

FINAL REPORT
for
NEW ZEALAND FOOD SAFETY AUTHORITY

TECHNOLOGICAL ISSUES
WITH
IODINE FORTIFICATION OF FOODS

by

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EXECUTIVE SUMMARY

Current estimates indicate that the majority of people in New Zealand and Australia are likely to have dietary iodine intake levels below their respective dietary reference intakes. An extension of permissions for voluntary iodine fortification of an increased number of foods and mandatory iodine fortification with potassium or sodium iodide or iodate are being considered as a possible means of improving the iodine status of New Zealanders and Australians.

Historically, most manufacturers in New Zealand and Australia use non-iodised salt in the preparation of processed foods. The potential for mandatory fortification with iodine requires consideration of the possible technological impacts of the addition of iodine on the stability of the food systems.

Iodine and its salts (iodides or iodates) are reactive inorganic chemicals. Iodide is a strong reducing agent, while iodate is a strong oxidising agent. Elemental iodine does not exist in nature, but is a key intermediate chemical in the conversion of iodate to iodide. Iodide can be oxidised to iodine by oxygen or other oxidising agents, particularly in acidic solution and in the presence of sunlight or various catalysts. Iodate is readily reduced, mainly to iodide, in reactions that are dependent upon pH and ionic strength. Ascorbic acid readily reacts with iodate to form iodide. Due to this highly reactive nature of iodine and its salts, research must be undertaken to determine the reactivity of iodine and its salts with food components and the technological feasibility of adding iodine to processed foods.

There is a paucity of published research detailing the impact of iodine reactions on food systems. Almost all research has involved the use of iodised salt as a replacement for non-iodised salt in processed foods. Much of the published research has failed to directly measure the iodine content of the foods under study, instead relying upon calculations of iodine levels from the added salt content. Despite these issues, the majority of work published has reported no significant influence of iodine on food quality parameters that were studied. There are some specific food systems where iodine has had an impact, including UHT milk and a lemon flavouring. In addition, there are some reports of changes in foods when iodine levels above 100 ppm were used. However, there is no published evidence for technological changes occurring in some common food systems foods when iodised salt is incorporated into the formulations. These food systems include bread, processed meats, salty snack foods, and some canned foods and cheeses.

Experimental work in the current pilot study found for iodine concentrations of 1 to 10 ppm – levels which would be typical of added iodised salt – there was no discernable impact on dough production and bread quality. This is consistent with the literature and also the current use of iodised salt in bread making around the world. However, higher levels of iodine (100 and 1000 ppm) did result in significant changes to the dough and bread. A range of food ingredients were also treated with 400 ppm (a high dose) iodide or iodate, and there were no qualitative changes observed even after 5 days' storage at room temperature. These food ingredients included starch, protein (egg and dairy), reducing sugars and tomato sauce. These results are consistent with published literature. Namely

that low levels (1 to 10 ppm) of iodine do not seem to affect a wide range of food systems, but concentrations of 100 ppm or greater may have an impact on some food products.

The use of iodine in oil which was heated at 180°C for two hours resulted in some significant changes in peroxide values, which reflected the oxidation of the oil. There appear to be chemical reactions occurring between iodine and the fatty acids. These changes occurred at 63.5 ppm addition of iodine and suggest further work is necessary in order to understand the ramifications of these changes on the lipid food system, and also possibly the bioavailability of the iodine complexes.

There is some volatility of iodine from food systems upon heating. The extent of this is dependent on the iodine salt used and the food system in question. For example, in bread approximately 40% of the iodine was lost when potassium iodate was used, while only 20% losses occurred when potassium iodide was used. Approximately 20% of the iodine was lost over two hours from a boiling starch solution (100°C), and sunflower oil heated for two hours at 180°C. Clearly, experimental work involving iodine in foods requires an accurate measurement of the true iodine concentration in the final food and cannot be calculated from a theoretical added amount.

Overall, there appears to be no observable reactivity of iodine in most food systems provided low iodine fortification levels are used. However, there are few scientific studies published on this matter and the range of food systems tested is particularly narrow. Existing results cannot be extrapolated to all foods. Clearly there are chemical reactions occurring in some food systems when iodine concentrations are increased above 100 ppm and these changes need further investigation.

The methodology for quantitatively extracting and recovering iodine from food matrices requires further study. The determination of different iodine species in foods (and other biological samples) is extremely complicated and requires substantial financial investment. Two methods are presently used for this determination, namely neutron activation analysis or combined ion-chromatography/inductively coupled plasma-mass spectrometry, but there are no published methods which quantify the extraction and recovery of iodine and its salts from complex food matrices. Iodine species (elemental iodine, iodide, iodate) determination is not possible for routine measurements and additional research is required to better understand iodine chemistry in a complex food matrix.

Fortification of iodine through the use of iodised salt, instead of non-iodised salt, in the formulation of some food systems is also supported, although the range of foods tested to date is relatively limited. The addition of iodine to foods should, in the first instance, be restricted to less than 100 ppm, although an actual, feasible maximum concentration has not been experimentally determined. Until further work is conducted, addition of iodine to foods high in unsaturated fats appears to be problematic. As bioavailability of iodine in foods is not accurately known, a national iodine monitoring programme should be introduced with any fortification strategy to ensure the intervention measures are effective.

1 INTRODUCTION

The iodine status of New Zealanders and Australians has decreased significantly over the past 10 years (Aitken, 2001). Whilst there is general agreement on the benefit of salt iodisation for the improvement of iodine status of the population, this appears to be inadequate to further secure sufficient iodine supply for the prevention of overt iodine deficiency disorders such as goitre and cretinism and of hidden iodine deficiency disorders such as growth retardation and mental impairment with particular focus on children. The use of salt for household purposes is decreasing, however it is undesirable to promote increased salt consumption as a means of improving iodine status.

In May 2004, the Australia and New Zealand Food Regulation Ministerial Council agreed that mandatory fortification of food with iodine should be considered as a possible means of improving the iodine status of New Zealanders and Australians and referred this work to Food Standards Australia New Zealand (FSANZ). In December 2004, FSANZ published an initial assessment report (Proposal P230) on iodine fortification. Options include extensions of permissions for voluntary iodine fortification of an increased number of foods, and mandatory iodine fortification.

Currently the only iodine salts permitted to be added to food are potassium- or sodium- iodide or iodate. The mandatory level of iodisation of salt in New Zealand and Australia is 25 to 65 ppm (mg per kg) iodine. It is possible to voluntarily include iodised salt in a range of foodstuffs. Many other countries mandate the iodisation of salt at varying levels, ranging up to 100 ppm of potassium iodide in the United States and Canada.

The majority of food companies in New Zealand and Australia use non-iodised salt for processed foods. Iodised salt is used in several countries around the world in baked goods (mainly bread) instead of non-iodised salt and there have been no reported technological issues associated with this level of use. However, the use of iodine as an ingredient in a wider range of processed foods has received little research attention.

Iodine salts may be volatile and lost through food processing operations. The World Health Organisation (2001) suggests there may be 20% loss of iodine through processing and another 20% through cooking and food preparation practices. The evidence for this, however, is not clear.

Iodine salts are also potentially highly reactive and may cause a variety of reactions in processed food systems. Iodide is a strong reducing agent and iodate a strong oxidising agent. Thus it is theoretically possible that reactions in foods involving iodine and its salts may potentially:

- cause colour reactions;
- increase oxidative reactions, hence reducing shelf life;
- decrease bioavailability of iodine; and/or
- reduce bioavailability of other nutritionally important substances.

The New Zealand Food Safety Authority (NZFSA) is interested in issues of technical feasibility around the addition of iodine to foods and as such wishes to undertake a review of this area. The objectives of this report were to:

- Undertake a comprehensive literature review on the addition of iodine to processed foods, the bioavailability of iodine from processed foods and the possible interactions of iodine with other food components;
- Define the chemistry, reactivity and mechanisms of reaction for iodine, iodides and iodates as inorganic chemicals;
- Identify possible food components, additives and processing conditions that may affect the stability and bioavailability of iodine in various food matrices;
- Identify possible food components and additives that may be affected by the addition of iodine to foods; and
- Experimentally determine the fate of iodides and iodates and their reactivity when added to various food matrices.

This report provides a review of the literature relating to the addition, or use of iodine and its salts in processed foods. It summarises fundamental iodine chemistry and identifies the potential reactivity of these compounds. Some preliminary experiments provide an indication of the volatility of iodine and its salts and whether there may be some observable changes in food systems through the addition of iodides and iodates directly to foods.

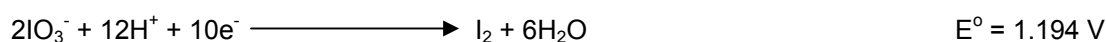
2 LITERATURE REVIEW

2.1 Iodine chemistry

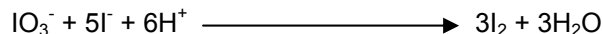
A comprehensive treatise of iodine chemistry is provided in Appendix A.

Iodine (symbol I, molar mass 126.9) is the heaviest, naturally occurring member of the halogens. Elemental iodine (I_2) does not occur in a stable form in nature and the two most common naturally occurring forms are iodide (I^-) and iodate (IO_3^-). While iodine does not occur in a stable form in nature, it is an important intermediate in iodine reaction chemistry.

The standard half-reactions for iodate and iodine are:



These indicate that both iodate and elemental iodine are oxidising agents and iodide is a reducing agent. These two equations can be combined to give:



Iodide can be oxidised to elemental iodine by oxygen or other oxidising agents, especially in the presence of catalysts, such as metal ions and moisture. The reaction between iodine and oxygen is very slow in neutral pH, but is rapid in acidic solution. The reaction is accelerated by sunlight and catalysts such as nitrite and cupric ion (Cu^{+2}). In a humid, acid environment, and in the presence of oxidising agents, iodide is readily oxidised to iodine, which is volatile (West and Merx 1995).

Elemental iodine is not a bioavailable form of iodine but is very reactive and undergoes various reactions, including:

- reduction to iodide;
- oxidation to iodate; and/or
- conversion to triiodide (I_3^-) through its interaction with excess iodide ion.

Elemental iodine readily sublimates and is rapidly lost to the atmosphere through evaporation and diffusion.

Iodate can be reduced to elemental iodine by a variety of reducing agents. However, the most common outcome of oxidation reactions with iodate is the formation of iodide. These reactions are dependent upon pH and ionic strength.

2.2 Iodine chemistry in food systems

Iodide, iodate and elemental iodine can undergo oxidation and reduction cycles in a food system. For example, iodine reactions within the food system may affect the bioavailability of iodine as a fortificant from the time of iodisation to consumption. However, there is very little published information detailing possible iodine reactions and their impact on food systems. Historically, iodine has been added as a fortificant to salt and most literature focuses on the use of iodised salt as a replacement for non-iodised salt in processed foods. The possibility of fortifying foods directly with iodide or iodate justifies a wider examination of the chemistry and reactivity of iodine and its salts in foods.

Lipid oxidation, degradation of ascorbic acid to dehydroascorbic acid (or reverse), reduction of ferric ions to ferrous ions (or oxidation of ferrous ions to ferric ions), and changes in protein functions due to formation of disulfide linkages between amino acids are some examples that theoretically could be mediated through the presence of iodine in food systems. Iodine and its salts could cause changes in colour, flavour, odour, texture, stability, and nutritional value of food matrices. For example, triiodide causes the development of a blue colour through its reaction with starch. Ascorbic acid is added as an antioxidant to many foods because it is a strong reducing agent and quenches any singlet oxygen present. Singlet oxygen is one of the most destructive and highly reactive oxygen species that is formed during oxidation reactions in foods. Ascorbic acid may react preferentially with iodate, if present, rather than oxygen and thus be lost as an antioxidant. In a similar manner when iron is present, iodate could potentially accelerate lipid oxidation by reducing ferric to ferrous ion, thus acting as a pro-oxidant. It is interesting to postulate the impact of food systems containing both iodine and ascorbic acid: the iodide/iodate pairing and ascorbic acid/dehydroascorbic acid pairing could have major implications on the stability of the food system.

Determining the rate of redox (oxidation-reduction) reactions and oscillating processes (iodate to iodide and reverse) induced by added iodine and its salts is very complex and can be significantly affected by many factors such as catalysts, reducing and oxidising agents, pH, temperature, and relative humidity. Some compounds present in foods act as reducing agents, such as sugars (glucose [dextrose] and lactose), aldehydes, ketones, some food additives (sodium metabisulphite, ascorbic acid, sodium ascorbate, and ferrous sulphate as an iron fortificant), sulphur compounds (sulfhydryl and disulphide groups), and amino acids (cysteine). These compounds and materials have very important roles in food systems, and these roles can be lost as a result of iodine-induced redox reactions, notwithstanding the concomitant loss of iodine as a fortificant.

In summary, elemental iodine does not occur naturally, but it is a key intermediate in iodine reaction chemistry. Potassium and sodium iodates are strong oxidising agents, while the iodide salts are reducing agents. As such, they are potentially important reactants in food systems. The chemistry of the reversible interconversion of iodate to iodide involves elemental iodine and thus a study of iodine and its salts in food systems must take into account all three forms.

2.3 International use of iodine in processed foods

The incorporation of iodides or iodates directly into foods has received very little research attention. The majority of work published in this area has involved the replacement of non-iodised salt with iodised salt in standard food formulations.

In South Africa, the iodisation of table salt (40 to 60 ppm) using potassium iodate as the fortificant is mandated. This is not a requirement for processed foods however. Harris et al., (2003) surveyed the use and analysed the iodine content of salt as an ingredient in 12 South African companies (six bread manufacturers, two bread pre-mix manufacturers, two margarine manufacturers and two flavour houses producing salty snack flavours). From the returned questionnaires, only one company (a bread manufacturer) claimed to use iodised salt as an ingredient. Three companies stated that they believed iodine would affect product stability, taste and the stability of flavours, where salt was used as a carrier. The authors measured the actual iodine content of the salt these manufacturers used and noted that four companies (one bread company, one margarine company and both flavour houses) actually used salt with a significant level (39 to 69 ppm) of iodine. The unintentional use of iodised salt as an ingredient in these foods suggests there is no adverse effect on these products.

Hard evidence for adverse reactions in foods is difficult to justify from published literature. Kojima and Brown (1955) found no undesirable effects of iodised salt on canned tomato juice, canned green beans, yellow sweet corn, bottled olives and canned or bulk sauerkraut. This study included storage for two to three months.

