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The Incidence of Metals in Food

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A Survey by the Association of Public Analysts

This paper comprises the first two parts of a report of the extent of regular investigations into the contamination of food by toxic metals. The collated results of 2 to 3 years' work by a representative proportion of laboratories in the United Kingdom will be presented. This present section is concerned primarily with the incidence of mercury.

PART I: GENERAL CONSIDERATIONS

From the very earliest days of food legislation (1860), Public Analysts have examined food for the presence of metallic compounds (including arsenic), whether introduced intentionally, by accident or occurring naturally. Numerous instances could be quoted, over the years, where investigations have shown that, apart from deliberate additions, the accidental contamination of food can occur by devious routes. Perhaps the most classical incident to mention was the finding of arsenic in beer in Lancashire in 1900 leading to the formation of a Royal Commission which made recommendations on the levels which should be accepted in food and drink. However, it was some 56 years later before general legislation[2] controlling the proportion of arsenic in foods was introduced, although during the intervening years, the work of Public Analysts had greatly contributed to an improving situation by taking action under the general provisions of the Food and Drugs Acts.

The reason for examining foods for the presence of contaminating metals is, of course, their potential toxicity and lead has been considered the primary danger, along with arsenic. Other metals which, for many years have been searched for by Public Analysts are copper and zinc in view of the symptoms associated with acute poisoning by these metals. With the increased use of canning in the food industry, tin has also been increasingly determined and in isolated cases, other metals, such as cadmium[3] or cobalt[4], have been shown to be the cause of particular outbreaks of food poisoning.

In recent years, the increasing use of pesticides has also involved Public Analysts not only in a search for such compounds as the organo-chlorine and organo-phosphorus pesticides but also in the examination of a variety of foods for lead, arsenic and mercury derived from sprays, sheep-dips, etc. Whilst therefore the reports[5,6] on the two years of the survey of pesticide residues in foodstuffs prepared by the Association of Public Analysts in collaboration with Local Authority organisations dealt, very largely, with organic pesticides, a significant section of the reports concerned the levels of arsenic, lead and mercury which had been found in these samples.

With this long interest in the metallic contamination of food, it is not surprising that Public Analysts have amassed a large amount of information on the occurrence of metals in a wide range of foodstuffs. It was appropriate, therefore, following the publicity at the end of 1970, in connection with the discovery of high levels of mercury in canned tuna fish in America, that the Council of the Association should decide to institute a survey of results of examinations made by its members during the last 2–3 years and this paper is the result of this decision.

It is intended to report on a number of metals and separate parts of this paper will deal with individual elements. However, there are a number of matters of a general nature in connection with the survey which are applicable to most, if not all, the elements concerned and these will be considered in this first part of the paper.

Methods of Analysis

It must be appreciated that the Public Analyst regularly examines a large number of samples for the presence of metals and the greater proportion of these samples will be acceptably free from excessive contamination. This work is done as part only of a full examination of samples under the Food and Drugs Act which are not normally submitted for examination for metals alone. Whilst, therefore, the most sophisticated methods of analysis will be employed for those samples where a possible infringement of a standard is likely, the great majority of samples needs to be checked against such a standard without the requirement of a high degree of accuracy (in scientific terms). The samples are generally submitted to tests which can rapidly indicate the approximate levels of contamination and different Public Analysts devise different methods of carrying out these sorting tests. In some cases, a pass/fail type of test is applied, whereas in others a rough indication of the amount actually present will be obtained.

The present survey is based upon the results obtained by Public Analysts in the normal course of their work and therefore upon the type of examinations outlined above. For the purpose of deriving an average content of a particular metal, the pass/fail type of test is of little value and these results have therefore been omitted from the survey. The results that have been included have generally been obtained by the type of test which will give an approximate result which may be considered to be accurate to within $\pm$ 20 per cent. or less and this should be borne in mind when interpreting the results of the survey. The major exceptions are the estimates of mercury where, generally, the results are all quite accurate, since "sorting tests" offer little saving in time over the methods of exact determination.

