegetables is in the same order as the total nitrogen content.

In order to further explore the role of the Maillard reaction in the loss of S(IV), positively charged and neutral components were selectively separated from acidified extracts by means of ion exchange. When extracts were adsorbed onto a sulphonate-type resin (Dowex 50W-X8) in the H^+ form and eluted with water followed by 2M ammonia solution, the recoveries of reducing sugar and amino compound were as shown in Table 3 where the results are from three determinations. The presence of amino compounds in all the reducing sugars fractions is probably inevitable since they could pass through the column as Schiff's bases. In order to assess the amount of amino-nitrogen which was in the form of protein, extracts were dialysed against water when of the order of 10% of the amino groups were retained by the

TABLE 3

Recovery of Glucose and Fructose, and Amino Compounds, when Vegetable Extracts are Fractionated on Dowex 50W-X8 (H^+ form) Ion Exchange Resin

	Recoveries (%)			
	Elution with water		*Elution with 2M NH_4OH*	
	Glucose + fructose	*Amino groups*	*Glucose + fructose*	*Amino groups*
Sprouts	103 ± 2	5·4 ± 0·9	ND	93 ± 1
Cabbage	98 ± 1	1·3 ± 0·1	ND	95 ± 1
Carrot	99 ± 0	3·8 ± 0·6	ND	95 ± 1
Swede	101 ± 2	5·2 ± 0·5	ND	93 ± 1

ND, Not detected.

TABLE 4
Reactivity, Towards S(IV), of Vegetable Extracts before and after Fractionation on Dowex 50W-X8 (H^+ form) Ion-Exchange Resin and after Adding Back Components Removed during Fractionation

Extract fractions	*10^4 × Rate of loss of S(IV)* (M h^{-1})			
	Sprouts	*Cabbage*	*Carrot*	*Swede*
Neutral	2·66	1·78	1·34	1·72
Neutral + glycine	2·66	1·34	1·60	1·50
Amino	2·46	1·14	0·42	0·54
Amino + glucose + fructose	2·84	1·46	0·48	1·34
Whole extract	3·64	2·66	2·14	2·74

dialysis membrane (molecular weight cut-off, 12 000). Kinetic experiments were carried out using the individual fractions and a mixture of the neutral fraction with an amount of glycine equivalent to the amino-nitrogen content of the original extract, and the amino fraction with the appropriate amounts of glucose and fructose added. The rates of loss of S(IV) are shown in Table 4 where they are compared with controls using the original extract. It is evident that in all cases the separated fractions are less reactive towards S(IV) than the original extract but the addition of the appropriate amount of hexose or glycine does not restore the reactivity to that of the extract. Whilst it is known that different amino acids influence the Maillard reaction to different extents, and hence the reactivity of glycine may not be representative of that of the mixture of amino compounds in the extracts, the effect of added glucose and fructose is expected to be most meaningful, but is found to be small. The significant reactivity of each isolated fraction suggests the presence of some other reactive component.

DISCUSSION

Loss of S(IV) on dehydration of vegetables

The results which demonstrate an approximately constant fractional loss of S(IV) when a range of vegetables are dehydrated in air, considerably extended the data of Gilbert & McWeeny (1976) who used a much more limited range of concentrations (1001 and 1744 mg SO_2/kg of cabbage, 198 and 257 mg SO_2/kg of potato and 463 and 662 mg SO_2/kg of carrot, measured in all cases only in the final product). If it is accepted that the fractional loss of S(IV) is independent of the vegetable or level of S(IV)

used, then the results obtained here give a mean loss of $51 \pm 6\%$ (mean $\pm$ standard deviation from fourteen measurements). This standard deviation represents a coefficient of variation of 11·8% which is similar to that found (12·6%) for the repeated determination of S(IV) in S(IV)-treated vegetables before dehydration, when amounts are expressed in terms of the dry weight of the vegetable. The assumption that the fractional loss of S(IV) in these experiments is invariant seems reasonable.