El Wakeil (1958) evaluated the effect of iodine/iodide mixtures, iodide in salt, and an iodophor on the quality of canned sweet corn, canned tomato juice and canned sauerkraut. With the exception of a flavour change in tomatoes at high concentrations (200 ppm) of the iodine/iodide mixture, there were no identifiable quality changes. It was noted that sodium thiosulphate, commonly used then for stabilising iodide in salt, caused substantial corrosion of the cans. This is no longer an issue as thiosulphate is not an approved additive for iodised salt.

Workers from the Morton Salt Company in the United States added iodised salt to commercially produced samples of bread, potato chips and frankfurters. There were no apparent adverse effects on the bread and frankfurters throughout processing or storage and sensory panels could not detect differences in the potato chips.

West and Merx (1995) cited reports that iodised salt using potassium iodide for manufacturing cheese, particularly Emmenthaler and Gruyere, had no discernable impact on flavour or quality. The authors themselves experimented with rice and potatoes boiled in water with and without iodised salt. They used four times the level of salt recommend by the World Health Organisation (2001) but found no significant difference in sensory properties such as flavour and appearance.

Wirth and Kuhne (1991) evaluated the use of iodised salt in a wide range of processed meat products. They could not find any changes in sensory properties, no influence on the curing characteristics of nitrite, and no additional nitrosamine formation.

These papers suggest that the replacement of non-iodised salt with iodised salt in the standard formulations for many food products will not cause any noticeable changes.

Skudder et al., (1981) found that 12.7 ppm iodine from added potassium iodate induced proteolysis in casein during ultra high temperature (UHT) processing of milk. Proteolysis was not induced with 6.3 ppm iodine from the iodate. This concentration of iodate was considerably higher than that anticipated to be added to iodised salt. In addition, Sevenants and Sanders (1984) found a reaction between iodide and the cresol component of lemon flavouring used in a cake mix. The resulting flavour was unacceptable and the authors recommended non-iodised salt be used to avoid the problem. This is because cresol is a key component of lemon flavour.

2.4 Use of iodine in processed foods in New Zealand and Australia

It has been suggested that a decline in the use of iodophors in the dairy industry may result in lower levels of iodine in dairy foods. However, Skeaff et al., (2002) refer to a government report that found no change in the iodine content of dairy products between 1988 and 1998. Cressey (2003) conducted analyses on different types of dairy products which had been analysed between 20 and 30 years earlier, in an attempt to compare iodine contents before and after iodophor usage. These included 13 products manufactured in New Zealand and three from overseas. Wherever possible, Cressey used the same methodology as that used in the earlier studies. There was no clear trend in iodine content over time, with one exception - butter. The iodine content of butter had clearly decreased over time.

The Dominion Salt Company has advised that most of the salt supplied to New Zealand food manufacturers is non-iodised salt (Personal communication, Russell Wallace, Group Marketing and Sales Manager, Dominion Salt Company, 2004).

The Tasmanian Iodine Supplementation Program began in October 2001 to encourage bakeries to use iodised salt in preference to non-iodised salt. Four of the six major bakery chains, along with a number of independent bakeries, agreed to participate. Estimates suggest that participating bakeries produced about 80% of the bread available for consumption. Salt manufacturers agreed to supply iodised salt at prices comparable to regular non-iodised salt. A survey in July 2003 found about 70% had changed to using iodised salt and none had reverted to regular salt. Of the non-participating bakeries, most baked from premixes or used frozen dough formulated interstate, to which salt was already added. The researchers concluded that the Iodine Supplementation Program has high

acceptance among small to medium sized bakeries with little impact on business, including time, cost and consumer acceptance. Unfortunately, there are no published results on the true iodine concentration of the bakery products. Iodine levels of bread baked with iodised salt were believed to be approximately 35 mcg per 100 g (Personal communication, Judith Seal, Department of Health and Human Services, Tasmania, 2004). The Supplementation Program is also monitoring milk, where iodine levels are about 200 mcg per L (Personal communication, Judith Seal, 2004; Turnbull et al., 2004).

2.5 Iodine retention

The retention of iodine in processed foods has received limited attention. The World Health Organisation (2001) recommends:

“in typical circumstances, where:

- iodine lost from salt is 20% from production to household;
- another 20% is lost during cooking before consumption; and
- average salt intake is 10 g per person per day,

iodine concentration at the point of production should be within the range of 20 to 40 mg iodine per kg of salt (i.e. 20 to 40 ppm iodine) in order to provide 150 mcg of iodine per person per day. The iodine should be added as potassium (or sodium) iodate. Under these circumstances median urinary iodine levels will vary from 100 to 200 mcg per litre”. It is unclear what evidence was used to support the indicated losses.

Kuhajek and Fiedelman (1973) found retention was:

- 70 to 80% during the processing and 10 days' frozen storage of white bread;
- 48 to 73% in potato chips after 13 weeks' storage; and
- 41 to 61% in frankfurters after refrigerated or frozen storage.

In an extensive study using 50 different Indian recipes, prepared in a hospital kitchen using different cooking procedures, Goindi et al., (1995) found the range of losses to be between 3 and 67%. The means ranged from 6 to 37%, however the variation in the results was very large. Some foods such as Kadhi, carrot, spinach, had losses in excess of 50%. The cooking method had a significant impact also:

- boiling (37% loss)
- steaming (20% loss)
- pressure cooking (20% loss)
- shallow frying (27% loss)
- deep frying (20% loss)

- roasting (6% loss)

There was no evidence the researchers assessed iodine losses as part of the methodology. Triplicate samples (250 mg each) were taken before and after cooking one batch of food. This level of sampling is of questionable value for complex food materials. However, the results do indicate that iodine is labile and lost from food systems during routine preparation processes.

In summary, the use of iodine salts in processed food systems has been studied predominantly in terms of the replacement of non-iodised salt with iodised salt in a range of processed foods. Most studies reported no significant impact of iodine fortification on the sensory properties or other qualities of the food. However, there were reactions with milk proteins undergoing UHT treatment and in lemon flavouring. There were some reactions observed in canned products when iodine concentrations were above 100 ppm. In most reports, the amount of iodine present in the food products was calculated from the amount of iodine in the added salt, rather than by direct measurement. Where studies did measure the iodine levels, it was clear that a considerable loss of iodine during processing was possible – sometimes as much as 70%. However, these studies used methods for iodine measurement which lacked sufficient controls and would be inappropriate today.

One of the issues which precludes unambiguous conclusions from these published studies is the limitations of adding iodine to foods via salt. Unless salt levels in foods are normally high, the levels of iodine would be low and the background levels naturally present in the foods may confound the results (for example, the controls may have similar levels of natural iodine). The published research on iodine in processed foods has not involved systematic and carefully designed experiments on the addition of iodine to processed foods, in order to be able to clearly establish the role that iodine may play in food chemistry. Researchers have generally assumed that the fortification process would be limited to replacement of non-iodised with iodised salt.

2.6 Iodine bioavailability

There are no recent data on the bioavailability of iodine from the diet. The methods to test bioavailability of iodine all require the use of radioisotopes. As there is only one stable isotope for iodine, stable isotope trace studies are not possible for ethical reasons (Hurrell, 1997). However, earlier literature provides a useful guide on iodine availability.

There are two aspects to the bioavailability of iodine:

- absorption of iodine in the gastrointestinal tract; and
- absorption of iodine from the bloodstream by the thyroid gland.

Inorganic iodide is readily and completely absorbed from the gastrointestinal tract (Keating and Albert, 1949). It is believed that iodate and protein-bound iodine are reduced to iodide for absorption. However, neither the reducing agent nor the site of reduction is clear. While iodine absorption from the gastrointestinal tract has been reported to be virtually 100%, the absorption of iodine by the thyroid gland was estimated to be around 10 to 15% under normal intakes (Lamberg, 1993). Using a 100 mcg radioisotope iodine dose, about 20% was taken up by the thyroid gland (Keating and Albert, 1949).

Very early human balance studies by von Fellenberg (1926) demonstrated high iodine absorption from most foods (approximately 90%) except from water cress. There was some evidence that iodine from plants may show a lower absorption rate, apparently caused by the poor release of iodine from the plant structure during digestion. Prolonged cooking of the seaweed “hijiki”, which is used in Japan, has led to an increase of urinary iodine excretion in men to 53% of dose compared to only 10% for the raw material uncooked (Katamine et al., 1987). However, as with other nutrients, mere balance techniques are imprecise and the assessment of iodine bioavailability is further complicated by analytical difficulties in measuring trace quantities in the diet and by possible contamination with atmospheric iodine.

Given the presence of various reducing and oxidising agents in foods there is a wide range of possible interactions between iodide and iodate with respect to their bioavailability. The various studies that used iodate as an iodine source for salt iodisation suggest that iodate bioavailability is extremely high. However, these studies have not included interactions within the food matrix, or *in vivo* changes during digestion and absorption.

Mannar and Diosady (1998) demonstrated that the reaction between iodate and ferrous salts used for dual fortification of salt with iodine and iron, could be problematic. The water-soluble, highly bioavailable ferrous compounds reacted with moisture and impurities in the salt, causing colour changes and iodine losses (Mannar and Diosady, 1998). Even encapsulation of ferrous sulphate with partially hydrogenated vegetable oil resulted in yellow colour changes in dual fortified salt when salt moisture content was high (Zimmermann et al., 2003).

In conclusion, there is almost no information on iodine bioavailability, either from pure iodine sources or from unprocessed and processed foods. All present data are based on limited studies using radioiodine in very small samples and specific foods from some decades ago. There are known reactions, particularly with mineral salts, where bioavailability appears to be significantly reduced.

2.7 Iodine methodology

The determination of different iodine species in foods (and other biological samples) is extremely complicated and requires both substantial investment in technical equipment and day-to-day operating expenses. Two methods are presently used for this determination, namely neutron activation analysis, or combined ion-chromatography/inductively coupled plasma-mass spectrometry (ICP-MS). However, there has been no work published which establishes the efficiency of iodine and its salts recovery from complex solid food matrices (Leiterer et al., 2001; Chai et al., 2004).

Determination of iodine species (iodide, iodate and elemental iodine) is not possible by these routine measurements. There are no known publications outlining iodine chemistry in a complex food matrix.

A commercially available iodine methodology involving ICP-MS was used for the experimental trials in this report, however several issues involving quantitative recovery of iodine from solid food matrices in the experiments highlighted the need for further research into methods development.

3 THE DETERMINATION OF IODINE STABILITY IN MODEL FOODS

3.1 Methods

3.1.1 Choice of iodine sources and concentrations

Potassium iodide and potassium iodate are the commonly used forms of iodine salts for universal salt iodisation. Because elemental iodine is a key intermediate in the reaction mechanisms of iodide and iodate, (see Section 2.1), elemental iodine was included in the experimental design.

Many food systems incorporate around 1.5% added salt. If iodised salt containing 65 ppm iodine was used, this would equate to adding approximately 1 ppm iodine. Literature data investigating iodine reactivity in food systems have reported iodine concentrations from 0.4 to over 150 ppm. Reactions in foods have not been reported below 12 ppm iodine, though many of these reports did not directly measure the true iodine concentration. For these reasons, a range of added iodine levels were chosen for the experiments, from 1 to 100 ppm.

Due to the fact that many foods have a low, natural level of iodine, screening experiments to establish if there is any potential reactivity of iodine in foods, requires the use of relatively high levels of iodine. This will ensure any observed effects can be clearly differentiated from background “noise”. Furthermore, there is clear evidence in the literature that iodine is readily lost as a result of food processing. However, there are no scientific trials that have established a consistent true level of volatility in foods. For some food matrices, loss of iodine could be as high as 70%. For these reasons, a high level of added iodine (1000 ppm) was chosen as part of the experimental plan. While it is recognised that this level of iodine is unlikely to be appropriate for use in foods, it is necessary as an experimental protocol for these screening experiments.

3.1.2 Choice of food systems

It is not possible to test all combinations of processed foods, additives and ingredients for their reactivity towards iodine. From the literature review it was clear that bread was a key food system which routinely incorporates iodised salt. As bromates and iodates have been used in the past as dough conditioners and therefore have a measurable impact on dough properties, the researchers chose a commercial bread producer to test the impact of iodine and its salts in this specific food matrix.

Iodine volatility will be affected mainly by heat. In foods at atmospheric pressure, either boiling or cooking in fat represent the most common heat processing practices which would maximise iodine loss. Although there are no published data on the reactivity of iodine and the lipid components of food systems, there is knowledge of the impact of iodine on fats from the fat processing industry, and it is also used as a method of defining fat composition (the “iodine value” is a measure of the degree of

unsaturation of fat). In addition, iodine is considered to be particularly reactive to starches, as the development of a dark blue colour with iodine is the reaction used to identify starches in foods. The two systems chosen for volatility studies, therefore, were a boiling starch solution at 100°C and sunflower oil maintained at 180°C. These two systems also provided the basis for assessing the impact of iodine on starch and iodine reactivity with unsaturated fatty acids.

A series of foods were selected in order to investigate the reactivity of iodine in different food matrices:

- egg white (protein, sulfhydryl groups)
- egg yolk (phospholipids)
- milk (dairy proteins)
- reducing sugars (glucose, lactose, sucrose)
- tomato sauce (used in many food products)
- pigments (anthocyanins and related plant colours)

While this is not a comprehensive selection of foods and food systems, it provided some key components which were reportedly influenced by iodine in processed foods, or theoretically could be reactive.

There was insufficient evidence in the literature on food processing to provide guidance on the types of iodine reactions that do occur in food. Decisions on choice of foodstuffs had to be confined to systems that would maximise the possibility of exposing whether the theoretical reactivity was a meaningful outcome, or not. Because of this lack of existing scientific evidence, and the limited time and resources available to complete this work, these experiments mandated a screening approach rather than a series of definitive trials.

3.1.3 Stability of iodine in oil

Three separate experiments using potassium iodide, potassium iodate and elemental iodine were conducted. Sunflower oil was chosen because of its high level of polyunsaturated acids and all experiments were conducted using the same bulk container of sunflower oil. Ameo sunflower oil with a best before date of 1 September 2005 was used.

