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Analytical Methods Section

Determination of trace quantities of selenium and arsenic in canned tuna fish by using electroanalytical techniques

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Fifteen brands and types of tuna fish were analyzed for selenium by using differential-pulse cathodic-stripping voltammetry. The cans with high and low concentrations of selenium were analyzed for arsenic by using differential-pulse polarography. Three samples with different levels of added As and a blank were analyzed for each can of tuna fish. Four sample-digestion methods with several variations of each were tested to determine the most reliable technique. An acid-digestion procedure using HNO_3 and $Mg(NO_3)_2$, $6H_2O$ with an 18-h pre-digestion step gave the best results, with an average recovery of 98·2%.

The selenium concentration of the cans analyzed ranged from 0·034 to 1·20 $\mu g\ g^{-1}$, with an average concentration of 0·68 ± 0·27 $\mu g\ g^{-1}$. The arsenic concentrations of the two cans analyzed were 1·62 $\mu g\ g^{-1}$ and 2·41 $\mu g\ g^{-1}$ in the low- and high-selenium cans, respectively.

The selenium concentrations found in the tuna fish are not excessively high and do not seem to pose a problem. The arsenic concentration of 2·41 $\mu g\ g^{-1}$ does, however, approach the maximum allowable level set by the FDA at 2·6 ppm.

INTRODUCTION

Although toxic metals are naturally present in the environment, industrial processes have resulted in an increased concentration of heavy metals in air, water, and soil. Subsequently, these metals are taken in by plants and animals and make their way into the food chain.

Traces of many heavy metals in food are a health hazard, but determination of the levels when various materials become dangerous is not so simple. Several elements are known to be essential at low concentrations, but at higher levels they are toxic. This is complicated even further if there is a very narrow range between the concentration at which the metal is considered essential and the concentration at which it is considered toxic. Some of the more common metals that pose problems in food are cadmium, lead, mercury, arsenic, and selenium. Some of the important considerations relative to arsenic and selenium are discussed below.

Arsenic, which is recognized as a cumulative poison and has been implicated as a carcinogen, is present in most food products owing to its use in agricultural chemicals such as insecticides. Arsenite, the trivalent As, is more toxic than arsenate, the pentavalent As. The no-effect level in rats for arsenate is 125 ppm, whereas it is only 62·56 ppm for arsenite (Doull *et al.*, 1980). Generally, the naturally occurring As is pentavalent, whereas that added to the environment is trivalent.

In 1955 in Japan, babies received a formula from powdered milk contaminated with As. Years later, there were incidences of leukomelanoderma and keratosis in these children. Mental retardation, epilepsy, and brain damage were also prevalent in these exposed children (Anon., 1977*a*). The administration of sodium arsenate to hamsters, mice, and rats has caused anencephaly, congenital malformations, cleft lip, fused vertebrae, eye defects, and forked ribs (Hood & Bishop, 1972). Potassium arsenate, however, was fed to four ewes during pregnancy at a dose of 5 mg kg^{-1} without effect (Jones & Boyer, 1979).

Several mutagenic studies have been carried out for sodium arsenate. Human leukocyte cultures exhibited chromosomal breakage after short-term exposure (Paton & Allison, 1972). Patients who had undergone As therapy more than twenty years earlier had much higher incidences of chromosomal aberrations than those who had not been treated with As (Anon., 1977).

Owing to its various toxic effects, it is necessary to limit exposure to As. A limit of 1 ppm for foods is set in Great Britain, while in the USA 2·6 ppm is allowed for most foods. Very little As is found in food products

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Table 1. Arsenic content of seafood*

Type	As (ppm)	Type	As (ppm)
Haddock	2·17	Kingfish	8·86
Oysters, fresh	2·9	Oysters, frozen	2·7
Scallop, fresh	1·67	Shrimp, shells	15·3
Shrimp, fresh frozen	1·50	Conch, fresh	3·1
Conch, dried whole	5·63	Clams, fresh frozen	2·52

* From Schroeder & Balassa (1966).

other than in fish and fish products. Table 1 shows typical levels found in a variety of fish. Arsenic concentrations above 1 ppm are present naturally in most fish and their products.

Selenium differs from the other trace metals mentioned in that it is an essential micronutrient. There is, however, a very narrow difference between the concentration at which it is known to be toxic and that at which it provides nutrition. The nutritional requirement for Se is thought to end at 0·1 ppm, and toxicity may begin at 0·4 ppm (Venugopal & Luckey, 1978). The toxicity of Se varies according to the chemical form and the species involved. Selenite Se(IV) is considered more toxic than selenate Se(VI). The minimum lethal dose (MLD) of sodium selenite given intravenously to rabbits is 1·5 mg Se kg^{-1} of body weight. The MLD of sodium selenate given under the same conditions is 2–2·5 mg Se kg^{-1} of body weight (Anon., 1978).

