

## FUMIGANT RESIDUES IN FOOD: BEHAVIOUR AND REGULATION

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This paper examines ways in which developments in methods for detecting and determining the nature and magnitude of residues in foodstuffs occurring after fumigation have led to a better understanding of their behaviour and significance. As a result of this new knowledge certain changes of approach on methods of regulating these residues have been proposed.

Fumigants are characterised by their considerable volatility in relation to other types of pesticides. When a foodstuff is exposed to a vapour or to a liquid which subsequently vaporises, some of the chemical is held by physical forces (sorption) and providing that no chemical reaction takes place, when the surrounding vapour is removed the sorbed fumigant gradually dissipates into the atmosphere. This process may be relatively slow if solution in constituents of the food, for example in oil or fat, has taken place, or if diffusion is restricted by a surrounding bulk of material. This applies particularly to the use of liquid fumigants on bulk cereals but to a lesser extent also to those which are applied as vapours, such as methyl bromide and ethylene oxide. However, it has for many years been accepted that after use in accordance with good practice no significant amounts of residues of unchanged fumigants such as ethylene dichloride, carbon tetrachloride, ethylene dibromide and methyl bromide would reach the consumer. On this basis some countries have exempted these compounds from the requirement for a tolerance in respect of the unchanged fumigant[1].

Developments in analytical methods in recent years have provided the means for detecting residues of these fumigants in raw foodstuffs such as cereals, nuts and animal feeding stuffs for weeks or months after treatment. These methods are generally based on the analysis of solvent extracts of the commodities by gas chromatography using one or more detectors[2,3] and are capable of detecting minimum levels of unchanged residual fumigant ranging from about 0.5 parts per million (mg/kg) down to 0.001 ppm or better according to the compound. With carefully selected conditions a multi-residue determination can be carried out on a single extract, but the considerable variation in sensitivity of some gas chromatographic detectors means that the estimation of lower levels of certain compounds e.g. ethylene dichloride, is best carried out under the optimum conditions for that substance.

The curves in Figure 1 demonstrate levels of carbon tetrachloride residues determined in fumigated maize samples over a period of 6 months[4]. Results are shown for whole maize aired freely in the laboratory at 10°C and 25°C, together with the effects of grinding the seeds part of the way through the aeration period.

