Food Chemistry **15** (1984) 141–155

Recent Developments in the Understanding of the Chemistry of Sulphur(IV) Oxospecies in Dehydrated Vegetables

B. L. Wedzicha, O. Lamikanra,
J. C. Herrera & S. Panahi

Procter Department of Food Science, University of Leeds,
Leeds, LS2 9JT Great Britain

(Received: 17 May, 1984)

ABSTRACT

The understanding of the mechanism of action of sulphur(IV) oxospecies as an additive to dehydrated foods is complicated by the low water activity environment and the possible interconversions between sulphur(IV) oxospecies. An analytical procedure, involving combustion analysis, Monier-Williams analysis and the determination of sulphate ion, shows significant differences in ionic composition of the additive in dehydrated carrot and cabbage, blanched at pH 5 and pH 9–10 respectively, before dehydration. A kinetic model for the sulphite-inhibited Maillard reaction is discussed in relation to dehydrated vegetables and it is possible that the importance of hydroxysulphonate adducts in the inhibition of browning is greater in the dehydration of vegetables than in model systems composed of relatively dilute solutions of reactants.

The possible involvement of sulphur-oxo free radicals in sulphited food systems has received little attention in the past. Solutions of sulphur(IV) oxospecies undergoing autoxidation are able rapidly to convert β-carotene to products containing 10 to 15 atoms of oxygen per β-carotene molecule when experiments are carried out in homogeneous solution. Significant differences exist between such homogeneous reactions and the heterogeneous systems formed when hydrocarbons are dispersed in foods. The conditions under which such systems are susceptible to 'sulphite-mediated oxidation' are discussed in order to reconcile the apparent anti-oxidant effect of the additive in many food systems with the pro-oxidant effect observed in model systems.

Food Chemistry 0308-8146/84/$03·00

INTRODUCTION

The ability of sulphur(IV) oxospecies, S(IV), to take part in a number of diverse chemical reactions by heterolytic and homolytic mechanisms is illustrated by the papers of Goodall (1984), Yang (1984) and Zoltewicz *et al.* (1984). It is not surprising, therefore, that the amount of S(IV) which may be recovered from a food to which it has been added is generally less than 100% and decreases with time, indicating chemical reactivity in food. This effect is very marked when the additive is used for the preparation of dehydrated vegetables, where its purpose is to control non-enzymic browning reactions. This application is of particular interest since the amounts of the additive which are required for successful inhibition of browning during dehydration, and on subsequent storage, represent the highest levels permitted in most foods. For example, residues of S(IV) of up to 0·031 mol kg^{-1} (2000 ppm SO_2) expressed in terms of dry weight are permitted in dehydrated vegetables in the UK, with the exception of cabbage and potato, for which the respective limits are 0·039 and 0·0086 mol kg^{-1} (2500 and 550 ppm SO_2). Furthermore, the conditions of elevated temperature, high concentration and ample supply of oxygen prevailing during air-dehydration are conducive to reaction between S(IV) and substrates in food, autoxidation of S(IV) and the formation of reaction products which may subsequently act as substrates for reaction with S(IV). The latter is illustrated by the formation of intermediates in non-enzymic browning reactions. The reactivity of S(IV) during vegetable dehydration is adequately demonstrated by Gilbert & McWeeny (1976) who report that well over half of the additive is lost during the dehydration of cabbage, carrot and potato. The products of reaction are mainly organic, although a small amount of inorganic sulphate is also formed.

Partially dehydrated and dehydrated foods are concentrated systems which are difficult to define chemically. This is unfortunate since the known preservative action of S(IV) is dependent on the nucleophilicity of sulphite ion, and the state of the additive with respect to its various ionic forms is therefore an important parameter of the system. The mechanism of the inhibition of non-enzymic browning in model systems is well understood, but its applicability to dehydrated vegetables has not been rigorously tested. Work to resolve some of these fundamental issues is taking place, and recent developments are reported in this paper.

Perhaps the most exciting new possibilities for chemical reactions of

S(IV) in foods arise from the homolytic reactions discussed by Yang (1984) in a variety of model systems, and the systems considered by Goodall (1984) which may be applicable at low water activities. The extrapolation of the findings concerning 'sulphite-mediated oxidations' to foods leads to serious implications concerning the oxidative stability of sulphited foods. The applicability of these results to sulphited vegetables is discussed in the final section of this paper.