Interpretation of Results

In a number of cases, the results obtained have been recorded in the form: "less than x parts per million". The method of interpretation of these results

is as follows: If "x" represents an appreciable level of contamination (e.g. the legal limit of the metal in the food) the results have been excluded from the survey because they would be likely to bias the result to an appreciable extent. When "x" is small compared with a reasonable limit, the result has been taken as $\frac{1}{2}x$. This is based on the assumption that the actual results are evenly distributed within the range 0 to x p.p.m., but no evidence is given in this paper to support or refute this assumption.

Classification of Foods

The survey covered a wide range of foodstuffs and some classification into different types was therefore essential. One of the desirable conclusions of such a survey as this would be to derive an average daily intake from food for any particular element being considered. In view of the fact that the Ministry of Agriculture, Fisheries and Food publish quarterly and annually[7] the total consumption of different classes of food it was decided to use the classification in these statistical returns as a basis for this survey. In addition to the classes used by the M.A.F.F., one or two additional classes were introduced for the purposes of this survey, such as "Herbs and Spices", "Beer and Cider" etc. However, perhaps the most topical was the decision, in the light of the information available, to split the M.A.F.F. classification "Other canned and bottled fish" into "Canned tuna fish" and "Other canned and bottled fish excluding tuna".

The total number of classes of foodstuffs was therefore 142, although in the reports on some elements, a number of similar classes have been combined, particularly where the numbers of samples examined were small.

Part II: Mercury

The occurrence of mercury in food has been of greatly increased concern to the Public Analyst in recent years, because of the use of organo-mercury fungicides in agriculture and elsewhere. The surveys of pesticide residues in food[3,4] carried out in 1966–68 included mercury determinations in selected samples and the results are summarised in Table I.

Thus at the end of 1968, on the evidence of the examination of over 400 samples, there was no indication of any serious problem of contamination with mercury in those foodstuffs which were thought, at that time, to be most likely to be exposed to this hazard.

In December 1970, the national press erupted with the news that the sale of canned tuna fish had been banned in the U.S.A. because a significant proportion (25 per cent.) of samples was found to exceed the limit (in the U.S.A.) of 0·5 p.p.m. of mercury. Immediately, the Government Chemist was asked by the Minister of Agriculture, Fisheries and Food to investigate the presence of mercury in canned tuna fish on sale in this country and by Christmas a report had been circulated of the levels found in about 100 samples. Simultaneously, most Public Analysts, on behalf of their local authorities, undertook

TABLE I

MERCURY IN FOOD: SURVEY OF PESTICIDE RESIDUES IN FOODSTUFFS BY THE ASSOCIATION OF PUBLIC ANALYSTS

	1966 to 1967		1967 to 1968	
Type of Food	Total No. of Samples	Mercury Content *parts per million*	Total No. of Samples	Mercury Content *parts per million*
Apples	48	less than 0·1	—	—
Cheese	—	—	49	0·1
			1	0·42
Eggs	48	less than 0·1	37	less than 0·1
	1	0·1	1	0·1
Tomatoes	45	less than 0·1	—	—
	1	0·1		
	1	0·24		
Milk	1	0·74	—	—
Miscellaneous	65	less than 0·1	140	less than 0·1
	3	above 0·1		

