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Adventitious metals in processed foods

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Primitive man consumed all his food in the raw state. If we could believe Charles Lamb (1823) an enthusiasm for roast flesh arose through the attractive aroma evolved when a pigsty caught fire. As one age succeeded another, roasting on an open hearth was superseded by cooking in utensils.

As soon as man secured a measure of domination over other animals, he began to exercise his ingenuity to obtain increased production of the foods yielded by them. The next advance was to preserve the surplus food for future use. To this end, processing in one form or another was devised, such as drying, salting, the addition of spices and preservation by means of fermented liquors. It is exactly 150 years since the first experiments on preserving food over long periods were made by Appert (1810).

Simultaneously with the progressive developments with flesh foods, attention has been directed to the promotion of increased yields of crops. Unfortunately, the concentration of plants of one kind in a relatively small space greatly increases the hazards of their destruction by pests, therefore chemical control is imperative to combat the depredations by insects and fungi. Some of the sprays used are compounds of toxic metals, and minute amounts of these are liable to persist and be carried into the finished products.

This survey is concerned with the presence of adventitious metals in processed foods, but no sharp line of demarcation can be drawn between raw materials and manufactured foods because most of the commodities delivered at the food factory have undergone some form of primary processing, for example curing of cocoa, drying of fruit or pulping of it in preparation for jam-making, extraction of gelatin from hides and rendering or refining of fats. On the other hand, commodities such as highly refined sugar, wheat flour, cornflour, confectioners' glucose, treacle, condensed milk, butter, dried eggs and wine and spirits are among the raw materials used in the food industry.

Adventitious metals may be present in many of the raw materials as received and further contamination is liable to occur in the factory. With canned foods, absorption of tin and iron by the contents progresses after the goods have left the factory.

When drawing up recommendations for limits of traces of metals in foods, the Food Standards Committee of the Ministry of Agriculture, Fisheries and Food is guided by what is judged to be good commercial practice; hence the limits proposed for certain scheduled foods are either above or below the general limits recommended for copper, lead and zinc, and the statutory limits for arsenic in beverages and solid foods. In the event of undesirable amounts of other metals being present in food sold for human consumption, it is open to the authorities to take action under the Food and Drugs Act, 1955 (Great Britain. Parliament, 1955) on the grounds that the food is not of the nature, or not of the quality, or not of the substance demanded by the purchaser. The onus is, therefore, on the food manufacturer to inspect the raw materials and to observe every possible precaution against the 'pick-up' of adventitious metals during processing. There is no doubt that increased vigilance exercised by the authorities and the manufacturers alike is leading to a salutary decrease in the level of metallic contaminants in foods. Though greater awareness of the means of prevention of metallic 'pick-up' has led to improvements in the construction of new factories, the former premises are often re-occupied by another food manufacturer and the chances are that he will take over some of the old equipment.

The factory

All paint used in the factory should be lead-free. Some fungicidal paints contain organo-mercurial compounds and are, therefore, unsuitable for places where food is being manufactured or stored. Coppock & Knight (1958) found that more mercury is extracted by condensation from emulsion paint than from high-gloss paint. Introduction of iron is a frequent cause of contamination of foodstuffs. Even at comparatively low levels, it can cause development of off-flavour in fats and discoloration of fruit products. Fall of rust from girders and overhead pipes can be prevented by using rust-resisting paint and taking precautions to avoid considerable condensation. This condition can be met by improving ventilation with extractor fans, and placing hoods over equipment from which steam rises, as well as by lagging cold-water pipes.

Wear of machinery, especially during grinding operations, worn plating, unsuitable joints and loose nuts and bolts are frequent sources of metallic contamination. Equipment should preferably be made from metals that are not readily subject to abrasion, for example, stainless steel. Stirrers and cutters should be thoroughly cleaned after use. After metal equipment is polished, either by burnishing or with metal polish, it should be thoroughly washed with hot water before being used again.

During a series of tests carried out at our laboratory for a member firm, it was noted that the production on Monday mornings invariably showed the highest copper content. It was attributed to the effect of the weekend cleaning of the equipment. A firm of whisky distillers asked us to investigate the cause of a haze which formed in the liquor and later settled out. The deposit contained a considerable quantity of copper. The source of contamination was eventually traced to exposure of copper owing to wear of the protective plating on the filter used.