The target iodine concentration was 0.5 mM (63.5 ppm). Potassium iodide (0.5 mM, 82.9 mg), potassium iodate (0.5 mM, 107 mg) and elemental iodine (0.5 mM, 63.5 mg) were added to 1 L of oil at room temperature.

The oil/salt mixtures were constantly stirred, using a magnetic stirrer, and heated to 180°C on a hot plate. "Zero" time was recorded once 180°C was reached. Samples (30 ml) were taken at times 0,

10, 20, 30, 60, and 120 minutes, transferred into air-tight brown glass containers and refrigerated until analysed.

Samples were analysed for total iodine content, fat oxidation and free fatty acid formation. Peroxide values provide a measure of fat oxidation. Free fatty acid analysis provides an indication of the breakdown of triglycerides in fats to form individual fatty acids and di-, mono-glycerides or glycerol. This is an important quality parameter in fat and oil processing.

3.1.4 Stability of iodine in starch solutions

A starch solution was selected as a model system for studying interactions of iodine with carbohydrate. In addition, the possibility that solution pH may impact on the reactions was tested.

Each experiment involved either potassium iodide (0.5 mM, 82.9 mg potassium iodide per kg of starch solution), potassium iodate (0.5 mM, 107 mg potassium iodate per kg of starch solution), or elemental iodine (0.5 mM, 63.5 mg elemental iodine per kg of starch solution). As iodine was not water-soluble, it was first dissolved in a small volume of ethanol prior to being added to the starch solution at room temperature.

A 1% w/w starch solution was prepared at room temperature. The appropriate iodine salt was added and the solution pH was adjusted to either pH 2, 5, 7, or 9 by appropriate addition of NaOH (pH 9 solution) or HCl (pH 2 and 5 solutions).

The starch solution/salt mixtures were continuously stirred with a magnetic stirrer, and heated to 100°C on a hot plate. "Zero" time occurred when the temperature reached 90°C. Samples (30 g) were drawn at 0, 10, 20, 30, 60, and 120 minutes, transferred to air-tight brown glass containers and refrigerated until analysed. Moisture loss was regularly measured (as loss of weight from the system) during the cooking process and these changes were used to adjust the final data.

3.1.5 Stability of iodine during bread processing

Bread was chosen as a model for the assessment of iodine stability during food processing, as it is a potential food vehicle for iodine fortification. Regular bread doughs were prepared in the test bakery at Goodman Fielder Ltd, Auckland. The base recipe was flour (78% extract, high protein bread flour), non-iodised salt, improver, softener, canola oil, yeast and water. Each batch made 2.4 kg of dough, which in turn gave three loaves of bread (each loaf of dough weighing 800 g before cooking).

A control batch of dough was prepared without addition of iodine. Four additional batches of dough were prepared, each containing either 1, 10, 100, or 1000 ppm iodine using potassium iodide. Four more batches of dough were prepared, each containing 1, 10, 100, or 1000 ppm iodine using

potassium iodate. The iodine salt was added to the dry ingredients before the dough was mixed. The lowest concentration of iodine (1 ppm) is within a similar order of magnitude had the non-iodised salt been replaced by iodised salt. Common flour oxidising agents (e.g. bromates and ascorbic acid) when used, are often incorporated into flour at 10 to 100 ppm. A high concentration (1000 ppm) in the dough was used to provide a concentration that would provide a meaningful evaluation of the volatility of the iodine salts.

The loaves were baked following the standard test bakery procedures for dough manufacture and proofing. At the end of baking and cooling, the loaves of bread were each approximately 700 g, meaning approximately 100 g had been lost during the baking and cooling processes.

Approximately 20 g samples each of the crust and separately the crumb from the centre of each loaf were collected, sealed in plastic bags and frozen prior to analysis for iodine concentration.

Colour changes and sensory evaluation were recorded by panellists from the Institute of Food Nutrition and Human Health (IFNHH), Massey University, Albany campus. In this instance, a 30 mm thick slice of bread was cut from each loaf and placed in a loose-fitting plastic bag to be used for visual evaluation of the bread. Cubes, approximately 30 mm in each dimension, were cut from the central part (i.e. not the crust) of each loaf the day after the bread was baked. These cubes were stored in a plastic bag until required for tasting.

Ten panellists were asked to visually examine the slices of bread. Comments were collected, including an assessment of which slices of bread “looked” the same and were there any obvious differences. The panellists were also asked to taste a cube of each sample and comment on any characteristics that they considered important. These data were collated and consistent comments about samples were noted.

3.1.6 Effects of addition of iodine on colour changes in foods

Whole milk, skim milk, egg yolk, egg white, tomato sauce, and sugars (glucose, lactose, sucrose) were selected to investigate the effect of an addition of elemental iodine, potassium iodide or potassium iodate on changes in food colour and smell. These foods are used in making various processed food products by their addition as whole or fractionated components. Also these foods contain key functional groups (proteins, pigments, free sulfhydryl and disulphide groups, and reducing sugars) that may be affected by the presence of iodine and its salts.

Whole milk, skim milk and tomato sauce were purchased from a local supermarket and used unchanged. Three solutions of sugars (3% w/w of glucose, lactose or sucrose) in deionised water were prepared. Eggs were separated into the white and yolk, and each was mixed separately in 500 ml of deionised water.

Because the changes were to be assessed visually and qualitatively by the researchers, a high concentration of iodine was chosen for these trials. Iodine, potassium iodide and potassium iodate were added to these foods at 400 ppm. This provided 237 ppm iodine for the potassium iodate salt, and 306 ppm iodine for the potassium iodide salt. Iodine itself was relatively insoluble, so for tests involving elemental iodine, only 12 ppm elemental iodine was used. It is acknowledged that this level of iodine would not be used in these foods, but the need to identify potential reactions outweighed the practicality of the level. If reactions did not occur at this level, they were unlikely to occur at the lower levels (1 to 10 ppm) that would likely be used commercially. There were no guidelines in the literature to suggest a useful working level for these trials.

Foods were treated in one of four ways:

- no added iodine, remain at room temperature;
- no added iodine, heat to boiling and cool to room temperature;
- added iodine (or iodide, or iodate), remain at room temperature; or
- added iodine (or iodide, or iodate), heat to boiling and cool to room temperature.

Where appropriate, samples were constantly stirred and heated in a beaker on a hot plate until they boiled. Comparisons were made amongst the four samples immediately after the heating /cooling process and also after five days' storage at room temperature.

3.1.7 Iodine analysis

The analysis of the total iodine concentration of the oil, starch, and bread samples was carried out by RJ Hill Laboratories Ltd, Hamilton.

Further details to Section 3.1 are provided in Appendix B.

3.2 Results

3.2.1 Solubility and observed colour changes in model (oil and starch) systems

Neither potassium iodide nor potassium iodate dissolved in the oil samples. Crystals at the bottom of the oil container were visible during the entire heating process. Even without dissolution, some interactions between the salt crystals and the oil could not be excluded and the experiment was continued unchanged. Elemental iodine dissolved completely and led to an immediate colour change of the oil to a brown colour from dissolved iodine, which turned a deeper orange colour as the oil was heated and then became colourless as heating continued at 180°C.

Both potassium iodide and potassium iodate dissolved readily in the aqueous starch solutions. No colour changes were observed for either salt immediately following their solubilisation. Elemental

iodine did not dissolve in water and it was pre-solubilised in a little ethanol before adding to the starch solution. Elemental iodine reacted typically with starch, resulting in a dark blue colour. Once the starch solution was heated, this colour disappeared. Starch solutions containing elemental iodine were colourless before the solution had reached its sampling temperature (100°C).

There were no noticeable colour changes in either the oil or starch solutions during subsequent heating of iodide or iodate solutions. The starch solution heated with added elemental iodine remained colourless however the oil heated with added elemental iodine turned a deeper orange colour and then became colourless as heating continued at 180°C.

3.2.2 Stability of iodine in oil

Table 1 presents the results for the analysis of total iodine concentration in oil during heating.

Table 1: Total iodine concentrations (ppm) in sunflower oil during heating at 180°C

Sample	Heating time (minutes)				
	0	10	30	60	120
Control	0.011	nd	nd	nd	nd
KI	0.077	0.144	0.16	0.192	0.317
KIO ₃	0.029	0.755	0.307	0.277	0.261
I ₂	21.9	50.6	49.78	46.3	40

nd = not detectable (below detection limit of 0.001 ppm)

Iodine and salts were added at room temperature

"Zero" time represents the time when the oil reached 180°C

All original concentrations of iodine were 0.5 mM (63.5 ppm)

Iodide and iodate salts were only slightly soluble in oil (less than 1 ppm) and it was not possible to quantify volatility. Potassium iodide was slowly and progressively solubilised during the heating process whereas potassium iodate seemed to reach a peak concentration at 10 minutes then become less soluble. This may indicate that iodate is very insoluble in oil, but is converted via iodine to potassium iodide. The solubility of elemental iodine followed a similar pattern to iodate, peaking at 10 minutes of heating at 180°C then declining for the remainder of the heating process. Iodine concentrations from addition of elemental iodine were much higher (around 50 ppm) but at no stage did they reach the level added (63.5 ppm). Given iodine will react with double bonds in unsaturated fats, it is possible the method used to extract iodine from the samples may have failed to remove that covalently bound iodine. As iodine is relatively soluble in oil and would clearly partition preferentially into a lipid phase in foods, this suggests that in foods comprising both aqueous and lipid phases, any reactivity that oxidises the water-soluble iodide (to iodine) or reduced iodate (to iodine) would likely result in the movement of iodine from the aqueous to lipid phase.

3.2.3 Stability of iodine in starch solutions

The initial concentrations of iodine measured in the starch solutions containing added iodide, iodate and elemental iodine, were the same as the added amounts, indicating that the iodine was fully dissolved and easily recovered from the starch solutions. In general, about 20% of the iodine was lost upon boiling for 2 hours at 100°C.

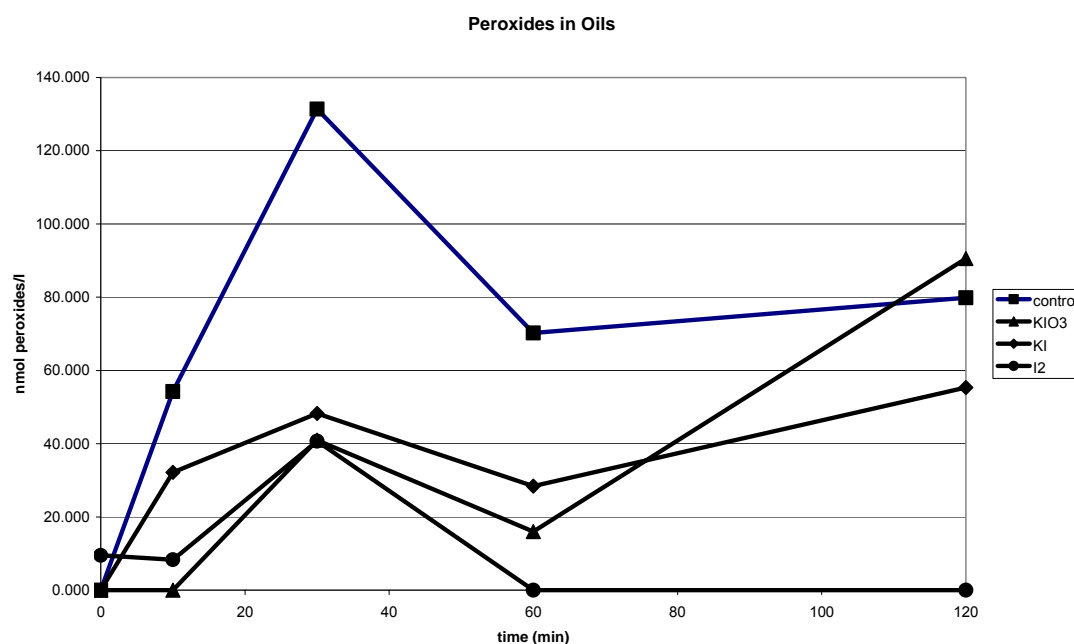
There appears to be some effect of pH on the inter-reactivity of the iodine moieties. For example, elemental iodine is relatively poorly recovered from starch solutions at pH 5 and 7, is better recovered at pH 2 and appears to be as recoverable as the other two salts at pH 9. It may be strongly bound to the starch at pH 5 and 7 and thus be unavailable for quantification using the methods employed.

Of particular interest is the fact that the typical blue colour of the reaction between starch and iodine is formed on addition of the iodine. However, this quickly disappears (even before the starch has gelatinised by heating at around 70°C) and by the “zero” time at above 90°C the starch solution containing added elemental iodine is colourless. This suggests the elemental iodine has been converted to alternative forms, probably iodide and iodate, and it no longer is present as elemental iodine. The data at acidic and neutral pH values indicate the iodine is strongly bound to the carbohydrate and not released during the extraction and analysis procedures used. The fact that the added iodine was fully recovered from the pH 9 starch solution suggests it is not bound to carbohydrate in alkaline solutions.

3.2.4 Peroxides in oil

Peroxides are intermediates in the development of oxidative rancidity in fats and oils. They accumulate early in the oxidation process, but are rapidly consumed as fat oxidation progresses. The relative progress of fat oxidation can be followed by identifying the peak of peroxide formation and comparing it amongst the various samples. In a given sample of oil, the earlier the peak, the faster fat oxidation is occurring.

Figure 1: Influence of iodine on peroxide formation in sunflower oil during heating at 180°C



Iodine and salts were added at room temperature

"Zero" time represents the time when the oil reached 180°C

All original concentrations of iodine, potassium iodide and potassium iodate were 63.5 ppm iodine in oil

The results showed an almost identical pattern of peroxide formation compared to the control (no added iodine), irrespective of the iodine moiety used, albeit at a significantly lower level than the control. The concentration of free iodine measured in the oil was high for the elemental iodine samples (above 40 ppm) and less than 1 ppm for the iodide and iodate samples. It appears, from the peroxide results alone, that these three iodine moieties reacted in the same manner with respect to peroxide formation. This result was completely unexpected and the researchers have found no literature reports which show this result or provide any explanation for the outcome.

Of special interest was the observation that fat which reacted with elemental iodine rapidly lost all peroxides and within 60 minutes of heating at 180°C there were no peroxides measurable in the fat. This observation was repeated in a second experimental trial. Iodide and iodate, however, caused a progressive increase in peroxide values with prolonged heating. This observation tends to support the hypothesis that iodine is reacting with the fat.