The main difficulty in interpreting the result is that it is independent of the composition of the vegetables. One explanation is that the loss could take place from a surface film of blanching liquor on the vegetable. The mechanism of loss could include release of gaseous SO_2 (which is always in equilibrium with ionic forms of S(IV)) or by autoxidation. The possibility of autoxidation of S(IV) in S(IV)-treated vegetables has not yet been considered in detail and the main problem is that vegetables contain sufficient amounts of simple sugars to act as effective antioxidants. Oxidation at the surface of the vegetable, where the concentration of antioxidant is likely to be the smallest, is the most straightforward way of accounting for the relatively small, but significant, amounts of sulphate ion formed in S(IV)-treated vegetables (Wedzicha *et al.*, 1984). The autoxidation of S(IV) in dilute solutions is, also, a first order kinetic process and, indeed, the amounts of sulphate formed in the dehydration of cabbage, carrot and potato have been found to be proportional to their initial S(IV) contents (Herrera Viloria, 1984).

The effects which take place in surface films depend on surface areas and surface structures. The areas of pieces of cabbage, carrot and potato were of the order of 280 nm^2. If peas are considered to be spheres with average diameters in the range 5–7 mm, their areas are of the order of 20–40 mm^2 whilst it is not possible to estimate the area of the surface exposed to blanching liquor when halves of Brussels sprouts are used. It is clear that the areas of all the surfaces are not the same. It is also difficult to imagine how at least half of the additive taken up by the vegetable can be held in a surface film. These difficulties could be reconciled if there is some transport of S(IV), from within the vegetable to the surface film, as the surface concentration is depleted. If this takes place by way of diffusion then it is expected to obey first order kinetics with respect to S(IV). Since the diffusion coefficients for small molecules are likely to be of similar magnitudes within the different vegetables, an invariant fractional loss of S(IV) during the drying operation can be expected from such a mechanism. This approach still does not explain the high yields of stable organic S(IV)-derived products (Gilbert & McWeeny, 1976) and is inconsistent with the observed low yields of sulphate ion, and it is suggested that internal diffusion of S(IV) to sites of organic reactant is another, and perhaps more important, limiting factor.

Reaction of S(IV) with vegetable extracts

The concentrations of extract and S(IV) used in kinetic measurements on Brussels sprouts, cabbage, carrot and swede extracts, were based on the relative amounts of vegetable and S(IV) which may be present during dehydration. Since 100 ml of extract is equivalent to 20 g freeze-dried vegetable, a mixture of 4 volumes of extract with 1 volume 0·05M S(IV) solution is equivalent to adding S(IV) to the original vegetable at approximately 4000 mg SO_2/kg vegetable. The actual concentration of extract was based on the amount of water required to rehydrate the vegetable to nearly 90% water content. The same concentration of S(IV) was used in the case of potato extract, for comparison.

Kinetic experiments, in which the rate of loss of S(IV) was measured, showed that the rate is of first order with respect to extract concentration. This was an unexpected finding since it is generally thought that irreversible binding of S(IV) is due largely to its inhibition of Maillard browning (Wedzicha, 1984) and the rate of loss of S(IV) in the S(IV)-inhibited Maillard reaction of glucose and glycine is of first order with respect to glucose and glycine (Wedzicha & Vakalis, 1988). If the reason for the loss of S(IV) in vegetable extracts is its inhibition of Maillard browning, then the reaction would have been of second order with respect to extract concentration. Further evidence which reduces the importance of Maillard browning is the observation that removal of amino compounds, or reducing sugars, from extracts does not cause the extract to become unreactive towards S(IV); instead, the rate of reaction is only reduced. Also, replacing the removed component with a pure amino compound or reducing sugar does not restore the reactivity to that of the original extract.

The main evidence supporting the involvement of the Maillard reaction is that the ranking of actual reactivities of the different vegetable extracts is similar to that of their Kjeldahl-nitrogen contents. However, the observation that, despite at least a two-fold difference in the rates of reaction of extracts of Brussels sprouts and carrot at the highest concentration used, the fractional loss of S(IV) on dehydration of these vegetables is similar, suggests that the reaction of the components of the extracts does not control the loss of S(IV) during dehydration.

It is well known that Brassica species contain large amounts of disulphide components which are capable of reacting with sulphite ion to form *S*-sulphonates which are not decomposed under Monier–Williams distillation analysis conditions. In dehydrated cabbage, for example, it has been suggested that some 30% of the free + bound S(IV) is in the form of *S*-sulphonates (Wedzicha *et al.*, 1984). The reaction of disulphide with S(IV) is of first order with respect to disulphide and S(IV) (Parker & Kharasch, 1959)

and kinetic measurements when the concentration of extract is varied with S(IV) concentration being kept constant should give rise to observed first order behaviour. Such reactivity could also account for the initial step in biphasic behaviour of concentration–time plots.

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