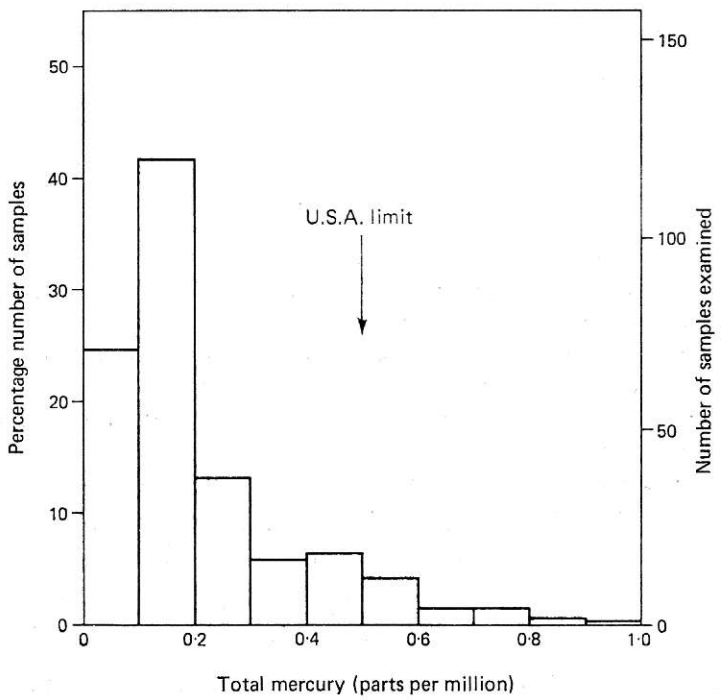

FIG. 1. Mercury in canned tuna fish (After the Association of Public Analysts).

similar examinations since local authorities are required, by law, to enforce all provisions of the Food and Drugs Acts. Public Analysts examined not only samples of canned tuna fish, but also canned salmon and other canned fish, together with a variety of other foods. The following tables have been prepared by summarising the results submitted by 21 Public Analyst laboratories

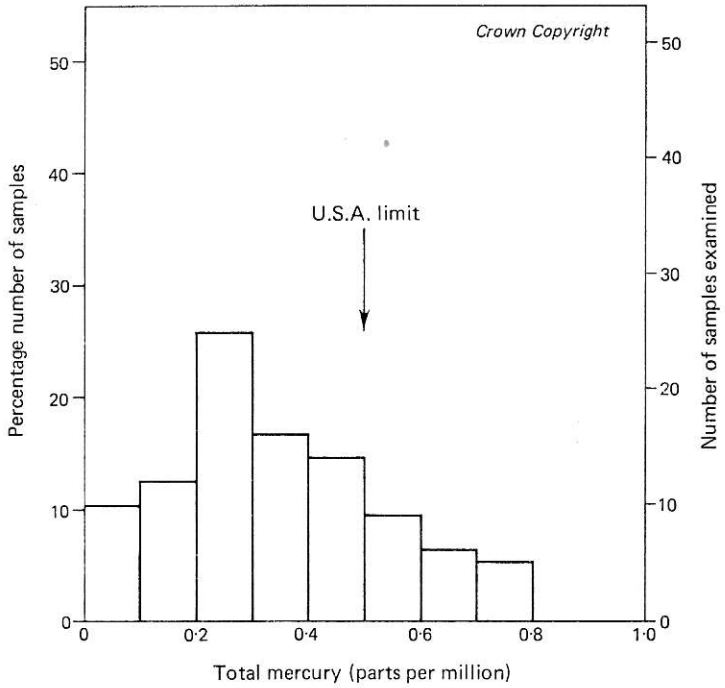

FIG. 2. Mercury in canned tuna fish (After the Laboratory of the Government Chemists)
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throughout the country. The greatest proportion of these results have been recorded in the period December 1970 to April 1971 but some, which were obtained prior to this period, have also been included (although none of these was of canned tuna fish). The results published by the Government Chemist on 22nd December 1970 for canned fish are also given for comparison.

Analytical Methods

The methods of analysis for mercury used in obtaining the results recorded in this paper were precise methods giving accurate results.

In general, an acid digestion procedure, using nitric and sulphuric acids under reflux, was followed by either a colorimetric estimation using dithizone or an estimation of the mercury by flameless atomic absorption techniques. Most analysts carried out the digestion method suggested by the Analytical Methods Committee of the Society for Analytical Chemistry[8]. In both the

dithizone method and the atomic absorption estimations, appropriate blanks and standards were carried through the procedures.