CHEMICAL FORMS OF SULPHUR(IV) OXOSPECIES IN FOODS

General considerations

When S(IV) is added to foods, it is considered to exist in three forms:

(a) free S(IV), that is the additive which is present as gaseous or aqueous sulphur dioxide, hydrogen sulphite, sulphite or disulphite ion;
(b) reversibly bound S(IV), that is the additive which is in reversible combination, as hydroxysulphonate adducts, with carbonylic constituents of food and which may be released during Monier-Williams distillation analysis (Monier-Williams, 1927), or by raising the pH of the system;
(c) irreversibly bound S(IV), which represents that additive which can no longer be measured as free or reversibly bound.

In dilute solution the concentration of the oxospecies making up free S(IV) may be calculated from the pH of the system given the dissociation constants of 'sulphurous acid' ($pK_1 = 1{\cdot}86$, Huss & Eckert, 1977; $pK_2 = 7{\cdot}18$, Smith & Martell, 1976; at 25 °C). Insufficient activity coefficient data are available to predict the behaviour at high concentration. Increasing ionic strength reduces the value of the pK of hydrogen sulphite ion, a value of 6·25 being reported in 'concentrated salt solution' (Shapiro, 1977). It is likely that hydrogen sulphite ion predominates in many sulphited foods.

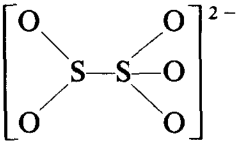
Hydrogen sulphite ion is in equilibrium with disulphite ion according to:

$$2HSO_3^- \rightleftharpoons S_2O_5^{2-} + H_2O$$

and the equilibrium constant for the reaction, given by:

$$K=\frac{[S_2O_5^{2-}]}{[HSO_3^-]^2}$$

has a value of 0·076M^{-1} at 25 °C at infinite dilution (Bourne *et al.*, 1974). In dilute solution, <0·01M, disulphite formation is negligible, but its degree of dissociation decreases with increasing concentration. Additionally, the value of the apparent equilibrium constant increases with increasing ionic strength, and disulphite ion is therefore favoured at high concentrations. At low water activities, when the amount of water present can no longer be neglected in the law of mass action expression, a further enhancement of disulphite ion formation is expected. Therefore, it is anticipated that, in dehydrated vegetables, hydrogen sulphite ion exists mainly in the form of disulphite ion. The implications of this deduction are unknown. Disulphite ion has the following S—S-bonded structure:



and does not bear the lone pair of electrons responsible for the nucleophilicity of sulphite ion, and to which is ascribed much of the heterolytic reactivity of S(IV). Disulphite ion is, therefore, unlikely to act as an efficient nucleophile, and conversion of hydrogen sulphite ion to this form could be one reason for the need for large amounts of the additive for successful preservation of dehydrated vegetables.

The extent to which hydroxysulphonate adducts are formed may be calculated for relatively simple dilute systems, such as wines and ciders (Burroughs & Sparks, 1973), given the concentrations of the carbonyl components and the dissociation constants of the respective hydroxysulphonates. Since the degree of dissociation of hydroxysulphonates decreases with increasing concentration, it is not unreasonable to expect that their formation will be enhanced as water is removed from a sulphited vegetable, but the extent to which this takes place cannot be predicted.

Irreversible combination of S(IV) with food components is considered to be synonymous with the formation of organic sulphonates and inorganic sulphate ion. Both C- and S-sulphonates have been identified in foods (Thewlis & Wade, 1974; Wedzicha & McWeeny, 1974), whilst sulphate is formed in small quantities (Mangan & Doak, 1949).

When S(IV) has undergone partial reaction with components of foods which are subsequently dehydrated it is therefore expected that the S(IV)-derived mixture will contain the following organic and inorganic species:

Organic	*Inorganic*
hydroxysulphonates	sulphate
C-sulphonates	sulphite
S-sulphonates	disulphite

It is assumed that, at the pH of food, all these components will exist as metal ion salts and that no significant amount of hydrogen sulphate ion is formed.

