

Mercury Content of Squid Loligo opalescens

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ABSTRACT

The mercury level has been determined in the edible and inedible tissues and in the whole raw and tinned Loligo opalescens squid. The method of measurement was cold-vapour atomic absorption spectrometry. The mercury levels were generally low, e.g. from $6\cdot 8 \pm 3\cdot 5$ to 18 ± 5 ($3\cdot 0$ to 28) µg kg⁻¹ wetweight for the edible and inedible parts of raw and tinned squid, and from 11 ± 3 to 14 ± 4 ($6\cdot 3$ to 23) for the whole squid. The level of mercury in tissues and carcasses examined was independent of the body weight of squid (p > 0.05). The results are compared with the levels found for different species of squid from various locations.

INTRODUCTION

Squid and other cephalopods are a popular food item in Japan, southeast Asia and Mediterranean nations. For example, in Japan the annual consumption of squid is about 5 kg per capita. Squid catches in the world increased in the 1974–1983 period from 688 600 to 1 139 800 tons and by Polish fishing vessels from 6700 to 110 300 tons (Blady & Byrka, 1986).

In view of the economic and nutritional value of squid, it is important to know the level of toxins such as heavy metals which are likely to occur in edible squid parts. The objective of the present paper relates to the occurrence of mercury in raw and processed squid.

MATERIALS AND METHODS

Squid (Loligo opalescens) were harvested during commercial fishing in the north-east Pacific Ocean (region of the Californian coast, Monterey) in

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August 1988. Approximately 10 kg deep-frozen $(-25^{\circ}C)$ squid were delivered to the laboratory.

The deep-frozen squid were the raw material for the commercially manufactured tinned squid 'Squid with salt and water added' and 'Squid in a piquant sauce'. In brief, the technology for the production of tinned squid is as follows: thawed whole squid are rinsed with flowing potable water, then packed in lacquered tins, flooded with hot brine (20%) or dosed with a piquant sauce, and sterilized in an autoclave.

The total mercury content was determined in the edible and inedible parts of the raw and tinned squid and in whole specimens. The sample weight was: 10.6-58.5 g for whole squid, 5.8-32.5 g for skinless mantle (tube), 3.8-18.2 g for arms and crown, 2.6-20.2 g for the intestines, 0.4-3.7 g for fin, 3.1-5.9 g for skin (pulled) and 0.85-1.10 g for pen (pulled).

For the determination of mercury the samples were wet-digested with concentrated nitric acid in a glass apparatus consisting of the round-bottom flask, partial condenser (30 cm long) and a water cooler. Five to twenty millilitres of 65% HNO₃ was added to the sample and the mixture was allowed to stand for 48 h, then the flask was gently heated for 3 h. After the flask had cooled, 10 ml of redistilled water was added and the flask was again heated, for 1 h. After cooling the water cooler and condenser were rinsed with 10 ml of redistilled water. The digest was filtered and, after appropriate dilution with redistilled water, hydroxylamine hydrochloride and stannous chloride in sulphuric acid solution were added to the sample (10 ml). Final determination of the Hg content was by cold-vapour atomic absorption spectrometry (AAS) using a UV mercury monitor LDC/Milton Roy.

The accuracy and precision of our measurements were determined during an obligatory participation in inter-laboratory trials, a quarterly sample check programme. We have checked our method also by analysing fish flesh: IAEA sample MA-A-2; gift from Dr Claudio Leonzio, University of Siena. Our result is $570 \pm 50 \,\mu\text{g}\,\text{Hg}\,\text{kg}^{-1}$ (n = 6) and is close to that obtained by Stoeppler *et al.* (1979) ($570 \pm 20 \,\mu\text{g}\,\text{Hg}\,\text{kg}^{-1}$) or Vos *et al.* (1987) ($546 + 1 \,\mu\text{g}$ Hg kg⁻¹). Moreover, the within-run reproducibility of the method was also controlled. The results of these measurements were satisfactory (running recoveries were from 80.8-101.3% in the range $3-85 \,\mu\text{g}\,\text{Hg}\,\text{kg}^{-1}$; coefficient of variation below 10%).