Accidental contamination may arise through loose pieces of steel wool and bits of wire detached from wire brushes used for cleaning, or rust from hoods that need repainting. As a result of temporary repairs being carried out, fragments of wire from flex and cables, particles of metal from drilling operations, and even red lead and bits of solder may find their way into food. Occasionally contamination has been found to occur through the impulsive act of a disgruntled employee who throws anything that is handy into the food.

Overalls worn by the workers should not be fastened with buttons made of metal or with metal attachments. When coins, paper clips, safety pins or other small articles are carried in overall pockets, there is a risk that they may fall out when the worker assumes a stooping position. Because hair clips are liable to become detached, women should wear caps.

Contamination by zinc has occurred in the past and still does occasionally through the use of galvanized containers. Enamel ware containing large quantities of antimony is unsuitable for use in a food factory. Much publicity has been given to the danger arising from its use as a recipient for fruit juice. Furthermore it is not generally appreciated that some plastic vessels contain a lead filler.

There are attendant dangers in the use of rodenticides containing zinc phosphide or arsenious oxide where food is stored.

Since water is added in the preparation of many foods and extensively used in cleaning operations, it is essential that the supply shall be as free as possible from lead and iron as well as from substances that promote the corrosion of service pipes. Wormwell & Nurse (1952) studied the effect of chlorination of flowing water on mild steel and brass and found that it was negligible when the free chlorine content was below 0·4 p.p.m.

Inspection of materials coming into the factory

Nails from crates, pieces of wire used to fasten bags, bits of broken wire baskets and wire gauze from sieves, shot in game, fish hooks remaining in fish and parts of wire ornaments worn by workers in the country of origin are among the metal objects that may be present in foodstuffs. Most of them can be removed by hand-sorting when the goods travel on conveyor belts or on rotating tables. As it is a tedious occupation some of the extraneous matter may escape detection owing to fatigue. In spite of aids such as magnetic and electronic devices for automatic separation, some of the foreign bodies can be missed and carried over to the next stage.

Fruits and vegetables are washed to remove as much pesticide residues adhering to the surface as possible, but this treatment fails to remove anything that is under the skin.

Many chemicals are used in food processing, for example salt in a wide range of foods, alkaline carbonates for the so-called solubilization of cocoa powder, citric and tartaric acids in boiled sweets and lemonade powder, acetic and lactic acids in pickles, raising agents for self-raising flour, hydrochloric acid for starch conversion, and polyphosphates in sausages. The manufacturer should either demand a guarantee that they are reasonably free from metallic contamination or else have them examined

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in his own laboratory. Routine chemical analysis of these substances in addition to the other commodities arriving at or leaving the factory is very time consuming. At present, the number of chemists engaged on such work in this country represents a considerable deployment of scientific effort.

In view of repeated warnings that young children are apt to place sweets in their mouths without removing the wrappers, it is necessary to have an assurance that the wrapping materials themselves and the printing inks used on them are free from harmful metals.

A firm making chocolate novelties in the form of watches covered them with foil and inserted metal winders in contact with the chocolate. After a time complaints were received from customers because the tips of the winders had turned green, probably owing to the action of traces of free fatty acid on the copper.

It is permissible to add certain metals and metallic oxides to foods for the purpose of colouring them. The oxide of iron known as 'bole', titanium dioxide, and silver and aluminium leaf for the external decoration of confectionery are included in the list of permitted food colours.

Canned foods

The shelf life of canned foods depends on a number of factors that vary according to the type of food. Some foods have a reasonable shelf life when they are packed in plain cans, whereas for other food packs a coating of lacquer is used to protect the tinplate.

When cans are made from sheet tinplate, cracks in the plating are apt to occur, particularly at the seams. Better protection of the steel is afforded if the tin coating is applied to the finished can; nevertheless, after either process, the film of tin is never absolutely free from minute pores which permit exposure of the steel to attack by the food. As lacquer is equally liable to crack, it is preferable to coat the cans than to use lacquered sheet. Breakage of the film is apt to occur also at the site of embossed coding numbers. Since the presence of oxygen favours attack of tin by organic acids, air should be removed as completely as possible. Exhaustion is more difficult to achieve in meat packs than in fruit packs. Because corrosion is accelerated at high temperatures, the cans should be efficiently cooled before they are stacked and they should be stored in as cool a place as possible.