Analysis

It is evident that the only method available to establish the state of S(IV) in dehydrated vegetables is that of direct analysis, this also being restricted to methods which do not involve dissolving the sample in water since rapid interconversion between ionic species is possible in aqueous solution. This condition may be satisfied by combustion analysis. Partial resolution of the ionic components of dehydrated sulphited vegetables may be achieved by subjecting samples to the following analyses:

(a) combustion of the sample in oxygen followed by measurement of the amount of sulphur present in the gaseous products and in the residue;
(b) measurement of the recoverable S(IV) when samples are analysed by the Monier-Williams technique;
(c) measurement of the amount of sulphate ion present.

In this work the analyses were carried out on vegetables which had been dehydrated in the presence of ^{35}S-labelled additive, thereby simplifying the measurement of sulphur, derived from S(IV), in each of the fractions.

The combustion analysis is based on the observation that gaseous products and residue after the combustion of metal salts of sulphonic acids, including hydroxysulphonates and S-sulphonates, and when disulphites are heated to above 600 °C, contain equal amounts of sulphur. In the case of S-sulphonates this is true only of the sulphur derived from the sulphonate group. On the other hand, the amount of gaseous product arising from metal sulphites and sulphates is negligible. Therefore, the gaseous product will contain sulphur according to:

$$S_{\text{gas}} = S_{\text{disulphite}} + \tfrac{1}{2}S_{\text{hydroxysulphonate}} + \tfrac{1}{2}S_{\text{C-sulphonate}} + \tfrac{1}{2}S_{\text{S-sulphonate}} \qquad (1)$$

and the residue will contain sulphur according to:

$$\begin{aligned} S_{\text{residue}} = {} & S_{\text{sulphate}} + S_{\text{sulphite}} + S_{\text{disulphite}} \\ & + \tfrac{1}{2}S_{\text{hydroxysulphonate}} + \tfrac{1}{2}S_{\text{C-sulphonate}} + \tfrac{1}{2}S_{\text{S-sulphonate}} \end{aligned} \qquad (2)$$

where each quantity refers to molar amounts of the respective sulphur-containing compound, and only the sulphonate group of S-sulphonates is considered. The amount of sulphur which may be recovered by the Monier-Williams distillation technique is given by:

$$S_{\text{Monier-Williams}} = S_{\text{sulphite}} + 2\,S_{\text{disulphite}} + S_{\text{hydroxysulphonate}} \qquad (3)$$

Combination of eqns (1), (2) and (3) gives:

$$S_{\text{residue}} - S_{\text{gas}} = S_{\text{sulphate}} + S_{\text{sulphite}}$$

and

$$S_{\text{total}} - S_{\text{Monier-Williams}} = S_{\text{sulphate}} + S_{\text{C-sulphonate}} + S_{\text{S-sulphonate}}$$

where S_{total} is the sum of the amounts of sulphur in the gaseous product and residue. Our present work is concerned with the specific measurement of the formation of C-sulphonates, and the contribution from S-sulphonates was eliminated using a modified Monier-Williams distillation procedure. This is based on the exchange reaction between S—^{35}S-sulphonate and inactive sulphite ion as follows:

$$\text{RS—}^{35}\text{SO}_3^- + \text{SO}_3^{2-} \rightleftharpoons {}^{35}\text{SO}_3^{2-} + \text{RS—SO}_3^-$$

For analysis, samples of dehydrated vegetables containing labelled additive were allowed to exchange with a large excess of inactive sulphite ion at pH 8; the mixture was acidified and sulphur dioxide was recovered by distillation. Under these conditions the amount of sulphur recovered is given by:

$$S_{\text{recovered}} = S_{\text{Monier-Williams}} + S_{\text{S-sulphonate}}$$

Analysis of sulphate ion was carried out by an isotope dilution technique.

The results of analysis of two dehydrated vegetable samples which require significantly different processing conditions are summarised in Table 1. The amount of S(IV) incorporated at the time of blanching was in the range 0·019–0·023 mol kg^{-1} (1200–1500 ppm SO_2) on a dry weight basis. Cabbage was blanched at a relatively high pH of 9–10 to preserve the green colour and showed a much higher level of sulphite ion than did carrot, which was blanched at approximately pH 5. In the case of the cabbage sample, the amount of sulphur shown to be in the form of hydroxysulphonate + disulphite + S-sulphonate is close to the difference between the amounts recovered by conventional Monier-Williams analysis and the modified procedure using exchange. Therefore, the major component responsible for some 30% of the added S(IV) is S-sulphonate. Indeed, cabbage contains more than sufficient dimethyldisulphide to account for this value (Dateo *et al.*, 1957). The absence of a large amount of hydroxysulphonate and disulphite ion is consistent with the high pH. In the case of carrot the amount of sulphite ion present is negligible as expected. Iodimetric determination of reversibly bound S(IV) shows 30% of the added S(IV) to be in the form of hydroxysulphonates, suggesting that some 50% is in the form of disulphite + S-sulphonate. Since the sulphur content of carrot is low, disulphite ion is the predominating species, consistent, again, with the pH of the environment.