Chronic Se poisoning is caused by the ingestion of excess Se over a longer period of time. There are two types of chronic Se poisoning in animals; blind staggers and alkali disease. Blind staggers is characterized by impaired vision, respiratory failure, and weakness of limbs. This usually occurs if the livestock consumes plants containing 100–1000 ppm of Se. Alkali disease occurs from the ingestion of plants containing about 25 ppm of Se (Doull *et al.*, 1980). Alkali disease is characterized by lack of vitality, loss of hair, hoof malformations, lameness, emaciation, anaemia, and necrosis of the liver.

Excess Se is known to have an adverse effect on reproduction in animals. Mice given Se produced fewer and smaller litters, and deaths before weaning were excessive (Schroeder & Mitchener, 1972). The feeding of 10 ppm of selenite to pigs lowered the conception rate and increased the proportion of piglets that were small, dead, or weak at birth (Wahlstrom & Olson, 1959). There is much controversy over whether Se should be considered a carcinogen. Non-metasticizing hepatic tumours were induced in rats by feeding them

Table 2. Selenium content of fish meal*

Type	Average (ppm)	Range (ppm)
East Canadian herring	1·95	1·30–2·6
Chilean anchovetta	1·35	0·84–2·6
Tuna	4·63	3·40–6·6
Smelt	0·95	0·49–1·23
Menhaden	2·09	0·75–4·2

* From Kifer *et al.* (1969).

Table 3. Selenium content of seafood and seafood products*

Type	Se ($\mu g\ g^{-1}$)	Type	Se ($\mu g\ g^{-1}$)
Lobster tail	0·681	Cod, fillet	0·465
Shrimp, shelled	0·604	Flounder, fillet	0·338
Oysters	0·659	Canned tuna	
Perch, fillet		#1	0·30
#1	0·35	#2	1·00
#2	0·23	#3	0·16
#3	0·44		

*From Morris & Levander (1970) and Holak (1976).

grain containing 5–10 ppm of Se. Hepatic carcinomas, hepatic adenomas, and precancerous neoplasms were observed by Venugopal and Luckey (1978) in 25% of the rats fed 4·3 ppm selenite. Epidemiological studies, however, have indicated a decrease in human cancer-death rates with increasing Se content of Crops (Shamberger *et al.*, 1972).

Although Se is an essential element, the excessive intake of Se has been shown to cause toxic effects. We should therefore be concerned with the distribution of Se in foods. Se is usually present in appreciable amounts in meat, seafood, and most grains (Morris & Levander, 1970). Most crop plants, grains, and grasses are not primary Se accumulators, but they can still contain up to 30 ppm of Se (Anon., 1976).

The Code of Federal Regulations Title 21 ¶573.920 specifies that Se can be added as a nutrient in animal feed in the form of sodium selenite or sodium selenate. In complete feed for chickens, swine, sheep, and cattle, the level cannot exceed 0·1 ppm. In turkeys, it cannot exceed 0·2 ppm in complete feed. These regulations were passed because the minimum dietary requirements for Se in animals, which range from 0·1 to 0·2 ppm, are not met in 70% of animal feeds. The toxic level in poultry and swine is considered to be 3·0 ppm, so the addition of 0·1–0·2 ppm of Se to feeds was considered to be safe by the FDA. Se levels in meat from cattle raised in seleniferous areas can be much higher and range from 1·17 to 8 mg per kg of body weight (Anon., 1976).

In fish, Se levels vary widely, both within and between species. Tuna fish were reported as having a range of 3·40–6·2 ppm, with an average of 4·63 ppm (Kifer *et al.*, 1969) This is considered very high. The Se concentrations reported for seafood and seafood products are listed in Tables 2 and 3. Since excessive amounts of Se are known to have toxic effects in man and animals, it is necessary to monitor the Se concentration in Se-accumulator species, primarily fish and grains, or species that are harvested from areas thought to be highly seleniferous.

EXPERIMENTAL

Apparatus

A Sargent–Welch Polarograph Voltammetric Analyzer Model 4001 was used to measure the concentrations of

arsenic and selenium in the various samples of tuna fish.

The cells used were standard cells equipped with an SCE (standard calomel electrode) reference electrode, a platinum-wire counter electrode, and a working electrode. The hanging-mercury-drop electrode (HMDE) used for the differential-pulse cathodic-stripping-voltammetry (DPCSV) determination of Se was Metrohm Model E410. The dropping-mercury electrode (DME) used for the differential-pulse-polarography (DPP) determination of As consisted of an Hg reservoir connected to a glass capillary equipped with a Sargent–Welch drop timer. A stopcock connected to a nitrogen tank was used to deaerate the solution prior to analysis and to maintain nitrogen over the solution during analysis. A Precision Scientific Company Mag-Mix Model 65904 was used to stir the solution. A Thermolyne Furnace Model 1400 and a Sybron Thermolyne Nuova II stir plate were used for sample preparations. For information on the principles of voltammetry together with a description of the methods, the reader should consult suitable analytical-chemistry textbook (for example, Christian & O'Reilly, 1986; Braun, 1987).