Discussion of Results

As might be expected, canned tuna fish was the one single food which Public Analysts obtained in the greatest number (287 samples). The distribution of the results is somewhat different from the results published by the Government Chemist in that a much smaller proportion of samples with high levels of mercury has been recorded by Public Analysts. The two histograms show this difference between the two sets of results. The proportion found

TABLE II

SURVEY OF MERCURY CONTAMINATION OF CANNED TUNA FISH (CLASS No. 42) IN 1970–1971

	Association of Public Analysts			Laboratory of the Government Chemist		
Range of Mercury Contents *parts per million*	Number of samples	Percentage of Total samples	Cumulative Percentage of Total samples	Number of samples	Percentage of Total samples	Cumulative Percentage of Total samples
0·00–0·04	28	9·(8)	9·(8)	—	—	—
0·05–0·09	43	15·(0)	24·(8)	10	10·(3)	10·(3)
0·10–0·14	79	27·(5)	52·(3)	—	—	—
0·15–0·19	41	14·(3)	66·(6)	12	12·(4)	22·(7)
0·20–0·24	24	8·(3)	74.(9)	—	—	—
0·25–0·29	14	4·(9)	79·(8)	25	25·(8)	45·(5)
0·30–0·34	12	4·(2)	84·(0)	—	—	—
0·35–0·39	5	1·(7)	85·(7)	16	16·(5)	65·(0)
0·40–0·44	15	5·(2)	90·(9)	—	—	—
0·45–0·49	3	1·(1)	92·(0)	14	14·(4)	79·(4)
0·50–0·54	8	2·(8)	94·(8)	—	—	—
0·55–0·59	4	1·(4)	96·(2)	9	9·(3)	88·(7)
0·60–0·64	4	1·(4)	97·(6)	—	—	—
0·65–0·69	0	0	97·(6)	6	6·(2)	94·(9)
0·70–0·74	4	1·(4)	99·(0)	—	—	—
0·75–0·79	0	0	99·(0)	5	5·(1)	100·0
0·80–0·84	2	0·(7)	99·(7)	—	—	—
0·85–0·89	0	0	99·(7)	0	0	100·0
0·90–0·94	1	0·(3)	100·0	—	—	—
0·95–0·99	0	0	100·0	0	0	100·0
1·00 and over	0	0	100·0	0	0	100·0
Total number of samples	287			97		
Mean		0·19(0)				
Standard Deviation		0·16(4)				
Standard Error of mean		0·009(7)				
Minimum		0·00				
Maximum		0·90				

TABLE III

SURVEY OF MERCURY CONTAMINATION OF CANNED SALMON (CLASS No. 40)

Range of Mercury Contents *parts per million*	Number of Samples	Percentage of Total Samples	Cumulative Percentage of Samples
0·00–0·04	47	47·(0)	47·(0)
0·05–0·09	23	23·(0)	70·(0)
0·10–0·14	12	12·(0)	82·(0)
0·15–0·19	4	4·(0)	86·(0)
0·20–0·24	10	10·(0)	96·(0)
0·25–0·29	0	0	96·(0)
0·30–0·34	2	2·(0)	98·(0)
0·35–0·39	0	0	98·(0)
0·40–0·44	1	1·(0)	99·(0)
0·45–0·49	0	0	99·(0)
0·50–0·54	1	1·(0)	100·0
0·55–0·59	0	0	100·0
0·60 and over	0	0	100·0
Total number of samples	100		
Mean	0·07(7)		
Standard Deviation	0·08(8)		
Standard Error of Mean	0·008(8)		
Minimum	0·00		
Maximum	0·50		

TABLE IV

SURVEY OF MERCURY CONTAMINATION OF SHELLFISH AND CRUSTACEANS, FRESH AND CANNED (CLASS No. 38)

Range of Mercury Contents *parts per million*	Number of Samples	Percentage of Total Samples	Cumulative Percentage of Samples
0·00–0·04	42	36·(0)	36·(8)
0·05–0·09	39	34·(2)	71·(0)
0·10–0·14	23	20·(2)	91·(2)
0·15–0·19	2	1·(8)	93·(0)
0·20–0·24	6	5·(2)	98·(2)
0·25–0·29	1	0·(9)	99·(1)
0·30–0·34	0	0	99·(1)
0·35–0·39	1	0·(9)	100·0
0·40 and over	0	0	100·0
Total number of Samples	114		
Mean	0·07(2)		
Standard Deviation	0·06(2)		
Standard Error of Mean	0·005(8)		
Minimum	0·00		
Maximum	0·35		