TABLE 1

Results of Analysis of S(IV) and S(IV)-derived Products in Dehydrated Cabbage and Carrot. (The amount of S(IV) added prior to dehydration was in the range 0·019–0·023 mol kg^{-1} (1200–1500 ppm SO_2) expressed on a dry weight basis.)

Species	*% Conversion*	
	Cabbage	*Carrot*
Sulphate	8·7 ± 0·8	10·0 ± 1·0
Sulphite	28·0 ± 2·0	3·0 ± 8·0
C-sulphonate	34·3 ± 0·3	5·0 ± 4·0
Disulphite Hydroxysulphonate S-sulphonate	29·0 ± 5·0	81·0 ± 1·0

INHIBITION OF MAILLARD BROWNING BY SULPHUR(IV) OXOSPECIES

Mechanism of inhibition

The mechanism of the Maillard reaction and its inhibition by S(IV) have been the subjects of several reviews (Reynolds, 1963, 1965; McWeeny *et al.*, 1974; McWeeny, 1981). The major pathway in browning is the amine-assisted dehydration of aldoses to 3-deoxy osuloses which may subsequently dehydrate to 3,4-dideoxy osulos-3-enes. The latter are the most reactive intermediates with respect to colour formation, which is accelerated by the presence of amines. If the aldose is glucose, then the corresponding intermediates are 3-deoxyhexosulose (DH) and 3,4-dideoxyhexosulos-3-ene (DDH).

The reaction of glucose with glycine is often taken as a model of Maillard browning. As this reaction proceeds in the presence of S(IV), two significant changes in the extent of combination of the additive take place. First, the amount of reversibly bound S(IV) increases with time, suggesting that carbonyl compounds which bind the additive more strongly than does glucose are generated. Secondly, some S(IV) becomes irreversibly bound (McWeeny *et al.*, 1969). The irreversible binding is the directed 3,4-addition of HSO_3^- to the double bond of DDH leading to 3,4-dideoxy-4-sulphohexosulose (DSH) (Knowles, 1971). Reversible and irreversible binding may be accounted for by means of the simple kinetic model shown in Fig. 1 (Wedzicha, 1984). In this scheme, I1 and I2 are unspecified intermediates, and k_0 and k_1 denote zero order and first order rate constants respectively. This model is applicable when the concentrations of glucose and glycine are large compared with that of S(IV) and indicates that the component responsible for the increased reversible binding of S(IV) as the reaction proceeds is DSH. This result shows that the rate of formation of DSH is independent of the

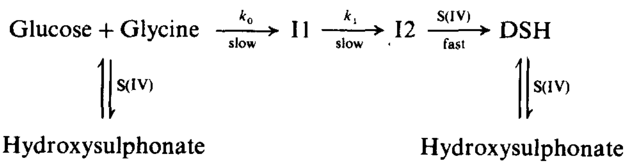


Fig. 1. Kinetic model for the reversible and irreversible binding of S(IV) in the system glucose (1M) + glycine (0·5M) + S(IV) (0·039M) at pH 5·5 and 55°C (Wedzicha, 1984).

concentration of S(IV); there is no evidence that kinetically significant interactions between precursors of DSH and S(IV), which would reduce the rate of formation of DSH, are taking place. Neither is there any evidence that the concentration of S(IV) is rate limiting at any stage.

Inhibition of browning in foods

It is clear that S(IV) inhibits the non-enzymic browning of vegetables during dehydration, but the extent to which the inhibition of browning contributes to the loss of S(IV) has not been established. Qualitative analysis reveals the presence of 3,4-dideoxy-4-sulpho osuloses arising from the inhibition of Maillard and the related ascorbic acid browning in dehydrated cabbage and swede (Wedzicha & McWeeny, 1974, 1975). Quantitative analysis data are limited. The amount of these sulphonates formed during the dehydration of swede represents a conversion of only 0·42 mmol kg^{-1} S(IV) (27 ppm SO_2) for a residual S(IV) content of 0·018 mol kg^{-1} (1140 ppm SO_2). In the case of cabbage, a sample which had been stored for 5 years contained sulphonates equivalent to the reaction of some 0·013 mol kg^{-1} S(IV) (800 ppm SO_2), all amounts being expressed on a dry weight basis (Wedzicha & McWeeny, 1975).