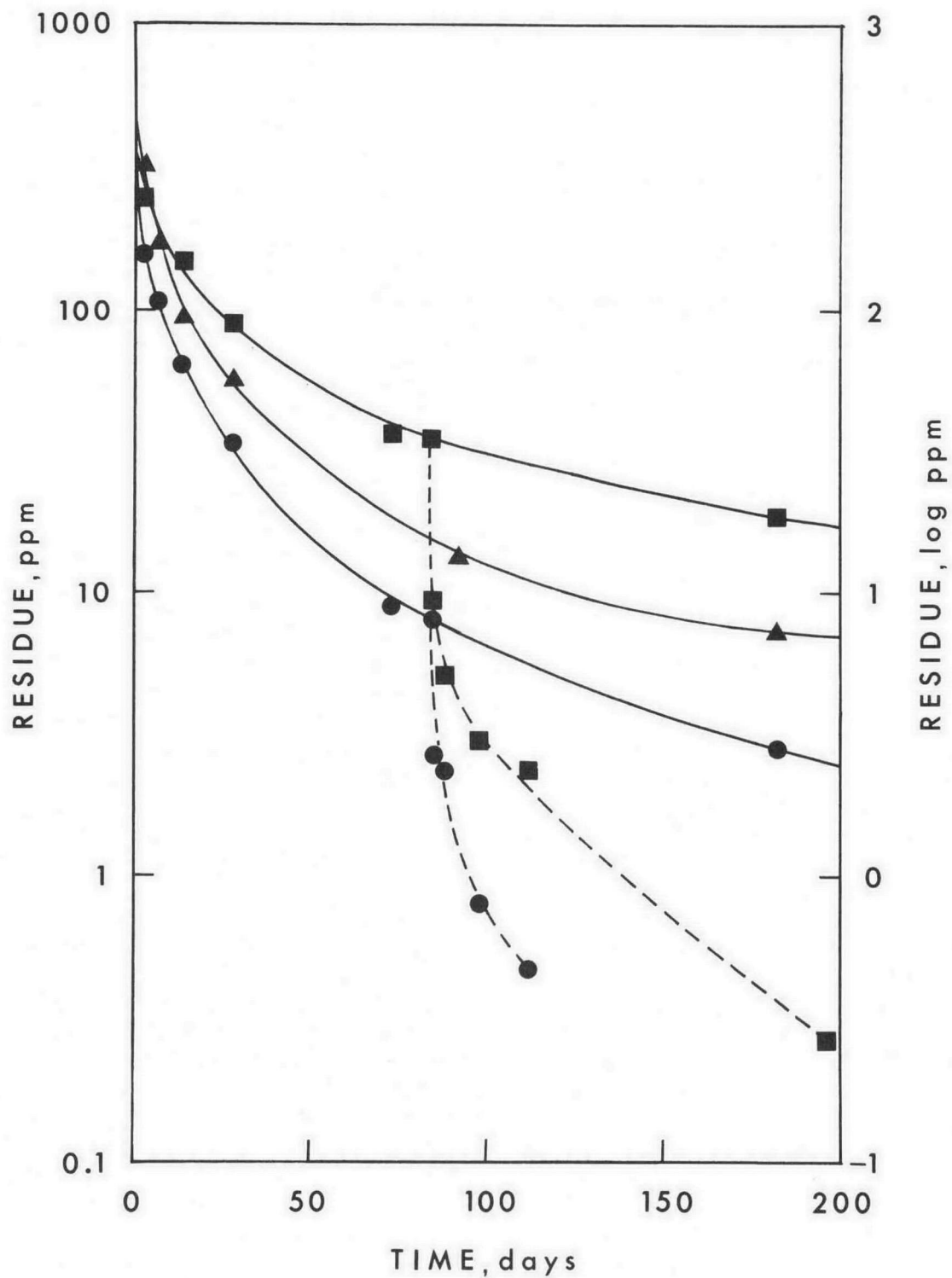


FIGURE 1. Loss of residual carbon tetrachloride from fumigated maize during storage.

Key

—	Whole maize	■	Fumigated at 10°C, stored at 10°C
—		●	Fumigated at 10°C, stored at 25°C
- - -	Ground maize	▲	Fumigated at 25°C, stored at 25°C

It can be seen that even under these favourable conditions, whilst the initial high residue level falls quite quickly, a proportion remains for a considerable period after treatment. There is recent evidence from field sampling of grain stored in farm bins that the disappearance of residual carbon tetrachloride and other liquid grain fumigants is much slower than this under bulk storage conditions[5].

Although subsequent processing and cooking may destroy most of such residue[6] there are undoubtedly instances where food-stuffs are consumed by man or fed to animals in the uncooked state, while evidence has been obtained of very small amounts of unchanged fumigants occurring in cooked foods[6,7]. In these circumstances it has been felt that amounts of such residues should be reduced to a minimum at each stage by adherence to good practice in treatments and in post-treatment handling.

The FAO - WHO 1971 Joint Meeting of Experts on Pesticide Residues[1] took the view that it was desirable, in the absence of sufficient toxicological data to allow higher tolerance figures on the basis of an acceptable daily intake, to recommend limits for such residues in cereals or cereal products at the point of consumption by man at about the present lower limits of detection. However, in view of the evidence on behaviour of volatile fumigant residues during storage and processing which had become available, the Meeting felt it possible to recommend "guide-line" residue levels for other stages in the trade movement of cereals, namely in raw cereals at the point of entry into a country or when supplied for milling, and a second lower level referring to milled cereal products to be subjected to baking or cooking. These recommendations were made in the knowledge that residues in food as offered for consumption should not then exceed an amount close to the limit of determination by currently available analytical methods.

Table 1 shows the three levels set by the FAO - WHO Expert Committee for five commonly used fumigants[1]. There was an additional provision made in respect of the upper set of figures. It was recognized that treatment might have been undertaken immediately before shipment or even on board ship and that in these circumstances, at the time of unloading, the residue levels could be changing rapidly due to the handling and movement through the air. The recommendations therefore stipulated that raw cereals be discharged or freely exposed to air for 24 hours before sampling for determination of fumigant residue levels. This policy was adopted in order to eliminate the possibility of rejection of a consignment on the basis of high residue figures which shortly afterwards could be well below the tolerance level, whilst at the same time recognising the value of some measure of control at a central point of distribution.

These proposals for "guide-line levels" were made by practical scientists well-versed in the modes of behaviour of these materials and in the patterns of commodity handling in commercial practice. However they represent a departure from the normal concept of a single tolerance for a pesticide residue referred to a

commodity and the system has at the present time not been incorporated into official procedures or proposals for harmonization such as those of the Codex Alimentarius Commission on Pesticide Residues.

