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Determination of Selected and Potentially Hazardous Elements in Caviar

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Abstract: Caviar, a gourmet food worldwide, was analyzed for Fe, Al, Mg, Cu, Sr, Mn, Zn, Co, Ni, Mo and other elements using Inductively Coupled Plasma Emission Spectrometry. The study was aimed to determine the prevailing concentration of trace elements in Caviar to evaluate nutritive value and the impact of long term toxicity. The data obtained will also serve as base line value for monitoring the extent of probable future contamination from surrounding marine atmosphere and/or the introduction of toxic elements during processing to formulate any curative action. The results were compared with a certified reference material analyzed under similar conditions. It was found that this food items contained elements of nutritive importance, whereas the toxic elements estimated are within the permissible safety limits.

Key words: Caviar · Toxic Elements · Inductively Coupled Plasma Emission Spectrometry · Analysis

INTRODUCTION

Data extracted from experimental studies of the interrelation between marine biota and terrestrial animals including humans indicated a potential for accumulation of various cations. The manifestations of metal toxicity are influenced by a wide range of parameter, including their concentration in the diet. Sometimes the presence of such elements even in small amount, disrupts the normal functioning of the animals. Development stages and nutritional variables must also be taken into account when evaluating the health effects of the potentially toxic elements. Investigations of the nutritional status and toxic potential of food are an integral part of any dietary evaluation as a means of protecting human health [1-4].

The caviar is the salted roe or eggs of certain large fish species, especially members of sturgeon family which are served as a gourmet delicacy. Sturgeon eggs are either black or slate gray, depending on the species. Red caviar is made from the roe of salmon, especially chum and silver salmon. Before packing the eggs are strained and salted. The best quality caviar is only slightly salted and is called malison. About 95% of the black caviar in the USA is imported from Iran, where the sturgeon is caught along the shores of the Caspian Sea. More than 60 metric ton caviar is imported from Iran, each year and most of it is preserved, pasteurized and sold in jars. The rest is sold fresh. The size of eggs varies from small grains to eggs as large as peas. Less costly varieties are the red eggs from North Atlantic salmon and the roes of whitefish, lake hersing cod and carp, which are usually dyed black when processed [5-8].

Although other analytical techniques can be used for decoding the elemental composition of marine biota, but selected the ICP-ES which is a food analytical technique and is not nuclear reactor dependent. The ICP-AES was also selected on the basis of range of elements covered, appropriate extent of sensitivity to suitability matrix effects of the elements [9-11].

METHOD AND PROCEDURE

Sampling and Preparation of Samples: The samples were collected using Market Basket Method [MBM] from markets in Islamabad [the capital], Lahore and Karachi [a metropolitan city] of Pakistan. Commercially packed caviar with commercial names “Paradise”, “Heaven” and “Like” were tested in the study. Major and minor elements were determined in these samples using Inductively Coupled Plasma Emission Spectrometry.

The samples were weighed and for analysis oven dried at 60°C for at least 48h till constant weight. The dried samples were then pulverized in an grinder [Braun, GmbH, Germany]. The samples were randomly selected and analyzed. The average water contents were found to be 76%.

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Table 1: Details of Equipment and Operating Parameters

1. Details of Equipment	
Spectroanalyzed System	A computer controlled analyzer system consisting of: JY-38 (VHR) monochromator with 3600 grooves mm^{-1} holographic grating(Jobine Yvon, France)
Practical Spectral band width	7.8
Theoretical band width	5.2
R.F. Source	40.68 MHz Crystal regulated (JY-2300) generator
Plasma Torch	Demountable modular torch (Jobin Yvon, France)
Nebulizer	Meinhard concentric nebulizer with 1.50ml min.-1 flow rate.
Computer	Apple lle with proper program Plasma
and aerosol carrier gas	software Argon
Spectrometer flushing gas	Nitrogen
Photo-multiplier tube	Hamamatsu R-306 (Japan)
2. Operating Conditions	
R.F. Power	1.0 K.W.
Reflected power	<5 V
Viewing height	10-15 mm above the load coil
Slits	Entrance 25 micron
	Exit 25 micron
Integration time	1000 MS
Flushing gas flow rates:	
Spectrometers	2.0 1 $min.^{-1}$
Channels	0.8 1 $min.^{-1}$
Plasma gas flow rates	12.0 1 $min.^{-1}$
Coating gas	0.35 1 $min.^{-1}$
Carrier gas (nebulizer)	0.8 1 $min.^{-1}$
Wavelength (nm)	As admissible for individual element

Reagents: All chemicals and reagents used were of spec-pure grade (Johnson and Matthey).