Reagents

SeO_2 (99%), As_2O_3, H_2O_2 (30%), $Mg(NO_3)_2.6H_2O$, HNO_3 (69·5%), HCl (37·6%) and H_3PO_4 (85·8%) were Baker Analyzed reagents. H_2SO_4 and Na_2SO_4 (anhydrous) were from MCB Reagents. Amberlite IRA-400 (Cl) analytical-grade synthetic anion-exchange resin (modified-amine form) was from Fischer Chemical. Continuous-vacuum, triple distilled Hg meeting ACS specifications was used.

The supporting electrolyte, 0·1M HCl was chosen because it gave a well-defined peak without interferences. A more concentrated supporting electrolyte of 1M HCl was found to interfere with the resolution of the Se(IV) peak.

Operating conditions

The effect of the deposition potential on the peak current was studied. A concentration of 3 μg in 0·1M HCl was used. A deposition potential of −0·35 V was chosen because it gave maximum sensitivity.

A scan rate of 0·2 V min^{-1} was found to give good resolution of the Se(IV) peak. As the scan rate was increased, the peak became distorted and drawn out. A pulse amplitude of 40 mV was found to give both good sensitivity and a well-defined peak. As the pulse amplitude increased to 80 mV, the peak became distorted.

A drop size of 3 scale divisions on the E-410 HMDE is reported by Metrohm to give a drop diameter of 0·76 mm with a drop surface area of 1·80 ± 0·05 mm (Anon., 1977*a*). This was the maximum size that could be used without causing problems by the drop dislodging from the capillary during stirring. A stir rate of 2 on the Mag-Mix was found to be adequate without creating enough turbulence to dislodge the mercury drop.

A purge time of 300 s was sufficient to remove the O_2 present in the sample. The deposition time of 90 s was adequate to form a sufficient amount of Se complex in the range of Se being analyzed. An equilibration time of 30 s was sufficient to cease all stirring and convection in the solution prior to stripping.

The electroactive form of selenium is Se(IV). Se(IV) gives two peaks at −0·08 and −0·55 V versus the SCE. The first reduction step results from the conversion of an adsorbed chloro-selenium complex to mercuric selenite. This peak was somewhat deformed, and the peak height was not directly proportional to the concentration. The second peak results from the reduction of mercuric selenide. This peak is well defined and was found to be directly proportional to the concentration over a range of 0–4 μg per 100 ml.

The electroactive form of arsenic is As(III). Two peaks are observed, one at −0·40 V and the other at −0·639 V versus the SCE. The first peak is due to the reduction to As(0), and the second peak is due to further reduction to AsH_3. The first peak is much sharper than the second, and it was found to be directly proportional to the concentration over a range of 0–7 μg of As(III) per 50 ml.

A supporting electrolyte of 1M HCl was chosen because it gave a very well-defined first peak without giving interferences. A scan rate of 0·2 V min^{-1} with a pulse amplitude of 40 mV was found to give a high resolution and a well-defined peak. Increasing the modulation amplitude resulted in a broadened peak.

A drop of one second was found to give a well-defined symmetrical peak. A purge time of 300 s was sufficient to eliminate O_2 from the sample.

Electroanalytical procedure

For the determination of Se, the 25-ml-digested sample was placed in a cell with 0·1M HCl (100 ml). The system was purged with nitrogen for 5 min. A deposition time of 60 s and an equilibration time of 30 s were followed by the stripping scan. After the stripping scan, a known amount of standard Se solution was added to the sample cell. The stripping procedure was then repeated after again purging the solution with nitrogen for 5 min. The standard addition method was used to determine the Se concentration to compensate for matrix differences.

The determination of the percentage recoveries for Se was carried out in the same manner as above, but, prior to sample digestion, a known amount of Se was added to the sample. Only 10 ml of the 25-ml-digested sample were used in the determination. This was necessary because the calibration curve for Se is linear only up to 4 μg per 100 ml.

For the determination of As(III), the removal of inorganic ions such as Pb(II), Sn(II) and (IV), and Tl(I) and (III) is necessary. These ions interfere owing to their reduction currents, which occur near the As peak at −0·40 V versus the SCE. Pb(II) will give a peak at −0·435 V, Sn(II) at −0·47 V, Se(IV) at −0·52 V, Tl(I) at −0·475 V, and Tl(III) at −0·45 V versus the SCE.

The presence of these ions will cause a much larger peak to appear near −0·40 V versus SCE, which will interfere with the determination of As. An ion-exchange purification technique was developed to remove these inorganic ions (Holak, 1976). In an HCl solution, Pb, Sn, Tl and many other metals exist as negatively charged complexes. These negatively charged complexes are adsorbed by a strongly basic anion-exchange resin, thereby effectively removing them from the solution. Arsenic, which is present as H_3AsOH_3, is uncharged and therefore is not adsorbed. This procedure, which was used for the As analysis, is described below.