We have demonstrated the importance of the Maillard reaction to the loss of S(IV) during the dehydration of cabbage, by the following series of observations:

(a) if freeze-dried unsulphited cabbage is extracted with water, the extract is reactive towards S(IV). This extract may be rendered unreactive by passing it through a column of cation exchange resin in the H^+ or Na^+ forms. Such treatment removes amino-compounds which participate in Maillard browning;

(b) if dehydrated cabbage is prepared using ^{35}S-labelled S(IV) as the additive and the distribution of radioactive components is analysed by means of chromatography on DEAE Sephacel (Pharmacia) with gradient elution using sulphuric acid, the chromatogram shown in Fig. 2 is obtained. This shows the same components as a chromatogram obtained for the reaction products in a mixture of aqueous extract of unsulphited cabbage (from (a) above) and ^{35}S-labelled S(IV) which had been allowed to react for 6 h at 80 °C. Similar chromatograms are also obtained when model systems containing glucose, glycine and ^{35}S(IV) are allowed to react and are subjected to chromatography.

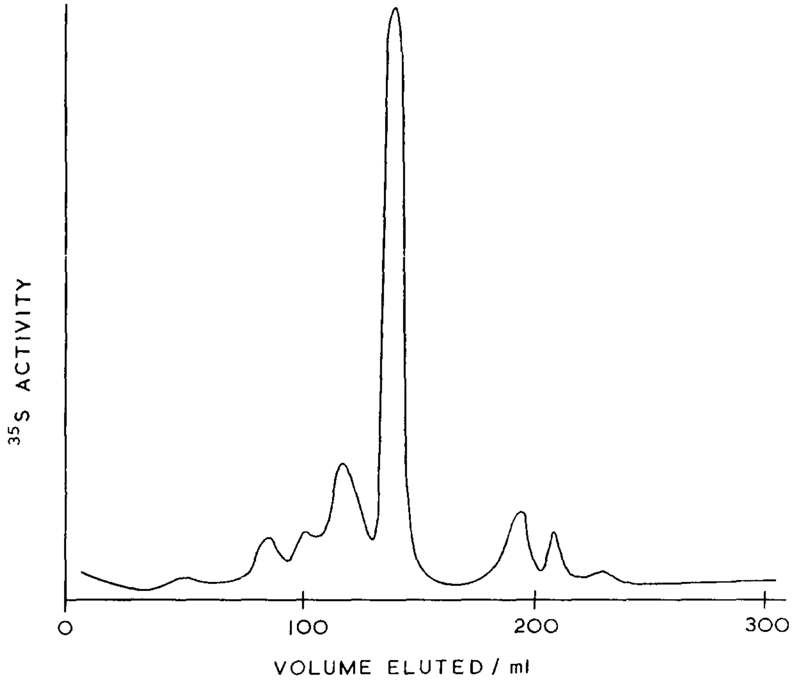


Fig. 2. Separation of S(IV)-derived reaction products in dehydrated cabbage prepared using ^{35}S-labelled additive. Separations were carried out on DEAE Sephacel with a sulphuric acid gradient.

Preliminary data show that, unlike model Maillard browning systems, the yield of C-sulphonate in vegetable dehydration is dependent on the amount of additive used. When used for the dehydration of potato, the amount of S(IV) which is added is sufficiently low to be rate-limiting as far as C-sulphonate formation is concerned. There are indications that the use of large amounts of the additive for the dehydration of carrot ($>0{\cdot}04\,\text{mol}\,\text{kg}^{-1}$, >2500 ppm SO_2) and cabbage ($>0{\cdot}06\,\text{mol}\,\text{kg}^{-1}$, >3900 ppm SO_2) leads to a reduction in the amount of C-sulphonate which is formed. This observation may be reconciled by noting that circumstantial evidence for the existence of the hydroxysulphonate of DH is available (Knowles, 1971) and, although such adduct formation was not significant in the relatively dilute system for which the kinetic model shown in Fig. 1 was devised, it may be appreciable in the much more concentrated, partially dehydrated or dehydrated food systems. Such reversible addition to the precursor of DSH could reduce the rate of formation of the latter.