The rate at which fruit acids attack steel base varies in different portions of the same sheet. These variations are not eliminated when steels that corrode at different rates are coupled with tin (Morris, 1933). Hoar, Morris & Adam (1939) carried out a statistical experiment on all kinds of steel base manufactured in Great Britain. They found that the shelf life of many fruits could be extended considerably by the use of steel with a high copper content (0·16–0·22%) and low phosphorus content (0·03–0·045%).

Under certain conditions, sulphides accelerate corrosion by acid solutions. Sulphur from spray residues renders iron permanently anodic to tin and causes acceleration of corrosion at a low pH. Sugar used for canned goods should be free from sulphites. The appearance of the interior surface of cans containing foods having an appreciable natural sulphur content may be improved by coating it with a sulphur-resisting lacquer containing zinc oxide which absorbs sulphuretted hydrogen and leaves a greyish film instead of the unpleasant-looking dark stains of the tin compounds.

Hydrogen 'swells' caused by the action of acids on the metal are actually more common in lacquered cans than in plain ones. Especially when cans are made from pre-lacquered tinplate, there may be a few points where tin is exposed. Action of corrosive substances is concentrated at these sites. Residual air in the can and oxygen carriers such as anthocyanin pigments favour solution of the tin with consequent exposure of the iron. Iron is initially anodic to tin, but soon becomes the cathode. Tin salts inhibit corrosion of iron, but when the rest of the can is covered with lacquer, the iron is unprotected electrochemically, hence it is open to attack by organic acids. In plain cans, because the surface area of tin is much larger than that of iron, anodic tin affords electrochemical protection which is greatest at high acidity. Broadly speaking, about two-thirds of the tin taken up from cans is present in the form of insoluble compounds with protein.

Removal of tin from plain tinplate is more severe with products of low acidity such as asparagus, meats and certain fruits. Prunes are a notable source of trouble. They produce hydrogen 'swells' very rapidly unless citric acid is added to the syrup. Enzymes in the stones of canned fruit are capable of remaining active after heat treatment that gives adequate protection against spoilage by micro-organisms. According to Dickinson (1957) the presence of an active β-glucosidase in kernels accelerates the corrosion of lacquered cans. A recent compromise that appears to prolong the shelf life of canned dried prunes is to pack them in cans having a lacquered body and plain base and lid in order to provide better electrochemical protection of the iron.

Lacquered cans are recommended for fruits and vegetables containing red or purple pigments in order to minimize the darkening of colour arising through combination with tin. Blackberries and blackcurrants assume a blue or violet colour in the presence of tin. The blackening of canned crab has been attributed to the copper content of haemocyanin (Monier-Williams, 1949).

There is a recommended limit of 250 p.p.m. for tin in canned foods (Ministry of Food: Food Standards Committee, 1953).

Arsenic

Under the Arsenic in Food Regulations (Great Britain. Parliament, 1959), a limit of 1 p.p.m. of arsenic was imposed for foods in general. Exceptions for certain scheduled foods include lower limits for beverages and ice cream and higher limits for dried herbs, liquid and solid pectin and spices. Residues of lead arsenate used for spraying fruit trees may be carried over into products such as pectin.

The regulations do not apply to fish (including crustaceans and molluscs) and products containing them for which a natural arsenic content in excess of 1 p.p.m. has been established. No doubt this exception is based on the extremely high levels of arsenic reported by Chapman (1926) in shellfish and crustaceans.

Lead

The contamination of foods by lead is widespread. Although it is usually present at very low levels, its presence in foods is a matter of great concern because it is a cumulative poison. As with arsenic, contamination arises through the use of lead arsenate as an insecticide. Contamination of canned foods through solder varies according to the type of container. The risk of entry is highest in cans with vent holes such as those used for packing meat. The recommended limit for lead in canned meat and canned fish is 5 p.p.m.