A 25-ml-digested sample was placed in a 100-ml beaker, to which concentrated HCl (2 ml) and anhydrous Na_2SO_4 (2 g) were added. The beaker was then covered with a watch glass and put on a steam bath for 20 min. This is necessary because, in samples that have undergone wet-ashing procedures with strong oxidizing agents such as HNO_3 or $HClO_4$, as will exist as As(V), which is not electroactive in most supporting electrolytes. It must therefore be reduced to As(III). Na_2SO_4 acts as the reductant and will quantitatively reduce As(V) to As(III). After cooling, the sample was placed in 1M HCl (50 ml). The sample was purged with nitrogen for 15 min. Ion-exchange resin (2 g) was added to the sample, which was then purged with nitrogen for 5 min prior to analysis. The standard addition method was used.

The determination of the percentage recoveries for As was carried out in the same manner as for Se, but, prior to sample digestion, a known amount of As was added to the sample.

Sample-digestion procedures

The determination of electroactive species by polarographic methods requires that the sample be in solution. When a solid sample is to be analyzed, the sample must first be digested. This can be accomplished in a number of ways, including wet digestion with acid or dry ashing in a furnace. Four different digestion procedures, including several variations of each method, were tested to determine which was the most reliable procedure, with the best recovery. All the sample-digestion procedures were performed in the hood.

The first digestion procedure was taken from a Metrohm Application Bulletin (Anon., 1977*b*). It consisted in a wet digestion with H_2SO_4 and HNO_3. A 1-g sample of the tuna fish was placed in a 100-ml beaker along with distilled water (20 ml), 96% H_2SO_4 (1 ml) and 65% HNO_3 (10 ml). The beaker was then covered and left standing at room temperature for 18 h. The sample was heated at a medium-heat level. All the samples except the blank turned black owing to carbonization. The samples were removed from the heat, allowed to cool, and then heated again after adding HNO_3 (10 ml) and H_2SO_4 (1 ml). This procedure was repeated twice for each sample. The samples were heated at a medium heat until they were very pale yellow. The heating was then increased until SO_3 mist, characterized by thick white fumes, appeared. The sample was cooled. Although not specified in the procedure because it was developed primarily for the determination of Pb, Cu, and Sn, 6M HCl (5 ml) was added to the sample to convert all the selenium to the electroactive Se(IV). The sample was boiled for 5 min, cooled, and then transferred to a 25-ml volumetric flask with distilled water. Upon analysis by DPCSV a recovery of 83·7% was attained.

Two variations of the above method were also tested. The amounts of acid added initially were doubled, and the addition of the distilled water was eliminated. The samples still turned black and H_2SO_4 (1 ml) with HNO_3 (10 ml) had to be added twice. Instead of boiling the sample after the addition of the 6M HCl (5 ml), the sample was slowly heated for 30 min. This first variation gave a recovery of 83·5%.

A second variation consisted in heating the sample on a very low heat after it had been allowed to stand overnight. The total heating time was increased from about 3 h to 6 h. The samples again turned black, which necessitated the addition of more acid. This was done twice. The samples were slowly heated for 30 min after adding the 6M HCl. This second variation gave a recovery of 86·7%.

The second digestion procedure was due to Adeloju *et al.* (1983). To a 0·2-g sample, H_2SO_4 (4 ml) and HNO_3 (10 ml) were added. Two glass beads were added to the beaker. The sample was slowly heated until all the sample material dissolved and HNO_3 fumes ceased to appear. Heating was increased until SO_3 mist appeared. The sample was cooled and concentrated HCl (12·5 ml) was added to the sample, which was then boiled for 30 min. The sample was cooled, diluted to a pH of 1·0 and analyzed. Since this procedure used only 0·2 g of sample, the Se peaks were barely discernible, and a recovery of only 43·8% was attained.

The above procedure was repeated by using a 1-g sample. The higher organic content caused the sample to turn black owing to carbonization. Further acid was added. After the solution had turned pale yellow, the heat was raised until SO_3 mist appeared. HCl was then added as above. The first variation also gave a poor recovery of 49·4%.

A second variation was tried in which all the modifications of the first variation were carried out but 6M HCl (5 ml) was added to the sample instead of concentrated HCl (12·5 ml). A recovery of 68·7% was attained. This was significantly greater than the 49·4% recovery. The lower recovery of 49·4% was probably due to the volatilization of Se as selenium (IV) chloride, which can occur in boiling concentrated HCl solutions. The use of the 6M HCl prevented this.

The third procedure, which was from Reamer and Veillon (1981), consisted in wet digestion with H_3PO_4, HNO_3, and H_2O_2. A 1-g sample was placed in the beaker with H_3PO_4 (1 ml) and HNO_3 (10 ml). The sample was covered and allowed to stand for 18 h. It was then boiled until it turned pale yellow, and 30% H_2O_2 was added slowly until the sample solution cleared. The sample was boiled for 5 min and transferred to a 25-ml

