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Determination of Silver in Foods by Neutron Activation Analysis

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ABSTRACT

Silver has been determined in a number of foodstuffs by neutron activation analysis. The results range from <1 to 530 ng g^{-1} dry matter and are highly variable, suggesting that random contamination of samples may occur. Higher concentrations of up to 31 μg g^{-1} dry matter were found in wild fungi. From these results, supplemented by others, the British dietary intake is estimated to be 4·5 μg Ag day^{-1}, which constitutes no hazard to human health.

Key words: Diet, food, fungi, neutron activation analysis, silver.

1 INTRODUCTION

Silver is an element which has rarely been determined in foodstuffs. Techniques with adequate sensitivity to determine existing levels include plasma emission spectrometry,[1] solvent extraction coupled with atomic absorption spectrometry[2,3] and neutron activation analysis.[4] The only foods which have been found to accumulate silver to any extent are certain fungi.[5–7]

In the present work the technique of radiochemical neutron activation analysis (NAA) has been applied to determine silver in miscellaneous foods and a few fungi. The accuracy of the method has been tested by analysing a number of certified reference materials.[8]

2 EXPERIMENTAL

2.1 Samples

Samples of foodstuffs were mostly supplied by the Plant Sciences department at Reading University (Nos. 001–010) and by the Laboratory of the Government Chemist (Nos. 106–908). Wild fungi were collected locally.

2.2 Apparatus

Gallenkamp Oven set at 85°C.
Gallenkamp Muffle Furnace set at 500°C, with a silica liner.
Phillips 250W Infra-red lamp.
MSE Centrifuge.
Nuclear Data Pulse height analyser with Ge(Li) gamma ray detector head.
Neutron activation was carried out in the University of London research reactor at Ascot, Berks.

2.3 Reagents

All chemicals used were of AR grade, or 'Specpure' for silver nitrate:

Ammonia, 19 M.
Ferric nitrate, 5% w/v.
Hydrochloric acid, 2 M.
Nitric acid, 8 M and 16 M.
Silver nitrate carrier, 20 mg Ag g^{-1} in 2 M nitric acid.
Silver nitrate standard, 10 mg Ag g^{-1}, freshly prepared.
Sodium sulphide, 2 M.

2.4 Methods

Samples were laid on polythene sheets which had been cleaned by soaking in 8 M nitric acid for 5 h and well rinsed with water. They were dried to constant weight at 85°C. Five grams dry matter was weighed in a silica crucible and heated at 500°C for 10 h. The ash was then sealed into a polythene packet. Spiking with ^{110m}Ag showed that losses of silver during this procedure were negligible.

Standards were made by weighing one or two drops of the standard silver nitrate solution on a small square of polythene film. The drops were evaporated to dryness under an infra-red lamp, and the film was folded and sealed into a packet. Packets containing standards and samples were activated in a flux of about 10^{12} neutrons cm^{-2} s^{-1} for about 60 h, and then left to decay for about 14 days.

The radiochemical separation of silver from samples and standards has been described in detail.[8] After adding 20 mg silver carrier, the ash was dissolved in 10 ml 16 M nitric acid; occasionally a few drops of 18 M sulphuric acid or 30% hydrogen peroxide were needed to aid the dissolution. The nitric acid was evaporated off and the silver was precipitated as silver chloride. This was dissolved in ammonia and scavenged with a precipitate of iron(III) hydroxide. The silver was then precipitated as silver sulphide, dissolved in nitric acid, reprecipitated as sulphide, dried, weighed and counted. Counting usually required 22 h and the areas under the gamma peaks at 0·66 and 0·88 MeV were obtained from a microcomputer. The counts were corrected for any weight losses of the silver carrier during the separation.

3 RESULTS

Results of the analyses are given in Table 1 in concentrations of silver g^{-1} dry matter (DM). The parts analysed were the edible portions used for human consumption.