One of the issues to be resolved is the complex chemistry which links iodide, iodate and iodine in any given food matrix. Conditions in the fat could easily have resulted in all three chemical forms being present in every sample tested. The methodology for iodine determination measures iodine as an element and does not discern its chemical form. Thus it was not possible to quantify the individual concentrations of iodine, iodide or iodate in the fat.

The results on fat oxidation, therefore, are inconclusive and confusing. It is unambiguously clear that iodine and its salts react with lipids at high temperatures. What this actually means and how it would be mediated in a more complex food system is not clear.

3.2.5 Free fatty acids in oil

The oil samples taken for total iodine analysis were also analysed for free fatty acids. The results showed that elemental iodine and its salts had no significant effect on the production of free fatty acids.

3.2.6 Iodine in bread

Comprehensive and extensive testing of dough and bread were not included as part of this trial – rather macroscopic and significant differences were the focus, together with volatility of iodine from the bread process.

Qualitative assessments during the dough making process clearly identified problems with high levels (100 and 1000 ppm) of iodide and iodate. However, there were no adverse affects noted for the 1 and 10 ppm additions. Baked bread looked normal for all iodide and iodate additions up to and including 10 ppm, but the 100 and 1000 ppm additions of iodate did cause significant changes in loaf volume.

Approximately 40% of the iodate and 20% of the iodide was lost from the central crumb during the baking process. The concentration of iodine in the crust was higher than the crumb.

The addition of iodide or iodate up to 10 ppm had no discernable effect on sensory characteristics (colour, texture, flavour) as tested by a small, informal taste panel. However, 100 and 1000 ppm iodate addition caused some significant changes in appearance, taste and crumb texture. Some visual differences in crumb texture and colour appeared to be evident when 1000 ppm iodide was used, but there were no flavour or taste differences noted. While it is important to recognise that iodate will cause some differences in bread quality at high levels (100 ppm and above), these levels are unlikely to be approved for food use. Consistent with all other published and anecdotal reports, there appears to be no significant impact of low levels of iodide or iodate on bread quality, especially if the method of iodisation occurs through the addition of iodised salt.

3.2.7 Effects of addition of iodine in various food systems

For these trials, 400 ppm iodide or iodate was used to ensure any potential reactions in the food systems tested would easily be observed. This is a high concentration of iodine (237 ppm for iodate

and 306 ppm for iodide) compared to the anticipated fortification usage, but the intention was to identify possible reactivity.

Full fat milk, skim milk, lactose, glucose, sucrose, egg yolk, egg white and tomato sauce were assessed over a 5 day storage period at room temperature. There were no observable differences in colour or smell over that entire period. In addition, various coloured plant materials were extracted with water (mainly anthocyanins and betaine) and a drop of the various iodine solutions were added in a spotting plate. There were no obvious changes in colour. While these observations were qualitative, the high levels of added iodine would have facilitated clear changes, if any occurred. No differences between control and iodine fortified samples were observed. The lack of visually observed changes in these systems, and after up to 5 days' storage, does not mean that there were no reactions occurring and it is important to recognise that iodine reactivity could still exist, but was not apparent at this macroscopic level.

4 CONCLUSION AND FUTURE WORK

4.1 Absorption and bioavailability of iodine from food sources

There is limited information available on the true absorption rate of iodine from the gastrointestinal tract. What literature is available suggests 100% absorption from the gastrointestinal tract, however these studies were conducted in the first half of the last century using small sample sizes and only basic analytical methodology. The definitive method for measuring the absorption rate of iodine is through the use of stable isotope techniques, however these cannot be used on humans for ethical reasons and therefore no accurate figures exist.

There is very limited information on the interactions between iodine and food components with respect to their impact on bioavailability from processed foods. However there are known reactions, particularly with mineral salts, where bioavailability appears to be significantly reduced.

4.2 Interactions of iodine with food components

This report combines published literature and a pilot experimental study to screen for possible interactions of iodine with food components during food processing.

The existing literature tends to suggest that iodine and its salts, when used as iodised salt to replace added non-iodised salt, will have limited impact on food quality. The experimental trials conducted in this study support those conclusions. However, these published studies have focused on very few food systems and at low iodine concentrations, often never directly measured. While the use of iodised salt to replace non-iodised salt is one method of adding iodine to foods, the levels of iodine that can be achieved by adding iodised salt to foods, are very low. There are no data to predict the outcome of adding higher levels of iodine directly to food during food manufacture.

Literature evidence, together with the results of the experiments outlined in this report, suggest there will be reactivity between iodine and some food components when the level of iodine is increased above 100 ppm. This suggests that consideration should be given to the fortification of foods being limited, in the first instance, to the use of low concentrations of iodine. There are insufficient data to establish what “low” means and a suitable threshold level cannot be defined at this stage, but must clearly be lower than 100 ppm.

Of particular importance is the potential impact of iodine and its salts on fat. Although there are no published data on the reactivity of iodine and the lipid components of food systems, there is knowledge of the impact of iodine on fats from the fat processing industry, and it is also used as a method of defining fat composition (the “iodine value” is a measure of the degree of unsaturation of

fat). While iodide and iodate are minimally soluble in oil, the complex chemistry which transforms iodate through iodine to iodide means that any of these chemical forms could potentially exist in foods. As iodine will react with unsaturated fatty acids, the impact of this on bioavailability of both iodine and essential fatty acids warrants further investigation.

For food systems such as bread, processed meats, salty snack foods, and some canned foods and cheeses, the use of iodised salt to replace non-iodised salt in the formulations does not create any observable technological issues. There are examples, such as milk for UHT processing, some flavourings, foods containing high levels of unsaturated fatty acids and some foods such as bread where iodine concentrations of 100 ppm and above were used and there was an observable reaction between iodine and the food matrix. Clearly, there are some technological issues surrounding the use of iodine in these food systems at levels above 100 ppm.

There are insufficient data available in the literature, or through the experiments conducted for this report, to be able to describe the range of foods which will be suitable, inert vehicles for the fortification of iodine to processed foods. It appears from world-wide use of iodised salt in bread that this is a suitable food, but this result cannot be extrapolated to all foods.

4.3 Quantification of iodine in food matrices

The methods for measuring iodine (and its variant chemical forms) in foods are inadequately developed and insufficiently robust to be confident in measuring low levels of iodine and those covalently bound forms of iodine in food matrices. This is an important area of work required for further studies on iodine in food.

Iodine is a volatile material that can be readily lost during food processing. The assumption that iodine concentration can be calculated mathematically in foods is flawed. Iodine losses depend upon the salt used. In bread, iodate is more volatile than iodide, while in boiling starch solution both iodine salts are equally volatile.

4.4 Overall

Care is required in promoting the use of iodine and its salts as fortificants in processed food systems without experimental evidence to justify their lack of reactivity. It appears a wide range of food systems can incorporate low levels of iodine without significant effects on food quality and sensory characteristics. However, iodine and its salts are effective redox chemicals which have the potential to react with food components when used at higher concentrations (e.g. above 100 ppm).

There is a need for a coordinated programme of research to establish suitable methods for measuring iodine and its salts in foods. These methods can then be used to ascertain the levels of iodine that can be added to foods without affecting bioavailability, or creating chemical reactions which would alter the characteristics or shelf life of the foods themselves.

In the meantime, there is some evidence that certain food systems could be used safely for the addition of iodine, should FSANZ choose to extend the voluntary permissions or apply mandatory options for iodine fortification of foods. However, further research on the addition of iodine to foods would be required.

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APPENDIX A - IODINE CHEMISTRY

1 Background

Iodine (symbol I, molar mass 126.9) is the heaviest, naturally occurring, member of the halogens. Lighter members in the group are fluorine (F), chlorine (Cl) and bromine (Br), and this set of elements occupies Group 17 in the modern version of the Periodic Table. Chemical nomenclature does not distinguish between the iodine atom (I) and the di-iodine molecule (I₂) – both are “iodine” and this can sometimes cause confusion.

Free iodine (as I₂) does not occur in nature, but the characteristic purple vapour of gaseous I₂ was first described by B. Courtois in 1811, by heating seaweed ash with sulphuric acid. An additional natural source of iodine was discovered when iodate (IO₃⁻) levels of 0.02 to 1% were found in the Chilean nitrate deposits. Iodine is the 60th most abundant element in the earth's crust (comparable with thallium) and today, most iodine is extracted from natural brines in Japan or Midland, Michigan, USA. The iodine concentration in seawater is only 0.05 ppm but some seaweeds can concentrate iodine up to 0.45% of their dry weight.

Table 1 lists some of the physical properties of iodine and its salts.

Table 1: Physical properties of some iodine compounds (Greenwood and Earnshaw, 1984)

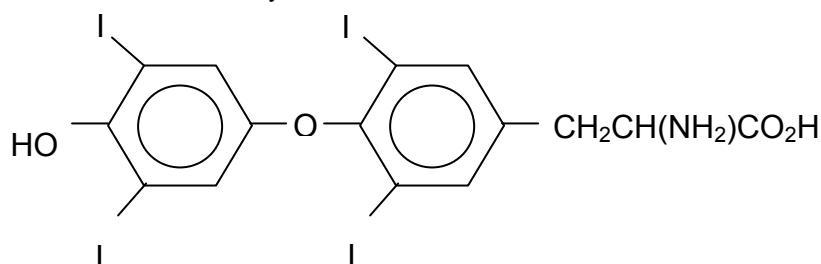
Compound	Molar Mass (g/mol)	Density (g/ml)	Mp/Bp (°C)	Sol. in H ₂ O (g/100 ml) (Temp.)	Solubility in other solvents (g/100ml)
I ₂ ^a	253.8	4.93	50 sublimes 116 decomp.	0.030 (25) 0.078 (50)	v. sol. most organic solvents and in aq. KI soln.
NaI	149.9	3.667	651/ 1304	184 (25) 302 (100)	v. sol. ethanol v. sol. acetone
KI	166.0	3.13	686/ 1330	127.5 (0) 208 (100)	sol. ethanol sol. acetone
NaIO ₃	197.9	4.277	decomp.	9 (20) 34 (100)	insol. org. solvents
KIO ₃	214.0	3.93	560/ > 1000	4.75 (0) 32.3 (100)	insol. org. solvents

^a Atomic radius of I atom = 133 pm

Soon after its isolation from seaweed, the starch-iodine blue colour was exploited by F. Stromyer (1814) as an analytical test sensitive to 2 to 3 ppm I₂.

In humans, the thyroid gland produces the growth regulating hormone, thyroxine (Figure 1), an iodinated amino acid. If iodine is insufficient, the thyroid gland enlarges in an endeavour to harvest more iodine - a condition known as goitre.

Figure 1: Chemical structure of thyroxine



Extracts from seaweeds had been used as a treatment for goitre from the 16th century, and in 1819 potassium iodide was introduced by J. F. Coindet, in Switzerland.

A number of radioactive isotopes of iodine can be produced artificially, including:

¹²⁹I (t_{1/2} = 1.6 × 10⁷ years, from uranium fission);

¹²⁵I (t_{1/2} = 60.2 days);

¹³¹I (t_{1/2} = 8.04 days); and

¹²⁸I (t_{1/2} = 24.99 min).

Those with shorter half-lives are used in medicine to follow metabolic pathways.

2 Compounds of iodine

The electron configuration of the iodine atom, [Kr]4d¹⁰5s²6p⁵, allows the attraction of one further electron to fill the 6p orbital, giving the I⁻ ion in the -I oxidation state, or the sequential loss of successive electrons from the 5s and 6p orbitals to give +I to +VII positive oxidation states¹. Most of these positive oxidation states occur as oxyanions (Table 2).

¹ Footnote – oxidation states. The use of signed Roman numerals for oxidation states is especially confusing in iodine chemistry, as we can have I (-I), I (+I), I (+III) etc. At this point, the author is quite sympathetic to the reintroduction of the old German symbol, J for iodine (German, jod).

Table 2: Oxyacids and oxyanions of iodine

Oxyacid	Oxyanion	Oxidation State	Name
HI ^a	I ⁻	-I	iodide
HIO	IO ⁻	+I	hypoiodite
HIO ₂	IO ₂ ⁻	+III	iodite
HIO ₃	IO ₃ ⁻	+V	iodate
HIO ₄	IO ₄ ⁻	+VII	periodate
H ₅ IO ₆	IO ₆ ⁵⁻	+VII	orthoperiodate
I ₂ O ₅ ^a		+V	iodine pentoxide

^a Included for completeness

In addition, a number of polyiodide cations (e.g. I⁺ to I₇⁺) and anions (e.g. I₃⁻ to I₁₆⁴⁻) are known. Many of these contain iodine in different oxidation states and the bonding modes have been the subject of much speculation, calculation and altercation.

The simplest of the polyiodide anions is the linear, I₃⁻, triiodide ion, which forms when I₂ is dissolved in aqueous I⁻ solution. Such solutions allow molecular iodine, I₂, to be “soluble” in aqueous media (Table 1) and are commonly used in volumetric analysis procedures involving iodine (Vogel 1936).

3 Biological applications

Potassium iodide solutions were used for the treatment of goitre in 1819. The “tincture of iodine” (I₂ plus KI dissolved in aqueous ethanol) was a time-honoured general antiseptic for wounds and water purification. However, as the treatment is painful and there is a reasonable proportion of the population allergic to topical iodine application (manifest as skin rashes), the use of iodine antiseptic treatments has declined.

Iodine is an essential trace element for human health and is absorbed into the blood stream as the iodide ion (following the same biochemical cycles as the chloride ion). Many areas of the world are iodine deficient insofar as background iodine levels are insufficient to provide the World Health Organisation recommendations of 0.15 mg per day. Much of New Zealand and Australia fall into this category and without iodine supplements, a high incidence of goitre is observed.

In 1938, the New Zealand Government recommended that table salt, supplemented with 20 to 30 ppm iodine, be available to the general public and this iodised salt is used today in many households. The legal limits for iodine in salt are a minimum of 20 ppm and a maximum of 65 ppm.

Recently, iodine levels in children in Tasmania and New Zealand have shown a disturbing decline and it has become obvious that the previous sources of iodine are not proving to be sufficient.

4 Analytical applications

The following are brief notes on various methods for the quantitative estimation of iodine.