Table 4. Percentage recoveries for various sample-digestion procedures

Method	Brand of tuna fish	Se found ($\mu g\ g^{-1}$)[a]	Percentage recovery[a]
Anon. (1977*b*)	Star-Kist albacore solid white	0·583 ± 0·012 1	83·7
Variation 1	Empress chunk light	0·76 ± 0·011 0	86·8
Variation 2	Empress chunk light	0·713 ± 0·008 2	83·5
Adeloju *et al.* (1983)	Key Food chunk light	0·280 ± 0·008 9	43·8
Variation 1	Key Food chunk light	0·300 ± 0·012 6	49·4
Variation 2	Chicken of the Sea chunk light	0·655 ± 0·259	68·7
Reamer & Veillon (1981)	Bumble Bee chunk light could not be determined owing to interference from H_2O_2		
Variation 1	Bumble Bee chunk light	0·520 ± 0·012 6	64·7
Variation 2	Bumble Bee chunk light	0·667 ± 0·025 0	81·6
	Bumble Bee chunk light	0·652 ± 0·033 5	79·0
Holak (1976)	Chicken of the Sea chunk light	0·757 ± 0·021 6	83·0
Variation 1	Chicken of the Sea albacore solid white	0·555 ± 0·075	98·5
	Bumble Bee chunk light	0·773 ± 0·012 1	96·9
(for arsenic)	Deep Blue chunk light	1·615 ± 0·0367 μg/g of As	94·3

[a] The average of three samples, with two standard addition determinations for each sample.

volumetric flask with distilled water and analyzed. A large peak occurred near the potential at which a Se(IV) peak should have appeared. The peak appeared in all the samples, including the blank. It was found to be due to the presence of H_2O_2 in the digestion procedure.

The above procedure was carried out again, this time with the addition of the H_2O_2 eliminated. However, the recovery of this variation was low at 64·7%.

Although the procedure specifies that the sample is to be boiled after standing overnight, it was felt that this resulted in a loss of Se. In variation 2, the sample was slowly heated for 5 h instead of boiled for 0·5 h. Although slowly heating the sample added greatly to the digestion time, it significantly increased the recovery to 81·6 and 79·0% for the two samples that were tested.

The fourth procedure, which was from Holak (1976) consisted in digestion with HNO_3 and $Mg(NO_3)_2 . 6H_2O$. A 1-g sample was placed in a beaker with HNO_3 (10 ml) and $Mg(NO_3)_2 . 6H_2O$ (4 g). The sample was then heated slowly until it became dry. This took about 5–6 h. After the sample was dry, the heat level was raised to a maximum until all the HNO_3 fumes were given off. The sample was then placed in a muffle furnace for 30 min at about 500°C. After cooling, 6M HCl (5 ml) was added to the sample, and it was placed on a steam bath until the white residue dissolved. The solution was then transferred to a 25-ml volumetric flask with distilled water. A recovery of 83·0% was attained.

Table 5. Sources of the tuna fish analyzed

Brand	Type	Code No.	Source[a]
Star-Kist	Chunk light	999X1-D5200	—
	Albacore solid white	791F3-ES557	—
Chicken of the Sea	Chunk light	C120A-RW620	West coast of Central and South America
	Albacore solid white	SMAIZ-W4K2H	West coast of USA
Bumble Bee	Chunk light	CLA4S-1XS41	Solomon Islands, near New Guinea
	Albacore solid white	SWP9J-L4362 (For Se)	Mid-Atlantic
	Albacore solid white	SWP1J-L7VHI (For As)	Mid-Atlantic
Key Food	Chunk light	SGB-40610	—
	Albacore solid white	M5LB-0028C	Atlantic
Deep Blue	Chunk light	SCB-40504 (For Se)	West coast of Central and South America
	Chunk light	SCB-40507 (For As)	West coast of Central and South America
American	Chunk light	M54-XB-32230	West coast of Central and South America
CHB	Albacore white flakes in oil	M3LU-NO9AB	West coast of USA
Season	Albacore solid white	751F8-ES646	—
Empress	Chunk light	41118-1TK	—
Progresso	Light in olive oil	RKM16-A7842	—
Genova	Solid light in olive oil	TLHAZ-53KBF	—

[a] Indicates source not available.
Unless otherwise noted, all fish were canned in water

A variation of the method was tried in which, after the addition of the HNO_3 and $Mg(NO_3)_2 . 6H_2O$, the sample was covered and allowed to predigest for 18 h. The procedure was then carried out as specified above. This predigestion step significantly increased the recovery to 95·5 and 96·9%, which was obtained for the analysis of two cans.

The sample-digestion procedure involving the use of HNO_3 and $Mg(NO_3)_2 . 6H_2O$ with an 18-h predigestion step was found to give an excellent recovery. It also eliminated the use of $HClO_4$ and benzene, two potentially dangerous compounds that are commonly used in digestion procedures. This procedure was therefore used for the digestion of all the tuna-fish samples in determining the Se concentration.

This procedure was also tested for the DDP determination of As. Coupled with the ion-exchange purification technique previously mentioned, a recovery of 94·3% was attained. No interferences were observed. This procedure was therefore used in the As determinations.

Table 4 gives a summary of the sample-digestion methods tested and the percentage recoveries attained for each.