The limits proposed for lead in beverages are 0·2 p.p.m. for soft drinks and spirits, and 0·5 p.p.m. for wines, beer and cider (Ministry of Agriculture, Fisheries and Food, 1959). The general limit for lead in other foods is 2 p.p.m., but narrower limits are recommended for staple foods such as refined white sugar and edible fats (0·5 p.p.m.) and confections such as ice cream and iced 'lollies'. Lead contents of iced 'lollies' varying from 1·5 p.p.m. to 11 p.p.m. were reported by Semple (1953). He commented that the lead was probably introduced from moulds made from tinplate containing lead or soldered with it. The higher limits for cocoa (5 p.p.m. on the fat-free solids) and curry powder (20 p.p.m.) are probably based on the consideration that they are subjected to grinding processes. A limit of 10 p.p.m. is recommended for tea. It is estimated that only one-fifth to one-third of the lead passes into the infusion (Ministry of Food: Food Standards Committee, 1954). It would be interesting to see some published figures for lead in instant tea, since this tea is made from an infusion.

Copper

Copper is an element essential to both plant and animal life. Nevertheless its adventitious presence can affect foods adversely. Even when present in very minute amounts it causes destruction of ascorbic acid, and when in contact with fats it catalyses fat oxidation. Copper causes discoloration of fruit products and it is believed to be a factor in the development of non-enzymic browning of starch-hydrolysis products. Its unwanted presence in wines gives rise to a haze that must be removed by 'fining'. The recommended tolerance in wines, liqueurs, cocktails, beer, cider and concentrated soft drinks is 7 p.p.m. and for other beverages ready-to-drink it is 2 p.p.m. The proposed general limit for foods is 20 p.p.m. (Ministry of Agriculture, Fisheries and Food, 1958). Exceptions include cocoa (70 p.p.m. on fat-free substance), coffee, chicory, gelatin and liquid pectin (30 p.p.m.), tomato purée (100 p.p.m. on dry solids), tea (150 p.p.m.), yeast and its products (120 p.p.m. on dry solids) and solid pectin (300 p.p.m.).

The main sources of extraneous copper are agricultural sprays and copper utensils. The latter, if brightly polished are reasonably resistant. In practice, 'pick up' occurs through the formation of a film of oxide which is more readily dissolved (Monier-Williams, 1949).

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Zinc

Zinc, like copper has a definite physiological function in the human body. Adventitious zinc is sometimes introduced into foods from solder. The commonest form of contamination is through drying foods on galvanized wire racks. There is a statutory limit of 100 p.p.m. in gelatin (Great Britain. Parliament, 1951). The recommended limit for beverages is 5 p.p.m. and for other foods, 50 p.p.m. (Ministry of Food, 1953). Herrings, shellfish and crustaceans and cereal and animal offals may, however, contain over 50 p.p.m. of naturally occurring zinc.

Iron

Iron is a nutritionally essential element. Under the Flour Order, 1953 (Great Britain. Parliament, 1953) the addition of iron at the rate of 1·65 mg/100 g to flours of an extraction rate of less than 80% is compulsory. Not all of the iron naturally present in foods is in an available form.

Unwanted iron can give rise to food spoilage. It catalyses fat oxidation. This property was used by Luckman, Melnick & Miller (1953) for testing the performance of anti-oxidants in fats. Iron combines with tannin substances in fruits to produce ink-like substances with an unpleasant flavour, and gives rise to discoloration and off-flavours in canned meats.

Other metallic contaminants

Nickel is used as a catalyst for hardening fats. Traces of it are sometimes found in the finished product. Palladium is also used as a catalyst.

Residues of mercurial pesticides may find their way into foods. During an investigation of the effect of mercurial aerosols on glasshouse crops, Beidas & Higgons (1957) found that penetration into the pulp of fruits occurs in 3 days. As much as 0·5 p.p.m. may be present in the fruit as harvested.

The hazards due to the use of enamel ware containing antimony have already been referred to. 'Pick up' may also occur from rubber rings used as seals for lids on glass containers and by the passage of liquids through hose made from rubber containing antimony.

From time to time, the use of aluminium utensils for food preparation has been questioned. When aluminium vessels are intelligently used, uptake by the food is trivial (Burn, 1932; Monier-Williams, 1935) and does not constitute a health hazard. Experiments by Beal, Unangst, Wigman & Cox (1932) indicate that no adverse effects are produced on human beings unless the daily intake approaches 200 mg.

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