TABLE 1
Silver Content of Dry Foods

Code No.	*Nature (origin)*	*ng Ag g^{-1} DM*
001	Rice, *Oryza sativa* (Pakistan)	43·6
002	Barley, *Hordeum vulgare* (Britain)	<1
003	Sorghum, *Sorghum bicolor* (Argentina)	95·4
004	Sorghum, *Sorghum bicolor* (Sudan)	158
005	Sesame, *Sesamum indicum* (Sudan)	197
006	Potato, *Solanum tuberosum* (Britain)	9·6
007	Carrot, *Daucus carota* (Britain)	48·7
008	Maize, *Zea mays* (Britain)	18·6
009	Broad Bean, *Vicia faba* (Britain)	3
010	Bean, *Phaseolus* sp. (Britain)	6·2
011	False Death Cap, *Amanita citrina* (Ascot)	144
012	Tawny Grisette, *Amanita fulva* (Ascot)	17700
013	Fly Agric, *Amanita muscaria* (Ascot)	5470
014	Boletus, *Boletus bovinus* (Ascot)	321
015	Bay Boletus, *Boletus badius* (Ascot)	4110
016	Brown Birch Boletus, *Boletus scaber* (Crowthorne)	874
017	Mushroom, *Agaricus bitorquis* (Shinfield)	31400
635	Carrot, frozen (Welwyn)	8
636	Carrot, frozen (Welwyn Co-op)	4
637	Carrot, frozen (Eltham)	64·6
638	Carrot, frozen (Wimbledon)	13·6
639	Carrot, frozen (Wimbledon)	74·5
640	Carrot, frozen (Greenwich)	35
642	Spinach, frozen (Eltham)	53·9
643	Spinach, frozen (Welling)	66
644	Spinach, frozen (Eltham)	9·3
645	Spinach, frozen (High Wycombe)	232
710	Spinach, frozen (Sainsbury)	199
711	Spinach, frozen (Sainsbury)	27·7
713	Bread, white (Independent)	<1
717	Bread, white (Sainsbury)	<1
719	Bread, white (Clarkes)	<1
720	Bread, white (Broomfields)	<1
722	Bread, wholemeal (Independent)	<1
725	Bread, white (Hovis)	<1
726	Bread, white (Vitbe)	<1
728	Bread, white (Tesco)	278
729	Biscuits (Sainsbury)	<1

(continued)

TABLE 1—*contd.*

Code No.	*Nature (origin)*	*ng Ag g^{-1} DM*
730	Biscuits (Tesco)	<1
732	Biscuits (Waitrose)	<1
733	Biscuits (Crawford)	<1
885	Beef (Tesco)	<1
887	Beef (Plumstead)	25·9
892	Lamb (Eltham)	4·5
895	Lamb (Tesco)	<1
898	Pork (Eltham)	527
900	Pork (Wimbledon)	2·2
905	Chicken quarters (London)	93·8
908	Chicken quarters (London)	14·9
106	Chicken liver (Healeys)	23·7
107	Chicken liver (Healeys)	56·9
108	Chicken liver (Sainsbury)	5·5
121	Chicken liver (Banham)	13·4

4 DISCUSSION

4.1 Comments

One conclusion that can be drawn from Table 1 is that apart from the fungi, none of which is commonly used as food in Britain, the silver contents of the foods are very low. Another conclusion is that the variation from sample to sample may be large and unpredictable. Compare for example the two pork samples, or sample 728 with all other bread samples analysed.

Silver contents of plant tissues must ultimately depend on silver supplied by the soil, while silver contents of animal tissues should be related to the intake of silver in the diet. The present results suggest, however, that at these very low concentrations, random contamination of foods is significant. Such contamination can readily arise from the use of silver cutlery or jewellery, or from dusts arising from photographic materials, and we believe that contamination has occurred before samples 728, 898 and probably 905 were analysed. Indeed, without 'clean room' facilities for preparing samples, all the samples studied may have been contaminated, though they do represent what people actually eat.

These results on the accumulation of silver by fungi, especially *Agaricus* spp., confirm the observations of others.[5-7] Since soils contain 100–400 ng Ag g^{-1},[9] the value of 31 $\mu g\ g^{-1}$ Ag found in *Agaricus bitorquis* represents a concentration factor of about a hundredfold. The mechanism of, and the reasons for, this accumulation of silver are unknown, though it may be that some fungi produce an argentophilic ligand to neutralise the toxic effects of the silver(I) cation in the soil.

4.2 Estimation of silver in British diets

In Table 2 an estimate is made of the daily intake of silver in the British diet. Values for the fresh weight (FW) of each type of food consumed per day are taken from the UK total diet survey,[10] modified to give a greater intake of beverages.[3] Mean silver contents for cereals, meats and vegetables were calculated from the

TABLE 2
Estimating Daily Input of Silver in Foods and Diet

Food group	*gFW eaten day^{-1}*	*ng Ag gFW^{-1}*	*Dietary intake μg Ag^{-1} day^{-1}*
Cereals	230	0·7	0·161
Meat	150	2·2	0·330
Root vegetables	180	2·4	0·432
Other vegetables	110	11·3	1·243
Fruit	170	8·0[3]	1·360
Fish	20	4·0[3]	0·080
Fats	80	2·0[3]	0·160
Milk	400	0·5[3]	0·200
Other beverages	600	0·8[3]	0·480
Total	1940		4·446

data in Table 1 after rejecting outliers. Silver contents of other foods were taken from reference 3. It seems that vegetables and fruit contribute about 50% of the British dietary intake of silver.

This estimate of a daily intake of silver of 4·5 μg agrees with estimates of 8·7, 9 and 7 μg for British,[3] Swedish[11] and Italian diets.[12] It is somewhat lower than values of 40, 70, 27 and 27 μg reported respectively for diets in the USA,[13,14] Britain[15] and Canada.[4] The chances of contamination and analytical error are strong when studying silver. The element is not known to be essential for any form of life, and the toxic effects of any of the above intakes are unlikely to be measurable. Hence it is not anticipated that any adverse consequences to human health will be caused by the silver present in current diets.

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