- (a) Iodometric analysis of iodate in iodised table salt: E. M. DeMaeyer, F. W. Lowenstein and C. H. Tilly, *The Control of Endemic Goitre*, WHO, Geneva, 1979.
- (b) Spectrophotometric methods using Br_2 (H_2O) to oxidise I^- with the excess Br_2 being destroyed by phenol: E. M. DeMaeyer et al.
- (c) ICP / MS: gives total iodine. *Anal. Chem.* 63 (1991) 219. Use of NH_4OH as the aqueous media to reduce “memory effects” in the spectrometer. Sensitive to 0.1 ppb.
- (d) Ion Sensitive electrode: not very reliable.
- (e) Colorimetric: direct urine samples using a redox indicator. D. Gnat, S. Chakev, F. Delange and F. Vertongen, *Hospital Saint-Pierre, Free University of Brussels*.
- (f) Ion Chromatography: used for I^- and IO_3^- in a mixture. H. Bruchertseifer et al. *Anal. Bioanal. Chem.* (2003) 375.

5 Redox reactions in aqueous solution

The current forms of iodine added to dietary supplements are iodide (I^-) or iodate (IO_3^-), either as sodium or potassium salts. Molecular iodine (I_2) is too volatile and is not in a bioavailable form.

Iodine, iodide and iodate are all quite reactive species and the following is a discussion of the redox chemistry of these substances.

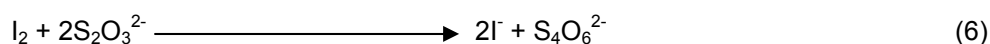
5.1 Electrochemistry

Chemical reactions in which electrons are transferred from one chemical species to another are named redox reactions. These can be expressed as the sum of two “half-reactions” where the left hand side of the equation is a reduction process (addition of electrons):



5.2 Iodide ion

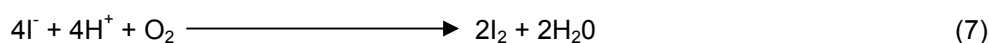
The iodide ion is used extensively as a reducing agent in the volumetric analysis of oxidising agents (iodometry) (Vogel 1936). For example, a known volume of permanganate (MnO_4^-) solution is added to excess acidic iodide solution and the amount of liberated iodine (I_2) is estimated by titration with standard thiosulphate ($\text{S}_2\text{O}_3^{2-}$) solution. In this way, the concentration of the permanganate solution can be measured.



Similarly, the reaction shown in Eq. 4 can be used to measure (IO_3^-) concentrations of $\geq 0.001 \text{ mol L}^{-1}$.

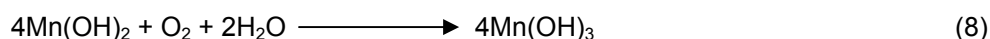
Table 4 lists a number of oxidising agents that can be analysed by reaction with iodide.

Of these, the reaction of iodide with molecular oxygen (O_2) (Eq. 7) is very slow in neutral media, but the rate increases with increasing acidity (decreasing pH). It is also accelerated by sunlight and by various metal ion catalysts (Kimura 1994).



A useful procedure that illustrates the potential for metal ion catalysis is the Winkler method for the determination of dissolved oxygen in potable waters (Massey University, 2004).

In this case, Mn(II) is the catalyst, and in basic solution, Mn(OH)_2 is rapidly oxidised by the dissolved O_2 to give Mn(OH)_3 :



The solution is then acidified with H_3PO_4 and the Mn(III) reacts with I^- to regenerate Mn(II) and to give I_2 (Eq. 9) which can be determined with thiosulphate (Eq. 6).

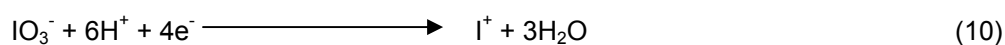


Table 4: Oxidising agents used in iodometry (Vogel 1936)

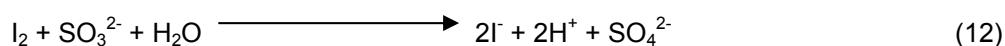
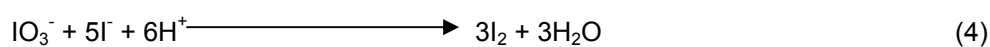
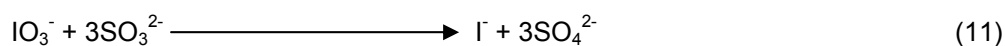
Oxidising Agent	E° (a[H ⁺] = 1) (V)
MnO ₄ ⁻	1.51
S ₂ O ₈ ²⁻ (needs a catalyst)	2.01
Cr ₂ O ₇ ²⁻	1.33
BrO ₃ ⁻	1.49
IO ₃ ⁻	1.13
ClO ⁻	1.48
IO ₄ ⁻	1.09
NO ₂ ⁻	0.983
Ce ⁴⁺	1.76
Cu ²⁺	0.34
Cl ₂	1.36
Br ₂	1.07
O ₂ (needs a catalyst)	1.23
Fe(CN) ₆ ³⁻ (needs Zn ²⁺)	0.36

5.3 Iodate ion

The iodate ion is also used in the volumetric analysis of reducing agents such as Sn²⁺, Cu⁺, Fe²⁺, Hg⁺, I⁻, hydrazine and peroxides. The normal procedure is to use greater than 4M HCl as the reaction media with the iodine stabilised in the (+I) oxidation state as ICl (the Andrews titration).



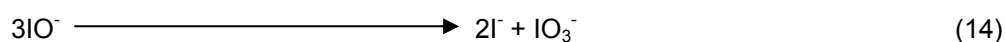
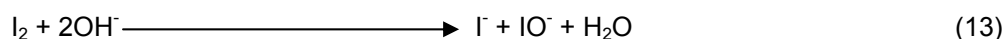
At lower acid concentrations, IO₃⁻ is first reduced to iodide, and the latter is subsequently converted to I₂ (e.g. with S(IV), As(III), H₂O₂ or I⁻ (Eq. 4) as reducing agents). The dependence of the reaction rates of (11) (4) (12) on [H⁺] and the relative concentrations of reacting species has led to the discovery of some spectacular “clock” and oscillating chemical reactions (see also Section 7).



Thus for the reaction sequence (11) (4) (12) (the Landolt reaction), step 11 is slow and I₂ (as indicated by the blue starch-iodine complex) will appear when all the SO₃²⁻ is used up.

5.4 Iodine

Even I₂ is a reasonable oxidising agent in acid solution and volumetric procedures are available using standardised I₃⁻ solutions (I₂ dissolved in excess KI) to determine Sn(II), S(IV) H₂S, S₂O₃²⁻ (Eq. 6) and As (III). At low pH, air oxidation (Eq. 7) can interfere and at higher pH (greater than pH 8), I₂ undergoes disproportionation reactions (15), (16).



5.5 Summary

The above sections illustrate the fact that both I⁻ and IO₃⁻ are reactive chemical species. Any chemical reaction that produces molecular iodine from these precursors could result in iodine loss from the system, due to the high volatility of iodine (Table 1).

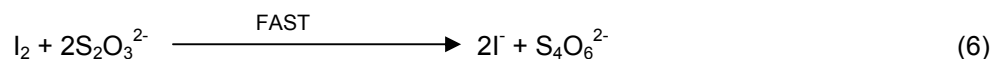
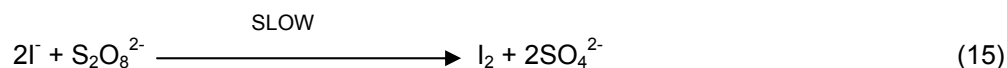
6 Kinetics and mechanism

The rates of all the reactions discussed above have been measured kinetically. With over 70 oxidising agents capable of oxidising I⁻ to I₂ and 70 reducing agents capable of reducing IO₃⁻ to I⁻ (or I₂), the amount of accumulated chemical knowledge is a quite overwhelming. Superimposed upon this information are a variety of catalytic and oscillating processes that have generated intense investigation.

These I₂ producing reactions are popular because the product is easily detected, either spectrophotometrically (λ max (I₂) = 460 nm : ε = 740 M⁻¹ cm⁻¹: λ max (I₃⁻) = 350 nm : ε = 25,000 M⁻¹ cm⁻¹) (Coumes et al., 1998) under dilute conditions, or with starch.

Many have been adopted into “clock” reactions (see Equations 11 to 12 for the Landolt reaction) to measure reaction rates.

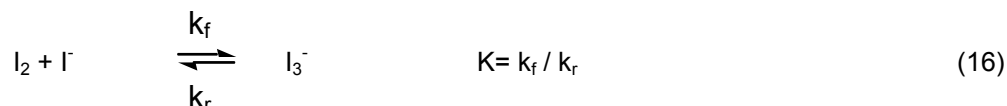
The reaction between I⁻ and S₂O₈²⁻ (peroxydisulphate) (Eq. 15) is quite slow at room temperature. If small increments of S₂O₃²⁻ are added the first formed iodine is rapidly converted back to I⁻ until all the S₂O₃²⁻ is consumed. The sudden appearance of I₂ is manifested by a blue colour in the presence of starch.



The reaction also becomes pseudo-first-order as the $[\text{I}^-]$ is effectively constant (House 1959).

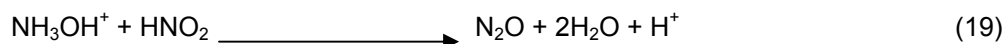
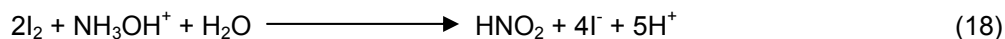
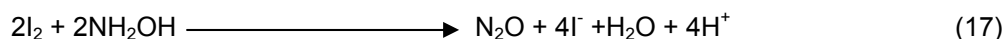
In certain systems and by careful choice of reagent concentrations, colourless-to-blue oscillations can be observed. One such demonstration experiment has been described by Briggs and Raucher (1973).

It should be noted that in all these I_2 producing reactions, excess iodide ion rapidly converts I_2 to triiodide (I_3^-) as the reaction proceeds. This generates a new reactant (I_3^-) which generally reacts more slowly than I^- with the oxidising agent.



At 25°C, the rate of the forward reaction for Eq. 16 is $6.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $K = 729$ (Palmer et al., 1984).

The reaction between I_2 and hydroxylamine (NH_2OH) in aqueous solution (Coumes et al., 1998) illustrates the complexity of a seemingly simple process. First, the stoichiometry is complex and depends on the pH, as the protonated hydroxyl ammonium cation (NH_3OH^+) reacts differently from free hydroxylamine.



Below pH 3.5, the reaction is first-order in I_2 and NH_2OH and is inhibited by I^- and H^+ . In most cases, in the $[\text{H}^+]$ range 0.0003 – 0.3 M, I_2 decreases monotonically with time with a concurrent increase in I^- . However, non-monotonic decay was observed when $[\text{NH}_2\text{OH}]_0 / [\text{I}_2]_0$ was less than 15, with $[\text{H}^+]$ and ionic strength about 0.1 M.

Under these conditions, the $[I_2]$ initially decreased, but then showed an increase (Eq. 20) followed by a further monotonic decrease. In the non-monotonic region, the $[HNO_2]$ was at a maximum at the second I_2 maximum. Under monotonic conditions, the overall rate can be expressed as:

$$\text{Rate} = -d[I_2] / dt = \{k_1 + k_2 [H^+]_0^{-1}\} [I_2]_0 [NH_3OH^+]_0 \quad (21)$$

With $k_1 = 2.2 \text{ M}^{-1}\text{s}^{-1}$ and $k_2 = 6.64 \times 10^{-2} \text{ s}^{-1}$ at 25°C in the $[H^+]$ range $0.03 - 0.0003 \text{ M}$.

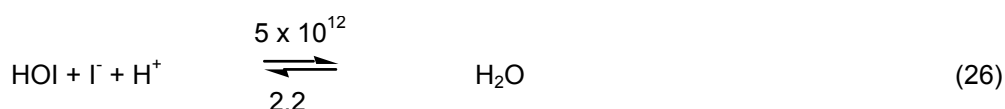
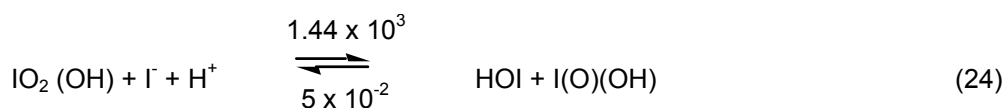
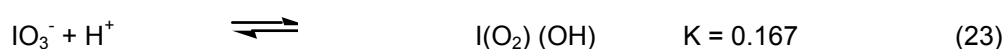
6.1 Oxidation of iodide

Table 5 attempts to summarise some of the available kinetic information where I^- has been used as a reducing agent.

For many oxyanions, the rate law takes the form of:

$$\text{Rate} = k_{\text{obs}} [\text{ox}] [I^-] [H^+]^2 \quad (22)$$

A mechanism involving iodide ion attack on one of the oxygen atoms has been proposed (Benson 1968). Using IO_3^- as an example, Eqs. 23 to 26 have been developed:



with the forward third-order rate constants in units of $\text{M}^{-2}\text{s}^{-1}$ (Simoy et al., 1991).

The reaction of I^- with inert complex ions e.g. $[Ir^{IV}C_16]^{2-}$, $[Fe^{III}(\text{phen})_3]^{3+}$ or octahedral Ni(III) (McAuley et al., 1984; McAuley and Xu, 1988) is almost certainly outer-sphere but an inner-sphere mechanism is proposed for square planer Ni(III) (Fairbank and McAuley, 1987).

One of the most important reactions of the iodide ion in the food industry is the potential for oxidation by atmospheric oxygen (Eq. 7). This reaction is very slow at room temperature but is catalysed by nitrite (NO_2^-) (Kimura et al., 1993) and cupric (Cu^{2+}) ions (Kimura et al., 1994). Unfortunately, we do

not have sufficient kinetic data to estimate the temperature effect, but as a general rule of thumb, reactions of this type double their rate every 10°C increase.

Using the data in Table 5, a half-life of several years at 100°C is estimated. This is in agreement with the work of Kuehne et al., (1991) who showed that there is no great loss of iodine (as iodate) during the cooking of nitrite stabilised bratwurst, even though the iodate was reduced to iodide during the cooking process.