Sources of tuna fish

The four main species of tuna are albacore, yellowfin, skipjack, and bluefin. These four species account for more than 95% of all tuna commercially caught. Canned tuna can be packed in a variety of media, including vegetable oils, olive oil, and water. Table 5 lists the sources of the tuna fish analyzed. The source refers to the area in which the fish was most probably caught as identified by the supplier. All the tuna fish were purchased in supermarkets throughout Brooklyn, NY, USA.

Other investigators have analyzed tuna fish for various toxic metals, including Cd, Pb, Hg, As, and Se. Table 6 lists the average concentrations that have been reported.

RESULTS

Fifteen different brands and types of tuna fish were analyzed for Se by using DPCSV. Three samples from each can with three different levels of added Se for each can were analyzed to determine recoveries. These results are presented in Table 7.

The types of tuna fish with the highest and lowest Se concentrations were analyzed for As by using DPP. Three samples with different levels of added As were also analyzed for each can to determine recoveries. These results are presented in Table 8.

Table 9 summarizes the average Se concentration for each brand and type of tuna fish. The standard deviations and relative standard deviations are also given. Table 10 summarizes the average As content of the two brands of tuna fish with the standard deviations and the relative standard deviations.

Table 6. Concentration of toxic metals in tuna fish

Metal and sample	Concentration ($\mu g\ g^{-1}$ unless otherwise noted)	Source
Cd	Less than 0·2	Fribergh *et al.* (1974)
Pb		
Fresh albacore muscle	0·3 ng g^{-1}	Settle & Patterson (1980)
Canned tuna fish	1·4	Settle & Patterson (1980)
Hg		
Yellowfin tuna	0·012–0·06	Matthews (1983)
Skipjack tuna	0·026–0·448	Matthews (1983)
Dogtooth tuna	0·38–4·4	Matthews (1983)
As	0·71–4·6	Anon. (1977*a*)
Se		
Average	4·63	Kifer *et al.* (1969)
Range	3·4–6·6	Kifer *et al.* (1969)
Canned tuna	0·49	Holak (1976)

DISCUSSION

The three light tunas that were identified as being caught off the west coast of Central and South America were found to contain 0·34, 0·68 and 0·90 $\mu g\ g^{-1}$ of Se. The Deep Blue tuna contained only skipjack and had the lowest concentration of 0·34 $\mu g\ g^{-1}$. The type of the other brands of tuna could not be identified. Bumble Bee light tuna, which was caught off the Solomon Islands near New Guinea, contained 0·77 $\mu g\ g^{-1}$ of Se, which was not very different from the value for the range found off the coast of Central and South America.

The brands with the highest and lowest Se concentration were also analyzed for As. Deep Blue light tuna, which had the lowest Se concentration of 0·34 $\mu g\ g^{-1}$ also had the lower As concentration of 1·62 $\mu g\ g^{-1}$. Bumble Bee albacore, which had the highest Se concentration of 1·20 $\mu g\ g^{-1}$ also had the higher As concentration of 2·41 $\mu g\ g^{-1}$. The Deep Blue skipjack tuna was caught off the west coast of Central and South America, whereas the Bumble Bee was from the mid-Atlantic.

The fifteen cans of tuna fish tested contained much less Se than reported by Kifer *et al.* (1969). They reported tuna having an average Se concentration of 4·63 ppm ($\mu g\ g^{-1}$) with a range of 3·40–6·20 ppm. The Se content of these fish was determined with fluorometry. Although the fish were reported to be from waters that were low in Se, tuna fish are highly migratory fish, and the area in which they were caught is not necessarily the area in which they lived. Since all the fish tested had excessively high Se concentrations, it is also possible that there was undetected Se contamination.

The concentration of Se in other seafood and seafood products (see Table 3) was found to be much lower than that reported by Kifer *et al.* (1969). Lobster, shrimp, cod, flounder, and perch had a range of 0·23–0·681 $\mu g\ g^{-1}$. Three cans of tuna fish were reported to have Se contents of 0·30, 0·16, and 1·00 $\mu g\ g^{-1}$. The fifteen cans of tuna fish analyzed fell well within the range, with only Bumble Bee albacore having a higher concentration. Table 11 compares the