HOMOLYTIC REACTIONS IN FOOD

The possible involvement of sulphur-oxo free radicals in sulphited food systems has been given little attention in the past. The pro-oxidant action of S(IV) as a result of homolytic reactions, in several systems explained by Yang (1984), appears contrary to the general belief that the presence of S(IV) is beneficial to the retention of carotenoids in dehydrated vegetables (Weier & Stocking, 1946; Nutting *et al.*, 1970; Arya *et al.*, 1979), dehydrated fruits (Woodroof & Luh, 1975), and in model dehydrated systems using sulphited cellulose as an adsorbent for β-carotene (Baloch *et al.*, 1977). We (Wedzicha & Lamikanra, 1983) have examined the products arising from the S(IV) mediated destruction of β-carotene referred to by Yang (1984). There is no evidence of sulphonation. Infrared spectra show a characteristic H-bonded OH band, and the increase in polarity as β-carotene is converted to products is well demonstrated by mobility on thin layer chromatograms. The products mixture is complex and can be resolved into at least ten components on alkylated dextran, but there is no evidence of extensive fragmentation or polymerisation. Microanalysis shows that the number of oxygen atoms combined per original β-carotene molecule is 10–15. This amount of oxygen is comparable to that found by Teixeira Neto *et al.* (1981) for autoxidation of β-carotene but, in contrast, the products of the S(IV)-mediated reaction do not show the carbonyl stretching, in the infrared spectrum, observed for autoxidation products (Ouyang *et al.*, 1980). It is likely, therefore, that in the products of S(IV)-mediated oxidation the oxygen exists in the form of hydroxyl groups and possibly also in the form of stable peroxides.

The experiments involving β-carotene and S(IV) were carried out in homogeneous solution according to the method of Peiser & Yang (1979), which required the presence of a large proportion of ethanol (75 % v/v) and a small amount of chloroform as well as water in the solvent to dissolve the organic and inorganic components. The use of such media is surprising in view of the well-known observation that the autoxidation of S(IV) is effectively inhibited by small amounts of alcohols. An unusual observation is that the addition of a catalytic amount of manganese (II) ion and of glycine or other amine overcomes this inhibitory effect provided that the amount of alcohol in the solvent is large (>30% v/v). Kinetic data show that the metal–amine complex is the catalyst for autoxidation under these conditions and e.s.r. studies, after the addition of nitroso-*t*-butane, as spin trap, show that the $SO_2^{\cdot -}$ radical is formed. These features are different from those of normal autoxidation of S(IV) but show some resemblance to the non-aqueous systems considered by Goodall (1984). Lizada & Yang (1981) have been able to oxidise Tween-stabilised emulsions of fatty acids in aqueous solutions of S(IV), where normal autoxidation of S(IV) was taking place. It is not possible to carry out S(IV)-mediated oxidation of *β*-carotene under these conditions unless some chloroform is also added. However, a simple dispersion of vitamin A/alcohol in an aqueous solution of S(IV) containing a catalytic amount of manganese(II) ion is rapidly oxidised in the presence of oxygen. When the vitamin is subjected to S(IV)-mediated oxidation in the ethanolic medium referred to above, the degree of oxygenation is similar to that expected for half of a *β*-carotene molecule. In aqueous dispersion the amount of oxygen introduced is some 30% lower.

It is suggested that an important factor in the S(IV)-mediated oxidation of hydrocarbons as dispersions in an aqueous phase is the ability of free radical intermediates to interact with the substrate. The known free radicals are polar and will, therefore, be solvated; and the degree to which the non-polar substrate for oxidation can interact with the medium, with the help of side-chains, is important. Thus, the ability of vitamin A/alcohol to interact with aqueous media is significantly greater than that of *β*-carotene. A similar effect has been noted in the free radical sulphonation of dodecene (Sakumoto *et al.*, 1975).