Table 5: Iodide oxidants

Oxidant	Rate Law	Rate Constant (25°C)
BrO_3^-	$k_o[\text{BrO}_3^-] [\text{I}^-] [\text{H}^+]^2$	$50.3 \text{ M}^{-3}\text{s}^{-1}$ ($\mu=1.0$)
$\text{BrO}_3^- + \text{Mo(VI)}$	$k_o[\text{BrO}_3^-] [\text{I}^-] [\text{H}^+] [\text{Mo(VI)}]$	$4.43 \times 10^4 \text{ M}^{-3}\text{s}^{-1}$ ($\mu=1.0$)
IO_3^-	$k_o[\text{IO}_3^-] [\text{I}^-] [\text{H}^+]^2$	$1.44 \times 10^3 \text{ M}^{-3}\text{s}^{-1}$
ClO_2^-	$k [\text{ClO}_2^-] [\text{I}^-] [\text{H}^+]^2$	
HCrO_4^-	$k [\text{HCrO}_4^-] [\text{I}^-]^y [\text{H}^+] [\text{edta}]^x$	
NO_2^-	$k_1[\text{HNO}_2] [\text{I}^-]^2 [\text{H}^+] + k_2[\text{HNO}_2]^2 [\text{I}^-]^2 [\text{H}^+]^2$	$k_1 = 3.7 \times 10^3 \text{ M}^{-3}\text{s}^{-1}$ $k_2 = 3.7 \times 10^{10} \text{ M}^{-4}\text{s}^{-1}$
IO_4^-	$k_1[\text{IO}_4^-] [\text{I}^-] + k_2 [\text{IO}_4^-] [\text{I}^-] [\text{H}^+]$	
MnO_4^-	$k_1[\text{MnO}_4^-] [\text{I}^-] + k_2 [\text{MnO}_4^-] [\text{I}^-] [\text{H}^+]$	
$\text{S}_2\text{O}_8^{2-}$	$k_o[\text{S}_2\text{O}_8^{2-}] [\text{I}^-]^a$	
O_2	$k_o[\text{O}_2] [\text{I}^-] [\text{H}^+]$	Cat. by NO_2^- and Cu^{2+}
Ce^{4+}		
Fe(CN)_6^{3-}	$k_1[\text{Fe(III)}] [\text{I}^-]^2 + k_2 [\text{Fe(III)}] [\text{I}^-] [\text{H}^+]$	$k_1 = 6.6 \times 10^{-4} \text{ M}^{-2}\text{s}^{-1}$ ($\mu=0.5$) $k_2 = 7.8 \times 10^{-3} \text{ M}^{-2}\text{s}^{-1}$ ($\mu=0.5$)
IrCl_6^{2-}	$k[\text{Ir(IV)}] [\text{I}^-]^a$	$328 \text{ M}^{-1}\text{s}^{-1}$ ($\mu=0.01$) $1380 \text{ M}^{-1}\text{s}^{-1}$ ($\mu=0.5$)
IrBr_6^{2-}	$\{k_1[\text{I}^-] + k_2[\text{I}^-]^2\} [\text{IrBr}_6^{2-}]$	$k_1 = 57.1 \text{ M}^{-1}\text{s}^{-1}$ $k_2 = 8.5 \times 10^3 \text{ M}^{-2}\text{s}^{-1}$

Ag(OH) ₄ ⁻	k ₂ [Ag(III)] [I ⁻] ^a	76 M ⁻¹ s ⁻¹
VO ₂ ⁺		cat. by Cu ²⁺
Ni(tacn) ³⁺	k ₂ [Ni(III)] [I ⁻] ^a	191 M ⁻¹ s ⁻¹
Co(III)	k ₂ [Co(III)] [I ⁻] ^a	341 M ⁻¹ s ⁻¹ (μ=1.0)
TiO ₂ ²⁺ (peroxo)	k ₂ [TiO ₂ ²⁺] [I ⁻]	3 x 10 ⁻³ M ⁻¹ s ⁻¹ (1MH ⁺)
TiO ₂ ³⁺ (superoxo)	k ₂ [TiO ₂ ³⁺] [I ⁻]	1.1 x 10 ⁶ M ⁻¹ s ⁻¹
(CH ₃) ₂ SNH ₂ ⁺	k ₁ [(CH ₃) ₂ SNH ₂ ⁺] [I ⁻] [H ⁺]	0.56 M ⁻² s ⁻¹
Hs(V)	{k ₁ [I ⁻] [H ⁺] + k ₂ [I ⁻] [H ⁺] ² + k ₃ [I ⁻] ² [H ⁺] ² }	k ₁ = 0.95 x 10 ⁻³ M ⁻² s ⁻¹
	[As(V)]	k ₂ = 0.26 x 10 ⁻² M ⁻³ s ⁻¹
		k ₃ = 0.71 x 10 ¹ M ⁻⁴ s ⁻¹
Sb(V)	{k ₁ [I ⁻] ² [H ⁺] ² + k ₂ [I ⁻] ² [H ⁺] ⁴ }[sb(v)]	k ₁ = 166 M ⁻⁴ s ⁻¹
		k ₂ = 38 M ⁻⁶ s ⁻¹
Bi(V)	k _o [Bi(V)] ^a	k _o = 161 s ⁻¹

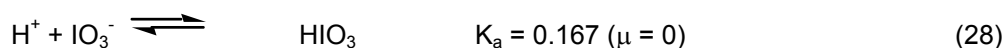
^a Independent of [H⁺]

6.2 Reduction of iodate

Several iodate reduction processes are also characterised by a rate law analogous to (22) (Table 6).

$$\text{Rate} = k_{\text{obs}} [\text{IO}_3^-] [\text{red}] [\text{H}^+]^2 \quad (27)$$

In acid conditions, HIO_3 is the most abundant species, with K_a increasing with increasing ionic strength (Birk 1978).



Consequently, all rate laws in Table 6 have a first-order (or higher) term in $[\text{H}^+]$. However, a proton anomaly exists with weakly basic reducing agents³.

Unfortunately, information for nitrite ion (NO_2^-) is missing from Table 6 but excess ascorbic acid reacts rapidly with iodate to give iodide (Samios et al., 1977).

Other potential reducing agents where kinetic data are lacking are sugars, aldehydes, ketones, thiols and amino acids.

Table 6: Iodate (IO_3^-) oxidations

Reducing Agent	Rate Law (Rate Constant, 25°C)
$\text{Fe}^{\text{II}}(\text{CN})_6^{4-}$	$k_3[\text{IO}_3^-] [\text{Fe}(\text{II})] [\text{H}^+]$ $k_3 = 32.1 \text{ M}^{-2}\text{s}^{-1}$
ascorbic acid	$k[\text{IO}_3^-] [\text{asc}] [\text{H}^+]$ $k = 3.8 \times 10^5 \text{ M}^{-2}\text{s}^{-1}$
NCS^-	$k[\text{IO}_3^-] [\text{NCS}^-] [\text{H}^+]^2$ $k = 4.5 \times 10^5 \text{ M}^{-3}\text{s}^{-1}$
I^-	$k_3[\text{IO}_3^-] [\text{I}^-] [\text{H}^+]^2$ $k = 1.44 \times 10^3 \text{ M}^{-3}\text{s}^{-1}$
$\text{S}_2\text{O}_3^{2-}$	$k[\text{IO}_3^-] [\text{S}_2\text{O}_3^{2-}] [\text{H}^+]^2$
$\text{Fe}(\text{II})$	$k[\text{IO}_3^-] [\text{Fe}(\text{II})] [\text{H}^+]$
IrCl_6^{3-}	$k[\text{IO}_3^-] [\text{Ir}(\text{III})] [\text{H}^+] / (1 + B[\text{IO}_3^-])$
$\text{V}(\text{III})$	$k[\text{IO}_3^-] [\text{V}(\text{III})]$
$\text{V}(\text{II})$	$k[\text{IO}_3^-] [\text{V}(\text{II})]$

6.3 Iodine oxidations

³ Footnote: proton anomaly. A proton anomaly means we cannot decide if the proton is associated with IO_3^- as HIO_3 or with, say, $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ as $[\text{HFe}^{\text{II}}(\text{CN})_6]^{3-}$. Both will give the same rate law.

Some representative I₂ oxidations are given in Table 7. In most cases, I₂ reacts more rapidly than I₃⁻.

Table 7: Iodine oxidations

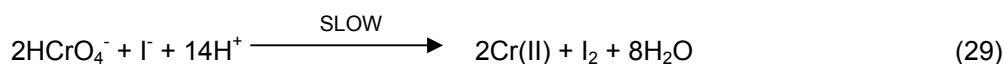
Reducing Agent	Rate Law (Rate Constant, 25°C)
I ^{-a}	$k[I_2][I^-]$ $k = 6.2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$
NCS ⁻	$k[I_2][\text{NCS}^-]$ $k = 6 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
S ₂ O ₃ ²⁻	$k_1[\text{S}_2\text{O}_3^{2-}][I_2] + k_2[\text{S}_2\text{O}_3^{2-}][I_3^-]$ $k_1 = 7.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, $k_2 = 4.2 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$
CN ⁻	$k = [I_2][\text{CN}^-]$ $k = 5 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$
U(IV)	slow
As(III)	$k_3[\text{As(III)}][I_2][\text{H}^+]^{-1}[\text{I}^-]^{-1}$
NH ₂ OH ^b	$k_0[I_2][\text{NH}_3\text{OH}^+]$ (see text) $k_0 = 8.2 \text{ M}^{-1}\text{s}^{-1}$
V ²⁺	$k_1[I_2][\text{V(II)}] + k_2[I_3^-][\text{V(II)}]$ $k_1 = 7.5 \times 10^3 \text{ M}^{-1}\text{s}^{-1}$, $k_2 = 9.7 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}$
Au(CN) ₂ ⁻	$k_2[\text{Au(I)}][I_2] + k_3[\text{Au(I)}][I_3^-]$ $k_2 = 2.8 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$, $k_3 = 4.40 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$

^a For comparison, not redox

^b I₃⁻ not reactive

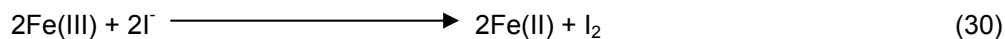
7 Catalytic and induced reactions

The oxidation of iodide ion by chromium(VI) in dilute acid solution (0.001 M) and at low Cr(VI) concentrations is very slow.

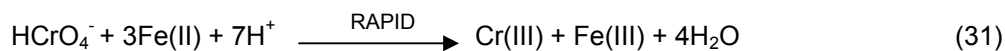


Similarly, the oxidation of I⁻ by Fe(III) is also slow.

SLOW



However, the reduction of Cr(VI) by Fe(II) is fast:



When these systems are combined it was found that iodide is rapidly oxidised to iodine in the presence of small amounts of iron(II).



Iron (II) is said to induce the reaction between Cr(VI) and I(-I) (Benson, 1968; Edwards, 1964) and is not a true catalyst, as it is not regenerated in the system.

Specific iodide ion catalysis is observed in the Ce(IV) plus As(III) reaction and the system has been developed as a kinetic method for the analysis of low levels (10^{-8} M) of iodide ion (Sandell and Kolthoff, 1934; Deraniagala et al., 1993).

8 References

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APPENDIX B - EXPERIMENTAL METHODS

1 Peroxides in oil

Peroxide concentrations in oil samples were analysed using the FOX II assay (Conlon et al. 2002) using a plate reader. Stock A was prepared by dissolving 49 mg ammonium ferrous sulphate with 38 mg xylenol orange in 5 ml water containing 300 μ l sulphuric acid (98%). Stock B was prepared on the assay day by dissolving 96.97 mg BHT in 100 ml absolute ethanol. Immediately prior to use the "reagent" was prepared by mixing 200 μ l Stock A with 20 ml Stock B. Hydrogen peroxide stock was prepared by dissolving 10 μ l of 30.4% hydrogen peroxide in 50 ml propan-1-ol (2 mmol/l). Twenty microliters of the sample (or control, standard, or blank) were placed in the wells of a 96-well microtitre plate and 180 μ l fresh reagent added. The plate was incubated at room temperature in the dark for 30 min and then read on a plate reader at 540 nm. Sample absorbance values were corrected for reagent blanks and concentrations calculated using the standard curve, corrected for the lipid blank.

2 Free fatty acids in oil

Prior to analysis, vials containing oils were shaken and allowed to stand at room temperature to ensure that oils were liquefied and well-mixed before weighing. An oil sample (approximately 30 to 40 g) was weighed accurately and placed into a 250 ml conical flask. Then 50 ml of pre-neutralised ethanol and 2 ml of phenolphthalein indicator (1% in 95% ethanol) were added to the flask. The mixture in the flask was heated using a hot plate to just boiling, then titrated with standard alkali (0.1 M KOH) to the point where a faint pink colour persisted in the alcohol layer for 30 seconds. The amount of total free fatty acids was calculated and expressed as the percentage based on oleic acid equivalents. In all cases, analyses of free fatty acids were done in duplicate.

3 Iodine analysis

Samples of biological origin (e.g. dairy products or foods) were digested with tetramethylammonium hydroxide (TMAH) at an elevated temperature and the extracts were chilled and filtered. Iodine was determined by ICP-MS. The method is based on the procedure of Fecher et al., (1998).

Approximately 1 g of the starch solutions and 0.5 g of the oil samples were weighed for analysis into pre-calibrated capped polycarbonate tubes. TMAH reagent (12.5% [w/v]) was added to all tubes. The oil samples were pre-extracted overnight (16 hours) by stirring the contents of the capped polycarbonate tubes using an orbital shaker with the tubes freely rolling on their long axis. This was done to enable the iodine to be selectively partitioned into the aqueous alkaline phase during the shaking treatment. All samples were then digested by heating tubes in a block pre-heated to 90°C for 60 minutes. Samples were then cooled and diluted to final volume with water and stored overnight in

a refrigerator. The chilled samples were then filtered through a 0.45 µm filter under reduced pressure ready for instrumental analysis. Digest batches also contained procedural blanks, an in-house quality control sample and suitably spiked samples.

Iodine was determined by ICP-MS, using a Perkin Elmer 6000 Series instrument as ¹²⁷I and quantified by comparison with standard samples of iodine.