TABLE V

SURVEY OF MERCURY CONTENT OF CANNED FISH, OTHER THAN TUNA, SALMON, CRUSTACEANS AND SHELLFISH (CLASS No. 41)

Range of Mercury Contents *parts per million*	Number of Samples	Percentage of Total Samples	Cumulative Percentage of Samples
0·00–0·04	39	41·(9)	41·(9)
0·05–0·09	30	32·(3)	74·(2)
0·10–0·14	11	11·(8)	86·(0)
0·15–0·19	5	5·(4)	91·(4)
0·20–0·24	5	5·(4)	96·(8)
0·25–0·29	3	3·(2)	100·0
0·30 and over	0	0	100·0
Total number of Samples	93		
Mean	0·06(8)		
Standard Deviation	0·06(6)		
Standard Error of Mean	0·006(8)		
Minimum	0·00		
Maximum	0·27		

TABLE VI

SURVEY OF MERCURY CONTAMINATION OF FRESH WHITE FISH (CLASSES Nos. 29, 30 AND 31)

Range of Mercury Contents *parts per million*	Number of of Samples	Percentage of Total Samples	Cumulative Percentage of Samples
0·00–0·04	13	41·(9)	41·(9)
0·05–0·09	11	35·(5)	77·(4)
0·10–0·14	5	16·(2)	93·(6)
0·15–0·19	1	3·(2)	96·(8)
0·20–0·24	0	0	96·(8)
0·25–0·29	0	0	96·(8)
0·30–0·34	1	3·(2)	100·0
0·35–0·39	0	0	100·0
0·40 and over	0	0	100·0
Total Number of Samples	31		
Mean	0·06(8)		
Standard Deviation	0·06(2)		
Standard Error of Mean	0·01(1)		
Minimum	0·00		
Maximum	0·30		

to exceed the U.S.A. limit of 0·5 parts per million was only 5·(2) per cent. compared with the result in the Goverment Chemist survey of 21·(6) per cent. Reports from the United States indicated that the Food and Drug Administration had found that approximately 25 per cent. of samples exceeded this limit. The results given in this survey therefore suggest that sampling over the whole of England and Wales has indicated a lower level of contamination than was shown in the previous results from the U.S.A. or by the Government Chemist.

The mean result for mercury in "Canned tuna fish" of 0·19 parts per million (with a standard error of 0·01 p.p.m.) is, however, significantly higher than that recorded for "Canned salmon" (0·08 $\pm$ 0·01 p.p.m.), for "Other canned fish" (0·08 $\pm$ 0·01), or for "Shellfish and Crustaceans" (0·07 $\pm$ 0·01). There is a remarkable constancy of the means in the fish other than tuna fish and this fact emphasises the higher level found in tuna fish, which is nearly three times the general level in other species of fish. These results clearly confirm, therefore, that canned tuna fish is much more likely to contain high amounts of mercury than the other fish sampled.

TABLE VII

SURVEY OF MERCURY CONTAMINATION OF FOODS OTHER THAN FISH

Class Number	Food	Number of Samples	Mercury Content Range *parts per million*	Mercury Content Mean *parts per million*
1	Liquid Milk	3	0–0·02	0·00(7)
4	Other Milk Products	5	0–0·04	0·01(4)
5	Cream	1	0	0
6	Natural Cheese	5	0–0·50	0·17
8	Beef and Veal	7	0–0·02	0·01
9	Mutton and Lamb	2	0	0
10	Pork	6	0–0·05	0·01(8)
12	Liver	2	0–0·09	0·04(5)
13	Other Offals	3	0–0·03	0·01(3)
14	Bacon and Ham (Uncooked)	2	0·04–0·05	0·03
15	Bacon and Ham (canned)	1	0·02	0·02
17	Corned Beef	1	0	0
19	Other Canned Meat	8	0–0·01	0·00(1)
24	Pork Sausages (uncooked)	5	0–0·07	0·02(4)
25	Beef Sausages (uncooked)	2	0·02–0·06	0·04
28	Other Meat Products	7	0–0·06	0·02(3)
32+33+34	Fresh Fatty Fish	8	0–0·10	0·02(5)
45	Eggs	6	0	0
46	Butter	1	0·01	0·01
48	Lard and Compound Cooking Fat	2	0·02–0·26	0·14
49	Suet and Dripping	1	0	0
52	Sugar	1	0·02	0·02
53	Jams, Jellies and Fruit Curds	1	0	0
55	Syrup, Treacle and Honey	1	0	0
56	Old Potatoes	4	0–0·07	0·02
58	Cabbage	3	0	0
59	Brussels	3	0	0
60	Cauliflower	3	0–0·05	0·02
61	Leafy Salads	6	0–0·05	0·00(8)
66	Other Green Vegetables	3	0·03–0·10	0·06