Since the S(IV)-mediated oxidation of unsaturated food components is possible in both aqueous solution and in dispersions, the probability of such reactions taking place in foods should now be examined. Oxidation of S(IV) to sulphate undoubtedly takes place in food. This may be to an extent of 20–30% in dehydrated vegetables, as reported by Mangan & Doak (1949), or in the region of 10% as shown in Table 1. There is, however, no report that the presence of the additive enhances oxidative changes in food. It is speculated that the success of S(IV) as an anti-oxidant arises from the physical state of the substrate for oxidation, in contact with an aqueous medium, and the presence of natural, or added, anti-oxidants in the aqueous and non-aqueous phases. The second contribution is demonstrated by the observation that, when *β*-carotene is solvent-extracted from carrot, the crude product is less easily oxidised in the presence of S(IV) than is pure β-carotene. When sulphited foods are packaged in containers which are impermeable to oxygen, residual oxygen in the head space may be removed by oxidation of S(IV). If, during the course of this oxidation, the unsaturated components of the food are protected in some way, for example, by a combination of physical effects and chemical anti-oxidant, the effect of S(IV) will be that of an anti-oxidant with respect to the oxidation of these components.

CONCLUSION

It is evident that any discussion of the fate of S(IV) in foods is centred around a small number of known reaction products which arise from the inhibition of browning reactions, or is concerned with analysis of unspecified sulphonates. The chromatogram shown in Fig. 2 indicates that the product-mixture arising from the inhibition of Maillard browning in a particular dehydrated vegetable (cabbage) is by no means simple, there being eight resolvable components shown. The most abundant component is sulphate ion. The preceding peak is due to DSH. Investigation of the other fractions reveals that they do not exchange sulphur with a solution of sulphite ion and are presumably not hydroxysulphonate adducts. S(IV) does not appear on this chromatogram; it is oxidised to sulphate during the work-up procedure. It is also intriguing, but not shown clearly on the chromatogram in Fig. 2, that a sulphur-containing component is eluted at the void volume of the column and is presumably not adsorbed. The implication of this result is that the component is not anionic and its formation is a departure from current expectation. There is clearly need for further investigation in this area.

It has been the view of workers engaged in studies on the fate of S(IV) in foods that the reaction products of interest will contain sulphur. It is, however, important not to lose sight of the possibility, as illustrated by the reactions of thiamine and the S(IV)-mediated oxidations, that products containing no sulphur may be formed, the additive acting only as an initiator of later reactions.

ACKNOWLEDGEMENTS

We are grateful to J. Lim who carried out the measurements reported in Table 1 as part of an M.Sc. project.

REFERENCES

Arya, S. S., Natesan, V., Parihar, D. B. & Vijayaraghavan, P. K. (1979). Stability of carotenoids in dehydrated carrots. *J. Food Technol.*, **14**, 579–86.

Baloch, A. K., Buckle, K. A. & Edwards, R. A. (1977). Stability of β-carotene in model systems containing sulphite. *J. Food Technol.*, **12**, 309–16.

Bourne, D. W. A., Higuchi, T. & Pitman, I. H. (1974). Chemical equilibria in solutions of bisulphite salts. *J. Pharm. Sci.*, **63**, 865–8.

Burroughs, L. F. & Sparks, A. H. (1973). Sulphite-binding power of wines and ciders. III. Determination of carbonyl compounds in a wine and calculation of its sulphite-binding power. *J. Sci. Food Agric.*, **24**, 207–17.

Dateo, G. P., Clapp, R. C., MacKay, D. A. M., Hewitt, E. J. & Hasselstrom, T. (1957). Identification of the volatile sulphur components of cooked cabbage and the nature of the precursors in the fresh vegetable. *Food Res.*, **22**, 440–7.

Gilbert, J. & McWeeny, D. J. (1976). The reactions of sulphur dioxide in dehydrated vegetables. *J. Sci. Food Agric.*, **27**, 1145–6.

Goodall, D. C. (1984). The formation of inorganic sulphur oxoanion systems from sulphur dioxide in non-aqueous solvents. *Food Chem.*, **15**, 93–111.

Huss, A. & Eckert, C. A. (1977). Equilibria and ion activities in aqueous sulphur dioxide solutions. *J. Phys. Chem.*, **81**, 2268–70.

Knowles, M. E. (1971). Inhibition of non-enzymic browning by sulphite: identification of sulphonated products. *Chem. Ind.* (*London*), 910–11.

Lizada, M. C. C. & Yang, S. F. (1981). Sulphite induced lipid oxidation. *Lipids*, **16**, 189–94.