Preparation of Samples: Samples weighing 500mg were taken in a 100ml flask. 5ml of ultra pure nitric acid was added to the sample and the mixture was then heated at 70°C for 30min. After cooling, 2.0ml of 70% $HClO_4$was added and then mixture was heated again at 250°C with occasional shaking until the while fumes evolved. The clear solution obtained was cooled and transferred into a 25ml measuring flask and the volume was made up to with doubly distilled deionized water. A blank was prepared under similar conditions.

Procedure: Inductively Coupled plasma [ICP-AES] analysis were carried out using a Jobin Yvon, computer controlled analyzer system consisting of JY.38 VHR-Monochromator. The conditions for the instrumental determination were optimized at the best compromised parameters. The details of equipment and operating parameters are listed in Table 1.

RESULTS

Commercially packed caviar with a fictitious name such as "Paradise" "Heaven" and "LIKE" were used for cationic compositional decoding of these this gourmet of elite. The level of toxic and essential elements determined is shown in Table 2. Generally, the level of concentration of different elements in caviar is very low. Most of them are found in ppb range except a few elements such as Fe, Al, Sr, Mg etc. It is covertly reported in literature [6,13-16] that concentration range of elements in different type of fish varies depending on the type, the surrounding environment and their own inclination to absorb and retain certain elements. (Table 3).

The lead, has a value of 0.166ngg^{-1}. The toxic effects of Pb involve several organs leading to pertinent biochemical effects. Cd was present at a mean of 4.02 to 9.85 ngg^{-1}. Cd is nephrologically toxic and carcinogenic. The critical concentration of Cd in the renal cortex, in 10% of the population is about 200μgg^{-1}. Liver and kidney Cd levels increases simultaneously until the average renal cortex. Cd concentration is about 300μgg^{-1} and the average liver concentration is 60μgg^{-1} [12], hence level of Cd in caviar is in a safe range.

Cu is essential to life and health and abundant to the point of excess in many foods. It is considered not significant health hazard. Cu has its safe limit in water less than <0.1 μgg^{-1}, according to the drinking water standards. Cu is involved in maintenance of vascular and skeletal integrity and function of central nervous system [14]. The suggested reference intake to humans is 3.5 mg/day. The concentration range of 0.13 to 0.289 μgg^{-1} Cu in caviar could be regarded as beneficial to human health.

Another nutritionally important element, Fe, is found at high levels in caviar. The recommended daily allowance for men (age group 19+ years) is 10 mg while for women in the age group (50+years), the recommended allowance is 15 mg per day. Cr is an essential nutritional element for humans for the role it plays in insulin activity. The studied caviar contained significant concentration of Cr, about 0.9 μgg^{-1} [13-15].

Hg considered to be a highly toxic element, was not found at detectable levels in the caviar. Its tolerance level

Table 2: The Mean Concentration of Various Toxic and Essential Elements in Caviar (processed)

S.No	Element	Concentration Paradise	Like	Heaven
1.	Al	1.284±0.531 μgg^{-1}	3.689±0.751μgg^{-1}	2.825±0.565μgg^{-1}
2.	Fe	5.360±0.982 "	7.461± 1.212 "	3.526±0.564 "
3.	Mn	158.1±11.6 "	228.653±29.98 "	321.448±98.2 "
4.	Sr	1.442±0.363 "	3.115±0.996 "	1.168±0.345 "
5.	Mg	497.4±24.6 "	209.8±37.95 "	350.258±15.74"
6.	Cr	0.880±0.096 "	0.278±0.025 "	0.542±0.044 "
7.	Zn	9.215±1.32 "	13.114±2.322 "	10.854±1.760 "
8.	Cu	132.6±12.3ngg^{-1}	169.3± 8.9ngg^{-1}	289±-25.2ngg^{-1}
8.	Cd	4.24±0.16 "	7.32± 1.14 "	9.62±2.88 "
9.	Co	37.36±4.38 "	16.74± 2.5 "	54.82±5.2 "
10.	Pb	16.05±2.6 "	29.85±56.81"	14.36±32.21"
11.	Ni	59.2±13.55 "	102.14±23.6 "	35.04±7.22 "
12.	Eu	16.35±7.66 "	11.54± 0.68 "	24.61±11.70 "
13.	Sm	24.93±7.21 "	12.65± 3.21 "	7.58±1.06 "
14.	Gd	10.92±2.69 "	18.64±3.41 "	11.35±1.24 "
15.	Tl	47.56±8.68 "	82.96±16.3 "	34.02±5.85 "
16.	Y	7.182±1.341 "	4.219± 0.76 "	11.247±0.99 "
17.	Dy	4.142±0.823 "	3.892±0.774 "	6.72±0.98 "
18.	Hg*	-	-	-
20.	As*	-	-	-

sought but were not detected.