continued over

TABLE VII *continued*

SURVEY OF MERCURY CONTAMINATION OF FOODS OTHER THAN FISH

Class Number	Food	Numder of Samples	Mercury Content Range *parts per million*	Mean *parts per million*
67	Carrots	3	0·01–0·05	0·02(7)
68	Turnips and Swedes	2	0	0
70	Onions, Shallots and Leeks	3	0–0·01	0·00(3)
72	Mushrooms	1	0	0
74	Canned Peas	1	0·02	0·02
85	Apples	42	0–0·18	0·00(8)
86	Pears	12	0–0·02	0·00(3)
88	Grapes	1	0	0
89	Other Soft Fruit	1	0	0
92	Tomatoes (Fresh)	14	0–0·05	0·01(2)
93	Other Fresh Fruit	1	0·01	0·01
94	Canned Tomatoes	11	0–0·06	0·01(9)
96	Other Canned Fruit	1	0·01	0·01
97	Dried Fruit	2	0–0·08	0·04
98	Nut and Nut Products	1	0	0
101	White Bread	7	0–0·08	0·02(2)
102	Wholemeal and Wheatmeal Bread	1	0	0
103	Other Bread	2	0·05–0·16	0·10(5)
104	Flour	8	0–0·06	0·02(5)
109	Oatmeal and Oat Products	3	0·02–0·03	0·02(7)
110	Breakfast Cereals	1	0·21	0·21
117	Other Cereal Foods	1	0	0
118	Tea	1	0	0
119	Coffee—Bean and Ground	1	0·06	0·06
122	Cocoa and Drinking Chocolate	1	0·06	0·06
124	Baby Foods	1	0·02	0·02
125	Canned Soups	1	0	0
129	Pickles and Sauces	4	0–1·4	0·36
	(ex. 1 result—1·4)	3	0–0·02	0·01(3)
130	Meat and Vegetable Extracts	2	0	0
134	Salt	1	0	0
135	Soft Drinks	2	0	0
136	Herbs and Spices	6	0–0·18	0·08(7)
137	Beer and Cider	3	0·01–0·02	0·01(3)
	Mean of all Results			0·02(6)
	Total number of Samples	248		

The results on foods other than fish, which have also been examined, show that the levels of mercury found in these foods are, generally, very low. In many classes of food the number of samples examined has been small and therefore the significance of a slightly higher than average mean for a particular class of food is probably small. For example, the mean level recorded for natural cheese is 0·17 parts per million, but of the five samples examined, three showed no detectable amount of mercury whereas the other two were 0·34 and 0·50 p.p.m., leading to the relatively high mean of 0·17. Similar considerations apply to "Lard and Compound Cooking Fat" (No. 48), "Other Bread" (No. 103), "Breakfast Cereals" (No. 110), and "Pickles and Sauces" (No. 129).

On the basis of this survey, therefore, there is no indication that any type of food (other than canned tuna fish) consistently contains high levels of mercury. Further work is desirable to enable the results from a greater

number of samples, over a wider range of foodstuffs, to be available. No doubt Public Analysts will continue to monitor fish and other samples for mercury content and it is intended that determinations of mercury in certain foodstuffs will form part of the work of a third year of the Survey of Pesticide Residues which it is proposed should be undertaken in 1972.

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