4 Quality Control (QC)

One sample of skim milk powder as an in-house QC sample was analysed in every batch because this type of sample matrix reflects the predominance of milk powders analysed at Hill Laboratories. The results for this QC are monitored to check for consistency of results from batch to batch. Typical results obtained for this QC from a number of sequential batches are 0.44 ± 0.035 mg/kg, 8.0%, n = 30 (mean; one standard deviation; %RSD; and results taken from 30 sequential batches for the current QC sample). Certified reference materials (CRM) were also analysed on a regular basis to check method accuracy (NIST 1549 Skim Milk Powder, NIST 8435 Whole Milk Powder, SRM 1515 Apple Leaves).

5 References

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APPENDIX C - EXPERIMENTAL RESULTS

1 Solubility of iodine in oil

Theoretically 0.5 mM iodine (63.5 mg iodine per litre of oil) was added to the oil at room temperature, before heating began. The control oil contained a natural, low amount of iodine which rapidly disappeared on heating at 180°C. The other results reflect the low solubility of potassium iodate and potassium iodide in the oil, as only 0.45% of iodide and 1.1% of iodate was recovered from the oil at the highest concentration (120 minutes and 10 minutes, respectively). Potassium iodide was slowly and progressively solubilised during the heating process whereas potassium iodate seemed to reach a peak concentration at 10 minutes then become less soluble. This may indicate that iodate is very insoluble in oil, but is converted via iodine, to potassium iodide. There were still crystals in the oil at the end of the heating period for both iodide and iodate.

Elemental iodine, while visually (qualitatively) completely dissolved in the oil, was only recovered at 31% of the added iodine at the start of the heating process. The reason for this was unclear, but may be related to the analytical procedures. Iodine is known to react across the double bonds of unsaturated fats and the method used to extract iodine from the samples may have failed to remove that covalently bound iodine. Further research work is required to establish this conclusion.

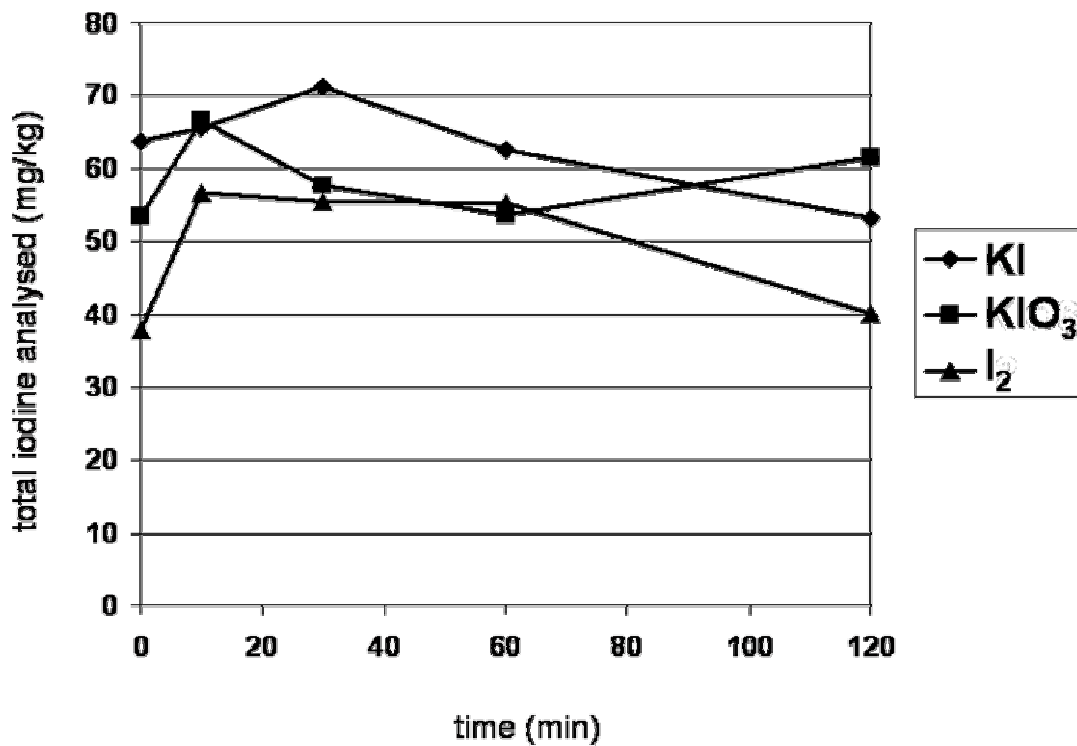
The solubility of elemental iodine followed a similar pattern to iodate, peaking at 10 minutes of heating at 180°C then declining for the remainder of the heating process. This increase in solubility at 10 minutes was accompanied by a deepening in orange colour which disappeared during further heating.

It can be concluded that potassium iodide and potassium iodate are both sparingly soluble in oil, reaching somewhere between 0.3 and 0.8 mg iodine per litre of oil during heating. Iodine, on the other hand, is relatively soluble in oil and would clearly partition preferentially into a lipid phase in foods. This suggests that in foods comprising both aqueous and lipid phases, any reactivity that oxidises the water-soluble iodide (to iodine) or reduced iodate (to iodine) would likely result in the movement of iodine from the aqueous to lipid phase.

2 Solubility of iodine in starch solutions

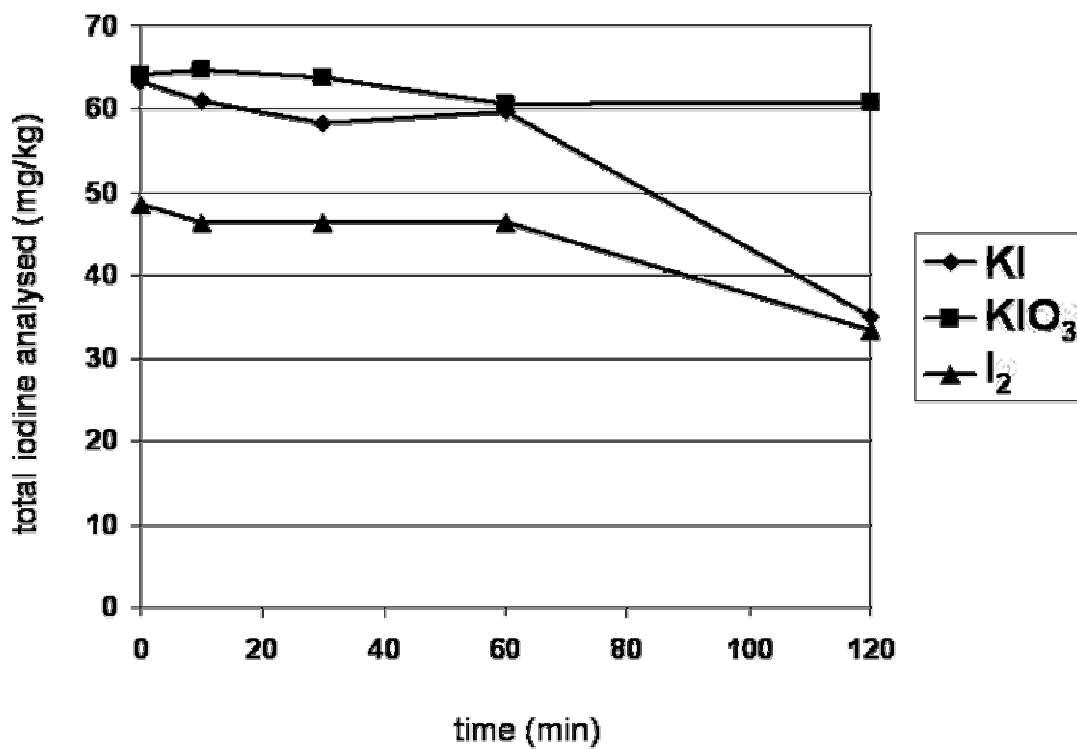
As for the oil experiments, potassium iodide, potassium iodate and elemental iodine were added to 1% w/w starch solution at differing pH values. Figures 2 to 5 show the results of total iodine analysis of starch solutions at different pHs. These data have been adjusted to compensate for both the observed evaporation of water that occurred during heating and the amount of sample (30 ml) removed for each sampling time.

Figure 1: Changes in total iodine concentrations on heating a starch solution at pH 2



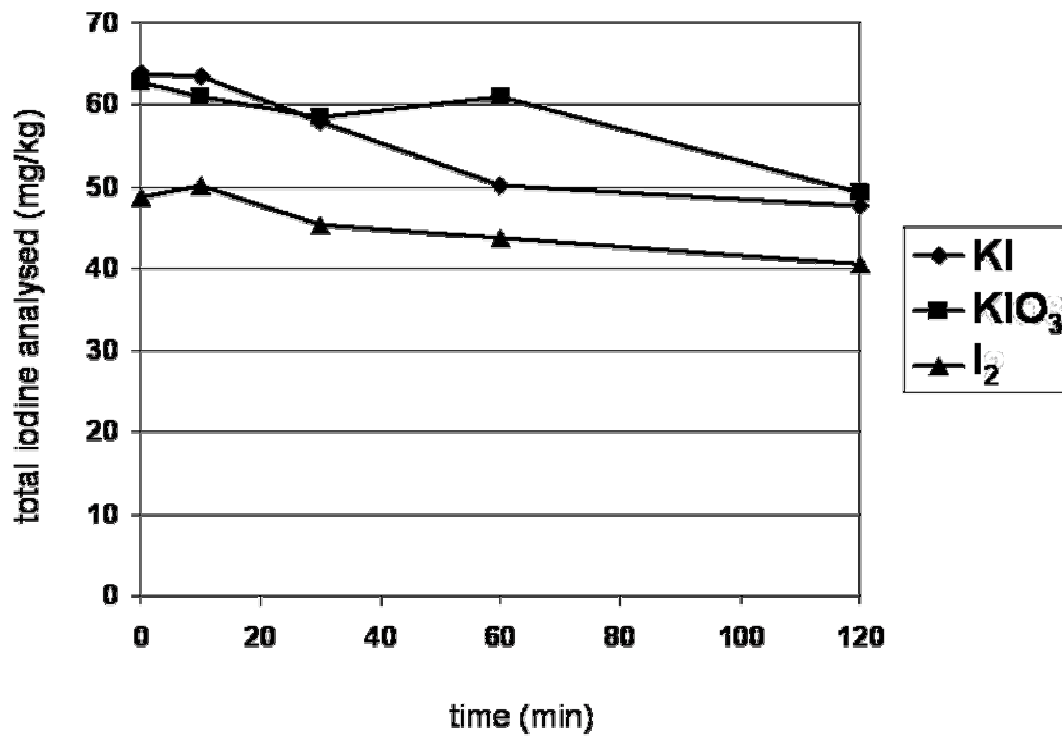
Iodine, potassium iodate and potassium iodide were added to give 0.5 mM iodine (63.5 mg iodine per kg)
 Starch solution was 1% w/w
 "Zero" time represents when solutions reached at least 90°C

Figure 2: Changes in total iodine concentrations on heating a starch solution at pH 5



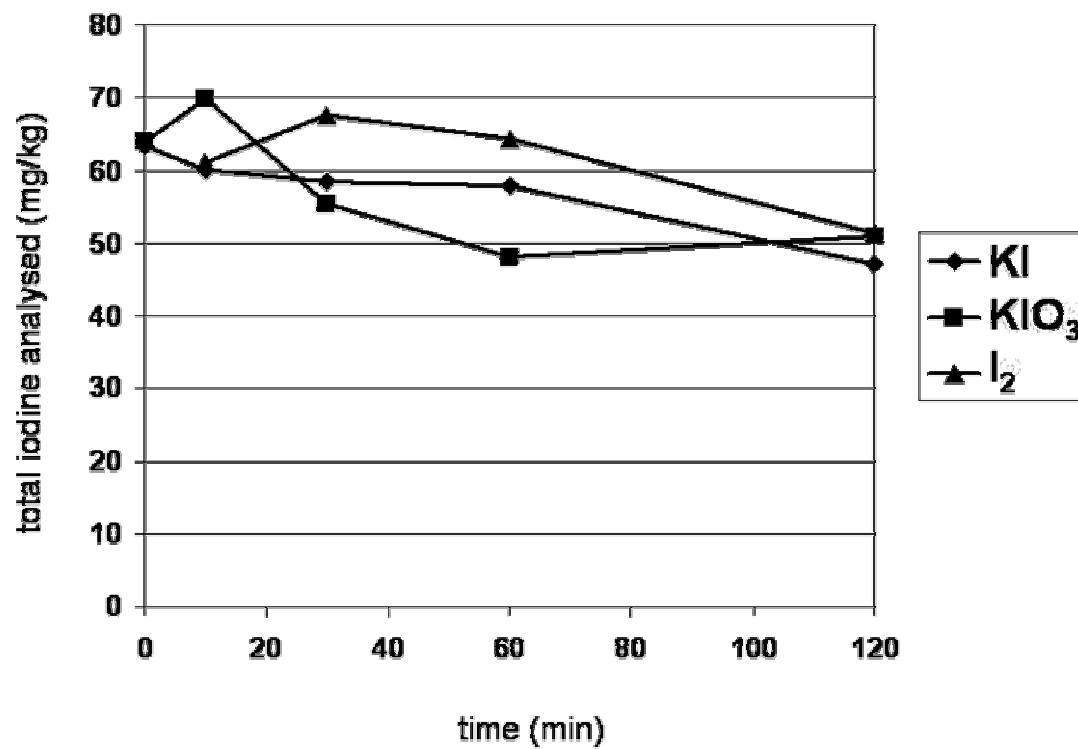
Iodine, potassium iodate and potassium iodide were added to give 0.5 mM iodine (63.5 mg iodine per kg)
 Starch solution was 1% w/w
 "Zero" time represents when solutions reached at least 90°C

Figure 3: Changes in total iodine concentrations on heating a starch solution at pH 7



Iodine, potassium iodate and potassium iodide were added to give 0.5 mM iodine (63.5 mg iodine per kg)
 Starch solution was 1% w/w
 "Zero" time represents when solutions reached at least 90°C

Figure 4: Changes in total iodine concentrations on heating a starch solution at pH 9



Iodine, potassium iodate and potassium iodide were added to give 0.5 mM iodine (63.5 mg iodine per kg)
 Starch solution was 1% w/w
 "Zero" time represents when solutions reached at least 90°C

The initial concentrations of iodine measured in the solutions containing added iodide and iodate were the same as the added amounts, indicating these salts were fully solubilised and easily recovered from the starch solutions.