Table 3: Intake of Normal Reference Man/Day [2, 13]

S. No.	Elements	Food	Units
1.	Al	45	(mg)
2.	Fe	12-16	"
3.	Mn	3.7	"
4.	Sr	1.9	"
5.	Mg	0.27-0.34	"
6.	Pb	44	"
7.	Ni	400	"
8.	Cr	150	µg
9.	Cu	3.5	"
10.	Cd	1.50	"
11.	Co	300	"

Tabel 4: Comparison of SRM-1577 (Bovine Liver) with Experimental Values

S. No.	Elements	Experimental Values	Certified Values	Units
1.	Fe	191.92±9.88	194±20	μgg^{-1}
2.	Cu	150.69±6.40	158	"
3.	Mn	9.22±6.17	9.9±0.8	"
4.	Zn	161.86±14.83	123±8	"
5.	Cd	423±18.87	440	ngg^{-1}
6.	Ni	223.42±17.87	-	"
7.	Cr	667.32±9.81	650	"
8.	Co	190.13±18.4	210±50	"
9.	Pb	131±25.77	139	"

in mammals lie between 100 to 400 μgg^{-1} weight. Caviar is also rich in Mn, with concentrations range from 158-321 μgg^{-1}. It is essential for growth, reproduction and skeletal development. Since human body can not distinguish between Sr and Ca. Hence in case of Ca-deficiency, it absorbs Sr efficiently. Thus Sr can act as an substitute for Ca as it plays an important role in the bone formation and in the strengthening of bones like Ca. Its concentration was found to be around 01.442μgg^{-1} [16- 18]. Zn is present in a safe range of 9.2 to 13.8 μgg^{-1}. Perhaps the presence of Zn renders a glow on human skin.

Mg plays a crucial role in the human body. Its deficiency leads to muscle wasting and spasms, numbness and convulsions. However, hypermagnesmia may result in problems with renal function. Mg has a concentration up to 497.4μgg^{-1} which does not appear to have any harmful effect on human health. Inorganic As, a well known poison for humans but was not found in caviar. It is imperative to be emphasized here, that nutritional physiology of the trace elements is rarely confined to a single element in isolation from others [19]. It is due to the frequency of interactions at the absorptive and the cellular level, which may influence the minimum requirements and maximum tolerance levels. Indeed the trace elements interact with each other and with other nutrients to such an extent that the margin between the levels at which the effects on human health are beneficial and those that are toxic may be quite small or even overlap. Nevertheless, these studies are to be further extended to reveal further insights for nutritious importance or cumbersome and nuisance role of certain trace elements in the physiological potential of human beings.

Trueness of Method: To establish the authenticity of the analytical procedures used, a certified reference material, SRM 1577, bovine liver from NBS. USA was deciphered under similar conditions. Our experimental values synchronized well with the reported values within the confidence level limits, as shown in Table 4 The variation of our experimental values from the certified values indicate the accuracy.

Precision: The relative standard deviations for 5 replicate measurements of 1.0 mgL^{-1} levels were 2.0% and the detection limit was found to be 15µ g L^{-1}. The reproducibility of the method was calculated in terms of the relative variation coefficient, by the following equation.

Table 5:

S. No	Statistical Data for Copper*	Values
1	Geometric Mean, GM	132.64
2	Standard Deviation, SD	12.3241
3	Arithmetic Mean, AM	12.4
4	Median, Med	12.5

* The samples were taken for one kind only

** Experiments carried out on different days

$$\nu = 100/C\ [\sqrt{\Sigma}\ d^2/(n-1)]$$

Where

N = No. of replicates

C =Average concentration

The statistical treatment of data rendered an overall precision of 2.0- 9.3% of the concentration values. (Table 5). The elements not estimated, were below the limit of quantification (LOQ) which was calculated from the equation.

$$LOQ = 10\ X\ (S_{BL}/b)$$

where S_{BL} is the standard deviation of ten blank firings, whereas the b is the slope of the calibration curve. The calibration curve was found to be linear in concentration range 20-1000ng g^{-1} for Ni.

CONCLUSION

The samples analyzed were not contaminated with trace toxic elements which are prone to cause any hazard to human health or may disrupt the routine functioning of the human organs. Nevertheless, they contain some adequate concentrations of the essential elements. Their inadequacy, imbalances and hazardous effects are discussed.

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