TABLE 1. F.A.O./W.H.O. Guideline Residue Levels (P.P.M.)

	Carbon Disulphide	Carbon Tetra- chloride	Ethylene Dibromide	Ethylene Dichloride	Methyl Bromide
Raw Cereals, Point of Entry Into Country Or As Supplied For Milling	10	50	20	50	50
In Milled Cereals For Baking Or Cooking	2	10	5	10	10
In Bread Or Cooked Cereal Products	0.5	0.05	0.1	0.1	0.5

As another example of the impact of analytical method development on the subsequent examination of foodstuffs for residue for enforcement purposes, reference can be made to the identification and estimation of different types of bromine-containing residues which can arise as a result of the fumigation of produce with bromide compounds or alternatively by take-up of bromine from soil.

In national tolerance schedules such as those of the United States, which have long been used as a pattern in many other parts of the world, levels for "inorganic bromide" (now often referred to more specifically as "ionic bromide" or "bromide ion") in particular commodities appear which, in many instances, have been set according to amounts which have been shown in trials to occur as a result of fumigation with methyl bromide or ethylene dibromide according to good practice. Two important points can be made about these tolerance levels and their determination. Firstly, the analyses are almost invariably carried out by methods which determine total bromide. In the absence of additional analyses for organic bromine compounds it is by no means certain, especially after treatment with ethylene dibromide, that the bromine determined is present in the ionised form.

With the availability of the gas chromatographic methods already referred to for determining small amounts of unchanged residual fumigants, assays can now be carried out to find by difference how much of the total bromine content is in the ionic form. Alternatively bromide ion can be estimated by a method in which ionic bromide is reacted with ethylene oxide and determined as 2-bromoethanol by gas chromatography[8]. Because of the greater

toxicity of the original fumigants it is in any case desirable that the identity of any bromine-containing residue should be established unequivocally; it follows therefore that ideally, analyses for both ionic bromide and organic bromine compounds should be performed. Failing this, a method specific for ionic bromide should be used to determine compliance with a tolerance for "ionic" or "inorganic" bromide.

The second point concerning tolerances for ionic bromide in stored crops is that while they are partly designed to avoid excessive residues due to bad practice and in the case of methyl bromide treatments to give an indication of the presence of other fumigant reaction products, it is not at present possible to determine whether ionic bromide is present as an addition product from fumigation or has been taken up by the plant from soil. Unless there is a considerable body of data available on the average levels of "naturally" occurring bromide in crops it is impossible to judge whether a certain bromide level can be ascribed to fumigation; thus such tolerance levels are of limited value in controlling bromide arising from specific uses.

In the case of cereal crops such as wheat and maize there is abundant evidence that unfumigated produce seldom has a bromide content exceeding 10 ppm. In these cases the present tolerance of 50 ppm provides a means of regulating the use of bromine-containing fumigants on grain in storage. For other commodities such as tobacco and some vegetables, where it has been shown that it is possible for relatively large amounts of bromide ion to be withdrawn from soil and concentrated in the plant[9,10], it is probably impractical to specify a tolerance for bromide ion resulting from specific action such as fumigation with a bromine compound.

Bromide in plant material derived from soil can originate not only from soil fumigation with bromine compounds but can also result from the deposits left by sea-water on reclaimed land. This problem is particularly important in certain parts of Europe such as the Netherlands. Because this type of bromine content is chemically indistinguishable from at least part of that produced by fumigation, the FAO-WHO Joint Meeting of Experts on Pesticide Residues stated in 1971 that further data would have to be made available before decisions could be taken on the practicality of recommending tolerance levels for bromide ion in foods other than raw cereals.

The examples described are typical of a problem which is currently receiving a great deal of attention in fields other than pesticide residues, namely the tendency to set tolerance levels for impurities in isolation from consideration of the analytical and sampling methods available to enforce them.

In the present rapid state of development of analytical chemistry, the weight of technical opinion is against the rigid specification of methods of analysis, lest improvements in technique prove difficult to adopt quickly. Nevertheless, methods to be used in the fields under discussion must be capable of producing unequivocal results and some form of intercomparison or collaborative

method-testing is imperative. Providing that this requirement is met, the principle of equivalence of methods is probably better, scientifically and practically, than attempting to adopt one official method, on which agreement in the international field may prove to be unattainable in all but a few cases.

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