Iodine losses were observed for potassium iodide and potassium iodate during the heating process and this appears to be related to loss from the system. In general about 20% of the iodine is lost after 2 hours at 100°C. Iodide and iodate stability seems to be improved by lowering the pH of the solution.

3 Peroxides in oil

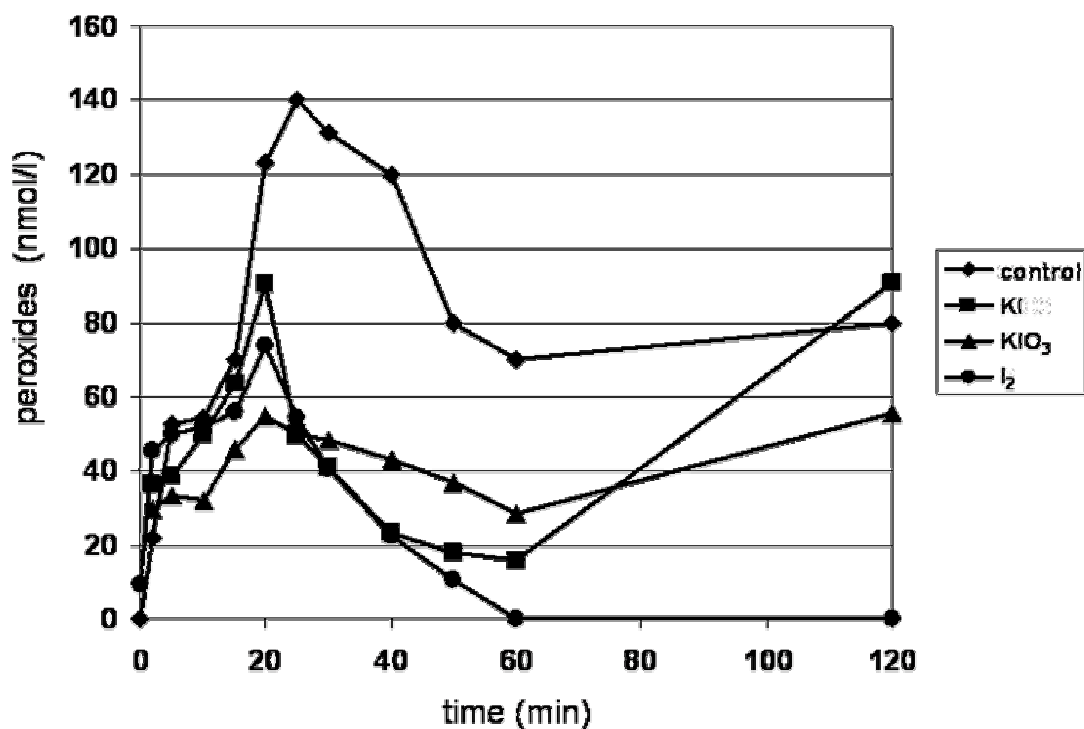
The addition of iodine, regardless of its form as iodide, iodate or elemental iodine, showed a similar rate of change as the control sample, but at a much lower level. There were insufficient data points available to properly interpret these observations. However, elemental iodine concentrations were particularly high in this oil and the zero peroxide values for all but the 30 minute period suggests the iodine had reacted with the double bonds in the oil and effectively stabilised them completely against fat oxidation. Iodide and iodate were present at much lower concentrations in the oil and may have only partially reacted with the fatty acid double bonds. As iodate is a potent oxidising agent and iodide a potent reducing agent, these data suggest that both forms of these salts could have been present in the oil. Unfortunately, there are no easy, reliable methods for measuring the different forms of iodine in foods.

This trial was designed to quickly assess possible interactions with fats. The results are inconclusive and confusing. It is also important to note, that despite iodide and iodate being relatively insoluble in the oil, these chemicals did have an effect on fat oxidation. The high temperatures used in this experiment can also be considered a form of accelerated shelf life testing.

While differences have been shown between oils containing iodine, compared to the control oil, peroxide values alone are insufficient to define whether these effects involve pro- or anti-oxidative action. It is possible that the mechanisms and results from each iodine salt are different. It is equally plausible to assume that iodide, iodate and iodine moieties could be present in all three solutions because of the reaction mechanisms that promote their chemical interchange.

This experiment was repeated using a new sample of sunflower oil. Iodine and its salts were added at 0.5 mM (63.5 mg iodine per litre of oil; 70.6 mg iodine per kg oil) and heated at 180°C for up to 2 hours. These results are shown in Figure 5.

Figure 5: Influence of iodine on peroxide formation in sunflower oil during heating at 180°C: trial 2



Iodine and salts were added at room temperature

"Zero" time represents the time when the oil reached 180°C

All original concentrations of iodine, potassium iodide and potassium iodate were 63.5 mg iodine per litre oil or 70.6 mg iodine per kg oil

The pattern of changes was the same as the earlier trial. The addition of iodine, regardless of its form as iodide, iodate or elemental iodine, resulted in a lower concentration of peroxides during the period of observation. This indicates an interaction between iodine and unsaturated fatty acids during heating. Added elemental iodine resulted in peroxides reaching a peak at 20 minutes, then returned to undetectable levels by 60 minutes. Iodide and iodate addition resulted in a peak at 20 minutes, a decline at 60 minutes and a dramatic increase at 120 minutes. As these two salts represent a reducing and an oxidising agent respectively, the similar pattern of peroxide change suggests these two salts may have reacted to give a balance of iodine chemical moieties that was similar in both samples of oil (for example, iodide may have formed iodate and iodine whereas iodate may have formed iodide and iodine).

It is not possible to draw further conclusions about rancidity or fat oxidation from these studies alone. Further work is required (e.g. sensory analysis, or additional chemical tests) to define organoleptic or fat oxidation changes in the oil. However, it is clear that there is a significant interaction between iodine, its salts and the oil components.

4 Free fatty acids in oil

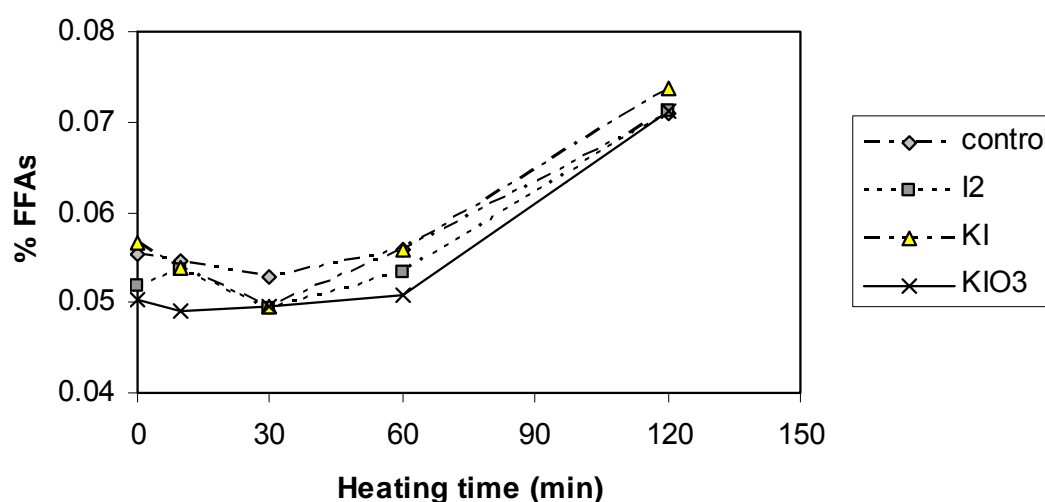
These results are shown in Table 1 and visually in Figure 6.

Table 1: Influence of iodine on free fatty acid (FFA) changes in sunflower oil heated at 180°C

Sample	Heating time (min)	% FFA
Control	0	0.0554 ± 0.0071 ^a
	10	0.0547 ± 0.0009
	30	0.0528 ± 0.0093
	60	0.0558 ± 0.0001
	120	0.0711 ± 0.0008
I ₂	0	0.0518 ± 0.0008
	10	0.0537 ± 0.0016
	30	0.0494 ± 0.0073
	60	0.0534 ± 0.0107
	120	0.0711 ± 0.0039
KI	0	0.0567 ± 0.0026
	10	0.0538 ± 0.0037
	30	0.0496 ± 0.0051
	60	0.0559 ± 0.0021
	120	0.0736 ± 0.0026
KIO ₃	0	0.0502 ± 0.0014
	10	0.0491 ± 0.0038
	30	0.0495 ± 0.0016
	60	0.0509 ± 0.0034
	120	0.0711 ± 0.0065

a) mean ± standard deviation (duplicate samples)

Figure 6: Influence of iodine on FFA changes in sunflower oil heated at 180°C



There were no significant differences between any of the samples. They all followed the same pattern of changes reflecting the hydrolytic cleavage of fatty acids from the oil as a result of heating alone.

5 Iodine in bread

Total iodine concentrations of the crust and crumb of the cooked loaves are shown in Table 2.

Table 2: Total iodine concentrations in bread fortified with potassium iodide or potassium iodate

Iodine source	Iodine added to uncooked dough (mg/kg dough)	Iodine added (mg loaf) ^a	Iodine analysed in cooked bread (mg/kg bread)	Iodine analysed in cooked bread (mg/loaf) ^b	Iodine retention (%)
CRUMB					
Control	n/a	n/a	0.15 ± 0.03	0.11 ± 0.02	-
KIO ₃	1,000	800	685 ± 10.6	480 ± 7.4	59.9
KIO ₃	100	80	67.9 ± 1.4	47.5 ± 1.0	59.3
KIO ₃	10	8.0	7.0 ± 0.2	4.9 ± 0.2	60.1
KIO ₃	1	0.8	1.1 ± 0.2	0.76 ± 0.13	84.3
KI	1,000	800	876 ± 9.9	613 ± 6.9	76.6
KI	100	80	92.2 ± 0.5	64.5 ± 0.3	80.6
KI	10	8.0	9.4 ± 0.3	6.6 ± 0.3	80.9
KI	1	0.8	1.1 ± 0.01	0.79 ± 0.005	87.0
CRUST					
Control	n/a	n/a	0.17 ± 0.03	0.12 ± 0.02	-
KIO ₃	1,000	800	844 ± 21.6	591 ± 15.1	73.8
KIO ₃	100	80	83.6 ± 1.2	58.5 ± 0.82	73.0
KIO ₃	10	8.0	8.3 ± 0.3	5.8 ± 0.2	71.4
KIO ₃	1	0.8	1.2 ± 0.09	0.85 ± 0.06	92.4
KI	1,000	800	926 ± 103	648 ± 71.8	81.0
KI	100	80	81.7 ± 6.8	57.2 ± 4.7	71.4
KI	10	8	8.9 ± 1.6	6.2 ± 1.2	76.8
KI	1	0.8	1.2 ± 0.1	0.85 ± 0.07	92.7

a One loaf of bread weighed 800 g of uncooked dough

b One loaf of bread weighed 700 g of cooked bread

n/a The actual concentration of iodine in the original dough (no added iodine) was not measured

The actual concentration of iodine in the uncooked dough was not measured directly, but clearly there was some present naturally, given that low levels still existed in the cooked bread.

Iodine was lost at all concentrations, for both added iodide and iodate. However, consistent with the relative volatility of the two salts, iodate losses were significantly greater than iodide. About 40% of the iodate and 20% of the iodide was lost from the crumb. Around 30% of the iodate and 25% of the iodide was lost from the crust region of the bread. The lowest level of added iodine (1 mg iodine per kg dough) appeared to have the highest retention of iodine. However, this is likely to be clouded by the experimental error measuring such low iodine concentrations: the 10 to 1000 mg iodine per kg dough samples provided the same level of iodine retention for each salt.

Some of the iodine that was “lost” would have evaporated and be permanently lost. It is possible that some iodine reacted with dough constituents (e.g. lipid, protein or carbohydrate) and was not extracted from the bread with the analytical techniques used. Such reactions may include the Maillard (non-enzymic browning) reaction. However, it would be expected that such reactions would

be more extensive in the crust rather than the crumb due to higher temperatures reached in the crust. The higher iodine retention found in the crust indicates the extraction procedures were effective and the amount of “bound” iodine was likely to be negligible. It should be noted, however, that no attempt was made to adjust these data for moisture content (of crumb and crust). As the crust would have a lower (not measured) moisture content than the crumb, this may account for the apparently higher retention of iodine in the crust.

The IFNHH taste panel found that breads with higher iodate concentration (100 and 1000 ppm) showed differences in appearance, taste, and crumb texture. The panellists described these differences as yellow or caramel in colour, darker or browner colour; the taste was slightly “sharp”, bitter, and artificial; the texture was chewy, doughy, and sticky. The majority of panellists did not like the 1000 mg/kg iodate bread.

Visual differences were noticeable also for bread containing 1000 ppm iodide but this did not seem to affect the eating characteristics. The panellists noted dark spots throughout the crumb in this bread, which tended to be pale yellow. The bread looked doughy and had a coarse crumb, but tasted acceptable to most panellists.

This was an informal panel evaluation with 10 people. It would appear the bread produced with 1 and 10 ppm iodine was the same as bread without any added iodine. Iodate definitely had a significant impact on bread characteristics (appearance and eating quality) at 100 and 1000 ppm iodine. Iodide had an effect at 1000 ppm iodine only, but this tended to be limited to appearance alone.

In conclusion there is a significant loss of iodine from bread during the cooking process. The extent of this loss depends upon the iodine salt being used. At low levels of iodine addition there appears to be little, if any, impact on the bread making process, or the eating quality of the finished product. This experiment only evaluated standard white bread, therefore the influence on other types of bread is not known.

6 Effects of addition of iodine in various food systems

There were no noticeable changes in colour or smell for all samples tested in this study during heating and storage of samples for five days after heating. No differences between control and iodine fortified samples were observed. These observations were visual and qualitative.

In summary, the various tests performed in this study suggest iodine and its salts may interact with some food components at high concentrations. A summary outlining these reactions is given in Table 3.

Table 3: Foods showing a reaction with iodine

Food	I₂	KI	KIO₃
Oil	Impact on peroxide formation Colour reaction	Impact on peroxide formation	Impact on peroxide formation
Starch solution	Colour reaction Binding to starch		
Bread		Changes in colour and sensory properties at high concentration	Colour reaction Changes in texture Changes in taste