Table 7. Results of the selenium analysis of tuna fish

Brand and type	Sample	Se found[a] ($\mu g\ g^{-1}$)	Sample	Se Added (μg)	Se Recovered[a] (μg)	Recovery (%)
Star Kist						
Chunk light	1	0·50	4	1·00	1·46	97·3
	2	0·51	5	2·00	2·25	90·0
	3	0·48	6	3·00	3·33	95·1
Albacore solid white	7	0·62	10	1·00	1·15	68·5
	8	0·72	11	2·00	2·70	101·0
	9	0·70	12	3·00	3·43	93·1
Chicken of the Sea						
Chunk light	13	0·91	16	1·00	2·03	108·0
	14	0·90	17	2·00	2·91	101·0
	15	0·90	18	3·00	3·85	98·5
Albacore solid white	19	0·55	22	1·00	1·52	98·1
	20	0·57	23	2·00	2·45	96·1
	21	0·55	24	3·00	3·27	92·1
Deep blue						
Chunk light	25	0·37	28	1·00	1·28	95·5
	26	0·32	29	2·00	2·21	94·4
	27	0·33	30	3·00	3·14	94·6
Bumble Bee						
Chunk light	31	0·78	34	1·00	1·70	96·0
	32	0·79	35	2·00	2·75	98·9
	33	0·76	36	3·00	3·60	95·7
Albacore solid white	37	1·20	40	1·00	2·17	98·2
	38	1·25	41	2·00	3·13	97·8
	39	1·16	42	3·00	4·13	98·1
Key Food						
Chunk light	43	0·67	46	1·00	1·58	96·3
	44	0·65	47	2·00	2·57	97·0
	45	0·65	48	3·00	3·56	97·2
Key Food						
Albacore solid white	49	0·84	52	1·00	1·79	96·8
	50	0·86	53	2·00	2·77	96·9
	51	0·86	54	3·00	3·74	96·9
American						
Chunk light	55	0·69	58	1·00	1·65	98·2
	56	0·66	59	2·00	2·50	93·6
	57	0·69	60	3·00	3·65	98·9
CHB						
Albacore white flakes in oil	61	0·47	64	1·00	1·40	95·2
	62	0·46	65	2·00	2·37	96·0
	63	0·49	66	3·00	3·36	96·8
Season						
Albacore solid white	67	0·59	70	1·00	1·58	98·8
	68	0·59	71	2·00	2·57	98·9
	69	0·59	72	3·00	3·52	97·7
Empress						
Chunk light	73	0·87	76	1·00	1·85	96·9
	74	0·92	77	2·00	2·84	95·6
	75	0·90	78	3·00	3·72	95·9
Progresso						
Chunk light in olive oil	79	0·77	82	1·00	1·75	98·3
	80	0·77	83	2·00	2·73	98·6
	81	0·79	84	3·00	3·80	100·5
Genova						
Solid light in olive oil	85	0·39	88	1·00	1·36	97·8
	86	0·40	89	2·00	2·33	97·5
	87	0·38	90	3·00	3·29	97·3

[a] The average of two standard addition determinations for each sample.

Table 8. Results of the arsenic analysis of tuna fish

Brand and type	Sample	As found[a] ($\mu g\ g^{-1}$)	Sample	As added (μg)	As recovered (μg)	Recovery (%)
Deep Blue						
Chunk light	91	1·62	94	1·00	2·46	93·2
	92	1·58	95	2·00	3·49	94·6
	93	1·65	96	3·00	4·39	95·0
Bumble Bee						
Albacore solid						
white	97	2·37	100	1·00	3·20	95·8
	98	2·45	101	2·00	4·15	94·7
	99	2·43	102	3·00	5·22	96·3

[a] The average of two standard addition determinations for each sample.

Se content of the canned tuna fish with the Se content reported for other foods.

The As concentrations reported for most foods excluding seafood are much lower than those found in the tuna fish (Table 12). As concentrations of other seafood fall within the range from 1·50 to 3·1 $\mu g\ g^{-1}$, with an average As content of 2·37 $\mu g\ g^{-1}$. The As concentration of the Deep Blue skipjack tuna was below the average with 1·62 $\mu g\ g^{-1}$. The As concentration of the Bumble Bee albacore fell close to the average with 2·41 $\mu g\ g^{-1}$.

The FDA maximum allowable limit for As in most fish and seafood is set at 2·6 ppm. This limit was not exceeded in either the Deep Blue skipjack or Bumble Bee albacore. The Deep Blue skipjack was found to contain a level of As of 1·62 $\mu g\ g^{-1}$ which is sufficiently far below this standard. Bumble Bee albacore, however, was found to contain 2·41 $\mu g\ g^{-1}$, which is closely approaching the FDA level of 2·6 ppm. Both cans do, in fact, exceed the limit of 1 ppm that is set in the UK. The UK standard, however, does not take into account that most of the As exists as As(IV) and not As(III), which is more toxic.

Table 9. Selenium content of fifteen brands and types of tuna fish

Brand and type	Se found[a] ($\mu g\ g^{-1}$)	Standard deviation	Relative standard deviation
Star-Kist			
Chunk light	0·50	±0·025	5·0
Albacore solid white	0·68	±0·054	7·9
Chicken of the Sea			
Chunk light	0·90	±0·015	1·7
Albacore solid white	0·56	±0·018	3·3
Deep Blue chunk light	0·34	±0·022	6·5
Bumble Bee			
Chunk light	0·77	±0·012	1·6
Albacore solid white	1·20	±0·040	3·2
Key Food			
Chunk light	0·65	±0·010	1·5
Albacore solid white	0·85	±0·010	1·2
American chunk light	0·68	±0·015	2·2
CHB Albacore white flakes in oil	0·47	±0·017	3·6
Season Albacore solid white	0·59	±0·006	1·0
Empress chunk light	0·89	±0·025	2·8
Progresso Chunk light in olive oil	0·77	±0·013	1·7
Genova solid white in olive oil	0·39	±0·026	6·7

Average of all determinations: 0·68 ± 0·268 $\mu g\ g^{-1}$

[a] The average of three samples with two analyses for each sample.