Mangan, J. L. & Doak, B. W. (1949). Behaviour of sulphur dioxide in dehydrated vegetables. *NZ J. Sci. Technol.*, **30B**, 232–40.

McWeeny, D. J. (1981). Sulphur dioxide and the Maillard reaction in food. *Prog. Food Nutr. Sci.*, **5**, 395–404.

McWeeny, D. J., Biltcliffe, D. O., Powell, R. C. T. & Spark, A. A. (1969). The Maillard reaction and its inhibition by sulphite. *J. Food Sci.*, **34**, 641–3.

McWeeny, D. J., Knowles, M. E. & Hearne, J. F. (1974). The chemistry of non-enzymic browning and its control by sulphites. *J. Sci. Food Agric.*, **25**, 735–46.

Monier-Williams, G. W. (1927). Determination of sulphur dioxide. *Analyst* (*London*). **52**, 415–16.

Nutting, M. D., Neumann, H. J. & Wagner, J. R. (1970). Effect of processing variables on the stability of β-carotene and xanthophylls of dehydrated parsley. *J. Sci. Food Agric.*, **21**, 197–202.

Ouyang, J. M., Duan, H., Chang, S. S. & Ho, C. T. (1980). Formation of carbonyl compounds from β-carotene during palm oil deodourisation. *J. Food Sci.*, **45**, 1214–17, 1222.

Peiser, G. D. & Yang, S. F. (1979). Sulphite mediated destruction of β-carotene. *J. Agric. Food Chem.*, **27**, 446–9.

Reynolds, T. M. (1963). Chemistry of non-enzymic browning I. The reaction between aldoses and amines. *Adv. Food Res.*, **12**, 1–52.

Reynolds, T. M. (1965). Chemistry of non-enzymic browning II. *Adv. Food Res.*, **14**, 167–283.

Sakumoto, A., Miyata, T. & Washino, M. (1975). Kinetics of the sulphonation reaction of 1-dodecene with sodium hydrogen sulphite. *Chem. Lett.*, 563–6.

Shapiro, R. (1977). Genetic effects of bisulphite (sulphur dioxide). *Mutation Res.*, **39**, 149–75.

Smith, R. M. & Martell, A. E. (1976). *Critical Stability Constants. Vol. 4. Inorganic Complexes.* Plenum Press, New York.

Teixeira Neto, R. O., Karel, M., Saguy, I. & Miztrahi, S. (1981). Oxygen uptake and β-carotene decolouration in a dehydrated food model. *J. Food Sci.*, **46**, 665–9, 676.

Thewlis, B. H. & Wade, P. (1974). An investigation into the fate of sulphites added to hard sweet biscuit doughs. *J. Sci. Food Agric.*, **25**, 99–105.

Wedzicha, B. L. (1984). A kinetic model for the sulphite inhibited Maillard reaction. *Food Chem.*, **14**, 173–87.

Wedzicha, B. L. & Lamikanra, O. (1983). Sulphite mediated destruction of β-carotene: the partial characterisation of reaction products. *Food Chem.*, **10**, 275–83.

Wedzicha, B. L. & McWeeny, D. J. (1974). Non-enzymic browning reactions of ascorbic acid and their inhibition. The identification of 3-deoxy-4-sulphopentosulose in dehydrated sulphited cabbage after storage. *J. Sci. Food Agric.*, **25**, 589–92.

Wedzicha, B. L. & McWeeny, D. J. (1975). Concentrations of some sulphonates derived from sulphite in certain foods and preliminary studies on the nature of other sulphite derived products. *J. Sci. Food Agric.*, **26**, 327–35.

Weier, T. E. & Stocking, C. R. (1946). Stability of carotene in dehydrated carrots impregnated with antioxidants. *Science*, **104**, 437–8.

Woodroof, J. G. & Luh, B. S. (1975). *Commercial Fruit Processing.* The AVI Publishing Co., Inc., Westport, Connecticut.

Yang, S. F. (1984). Reactions of oxidation intermediates of sulphite species with some cellular components of plants. *Food Chem.*, **15**, 113–24.

Zoltewicz, J. A., Kauffman, G. M. & Uray, G. (1984). A mechanism for sulphite ion reacting with vitamin B_1 and its analogues. *Food Chem.*, **15**, 75–91.