The FDA does not have any guidelines or regulations dealing with the maximum allowable Se concentration. The FDA, however, permits the addition of up to 200 μg Se per tablet as a dietary supplement. The FDA also allows the addition of Se as a supplement in animal feedstuffs (Code of Federal Regulations, Chapter 1, ¶573.90). The levels of 0·1 ppm allowed to be added to the feed of swine and chickens and 0·2 ppm allowed to be added to the feed of turkeys were shown not to increase significantly the Se concentration in the edible products of chickens, turkeys, and swine (Anon., 1973).

The Se concentrations found in the tuna fish analyzed do not seem to pose a hazard to man. The FDA considers 200 μg of Se to be safe, so even the highest level of Se found, 1·20 $\mu g\ g^{-1}$ would not appear to present a problem. Concern may arise, however, if Se toxicity already exists. The consumption of tuna fish in this case would give an additive effect.

CONCLUSION

DPCSV and DPP proved to be excellent techniques for the determination of trace quantities of Se and As. The sample-digestion procedure involving the use of HNO_3

Table 10. Arsenic content of two brands of tuna fish

Brand and type	As found[a] ($\mu g\ g^{-1}$)	Standard deviation	Relative standard deviation
Deep Blue			
Chunk light	1·62	±0·037	2·3
Bumble Bee			
Albacore solid white	2·41	±0·037	1·5

Average of the two samples: 2·02 ± 0·559 $\mu g\ g^{-1}$.

[a] The average of three samples with two analyses carried out for each sample.

Table 11. Comparison of the Se content of canned tuna fish with the Se content reported for other foods

Type of food	Average Se ($\mu g\ g^{-1}$)	Source
Canned tuna	0·68	—
East Canadian herring	1·95	Kifer *et al.* (1969)
Chilean anchoveha	1·35	Kifer *et al.* (1969)
Smelt	0·95	Kifer *et al.* (1969)
Menhaden	2·09	Kifer *et al.* (1969)
Tuna	4·63	Kifer *et al.* (1969)
Lobster tail	0·681	Morris & Levander (1970)
Shrimp, shelled	0·604	Morris & Levander (1970)
Flounder, fillet	0·338	Morris & Levander (1970)
Cod, fillet	0·465	Morris & Levander (1970)
Perch, fillet	0·34	Holak (1976)
Canned Tuna	0·49	Holak (1976)
Beef, pork, and lamb kidneys	1·76	Morris & Levander (1970)
Dairy products	0·078	Morris & Levander (1970)
Vegetables	0·012	Morris & Levander (1970)
Fresh fruit	0·007	Morris & Levander (1970)
Garlic	0·276	Morris & Levander (1970)
Mushrooms	0·125	Morris & Levander (1970)
Whole-wheat products	0·521	Morris & Levander (1970)
White-grain products	0·239	Morris & Levander (1970)

and $Mg(NO_3)_2 . 6H_2O$ prevented losses of the analyte. It was found to be an excellent digestion procedure.

Se and As accumulate in tuna fish to varying degrees. Albacore tuna tend to accumulate more Se than skipjack, yellowfin, or bluefin. Arsenic was also more concentrated in albacore. The higher concentrations are probably due more to environmental conditions than to the ability of certain species to be Se or As accumulators. Higher concentrations of Se and As were found in the albacore that were caught in the Atlantic than in those caught in the Pacific. Tuna, however, are migratory fish so the area in which they are caught is not necessarily the area in which they lived.

Table 12. Comparison of the As content of canned tuna fish with the As content reported for other foods[a]

Type of food	Average As ($\mu g\ g^{-1}$)
Canned tuna	2·02
Haddock	2·17
Oysters, fresh	2·9
Scallop, fresh	1·67
Shrimp, fresh frozen	1·50
Conch, dried whole	5·63
Kingfish	8·86
Shrimp shells	15·3
Clams, fresh frozen	2·52
Beef, stewing	1·3
Pork, liver	1·4
Pork, kidney	0·0
Pork loin	0·06
Lamb chop	0·35
Salt, table and sea	2·77
Mushrooms	2·9
Garlic, fresh	0·24
Whole-wheat grains	0·17
Butter	0·23

[a] Source: Schroeder & Balassa (1966).

The Se and As concentrations found in the tuna fish exceeded those found in most other foods except for seafood. Se and As seem to accumulate in fish, and food in general, more so than the other heavy metals except in the case of contamination. Fish and seafood do tend to lead to the accumulation of As and Se to greater degrees than most other foods.

The concentrations of Se found in the tuna fish should not be of concern unless Se toxicity already exists. Although the As concentrations were below the FDA standard of 2·6 ppm, the Bumble Bee albacore from the mid-Atlantic approached this level with 2·41 $\mu g\ g^{-1}$.

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