RESULTS AND DISCUSSION

A total of 104 squid were analysed for mercury content and all samples contained the metal. However, the level of mercury was relatively low, e.g. the total range was from 3.0 to $28 \,\mu g \, kg^{-1}$ (Table 1). Mercury is found in

N		
NO.	Mean	Range
16	11 ± 3	6.3-16
16	7.7	
16	7.3 ± 3.1	3.0-13
16	18 <u>+</u> 5	13-28
16	8.2 ± 3.1	3.5-16
4 (16)*	13 ± 4	8.5-17
16	6·8 ± 3·5	3.0-16
4 (16)	13 ± 3	10–17
16	14 ± 4	7.2-23
16 (32)	13	
16 (32)	13 ± 4	8.8-22
12 (24)	14 <u>+</u> 3	8.4-18
15 (30)	16 <u>+</u> 4	9.6-25
16 (32)	12 ± 5	4.2-24
	No. 16 16 16 16 16 4 (16) ⁵ 16 4 (16) 16 16 (32) 16 (32) 15 (30) 16 (32)	No. Mean 16 11 ± 3 16 $7 \cdot 7$ 16 $7 \cdot 7$ 16 $7 \cdot 3 \pm 3 \cdot 1$ 16 18 ± 5 16 $8 \cdot 2 \pm 3 \cdot 1$ 4 (16) ^b 13 ± 4 16 $6 \cdot 8 \pm 3 \cdot 5$ 4 (16) 13 ± 3 16 14 ± 4 16 (32) 13 16 (32) 13 ± 3 16 (32) 13 ± 4 12 (24) 14 ± 3 15 (30) 16 ± 4 16 (32) 12 ± 5

TABLE 1 Total Mercury Content of *Loligo opalescens* squid ($\mu g k g^{-1}$ wet wt)

^a Calculated values (arithmetic mean weighted).

^b Number of samples and number of squid (in parentheses).

"Squid in brine with salt and water added'.

"Squid in a piquant sauce'.

tissues of marine fish mainly in the form of methylmercury. In the study of Chvojka (1988) the methylmercury concentration averaged 87.9% of total mercury found in axial white muscle of yellowtail kingfish, while in a single specimen of squid analysed by Cappon and Smith (1982) the methylmercury content was $29 \,\mu g \, kg^{-1}$ and $53 \,\mu g \, kg^{-1}$ for inorganic mercury. Methylmercury is a highly toxic cumulative compound that, ingested by man, causes irreversible and severe effects (Tollefson & Cordle, 1988). Mean and maximum mercury levels in edible muscle meat of squid analysed (mantle, fin and arms, crown and head-cleaned), were far below the action level of $500-1000 \,\mu g \, kg^{-1}$ set for fishery products by the health authorities in some countries.

The fin (with skin), skin and arrow of the raw squid contained somewhat higher levels of mercury in comparison with skinless mantle, arms, crown and head and intestines, e.g. from $13-18 \,\mu g \, kg^{-1}$ and $6 \cdot 8 - 8 \cdot 2 \,\mu g \, kg^{-1}$, respectively. In the case of tinned squid the levels of mercury found in inedible intestines and edible mantle and arms and crown are comparable (Table 1). The correlation between mercury level and the body weight or a particular tissue weight was not statistically significant (p > 0.05).

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Species, site of sampling and year	Tissue	No.	Mean ± SD	Runge	Reference
<i>Loligo forbesi</i> Atlantic, northeast, 1971 Atlantic, northeast, 1972	Mantle Mantle	1 (9) ^a 1 (9)	90 150		Portman (1979)
Loligo opalescens Pacific; California, 1971 Pacific; California, 1988	Whole Whole Mantle ^b	50 16 16	36-64 11 ± 3 7·3 ± 3·1	(10-240) (6·3-16) (3·0-13)	Hall <i>et al.</i> (1978) This study
<i>Loligo patagonica</i> Atlantic; southeast, 1986	Mantle ^c	ę	12±0	(12–12)	Falandysz (1989)
<i>Loligo pealei</i> Atlantic; northeast, 1971	Mantle ^c Whole	110 23	20-140 50 <u></u>	(nd-390) (20-125)	Hall <i>et al.</i> (1978)
Loligo vulgaris Atlantic; NW Africa, 1976 North Sea, 1976	Mantic Mantie	0 0	320 100	(85–530) (85–130)	Stoeppler et al. (1979)
Irish Sea, 1976 Atlantic, NW Africa	Mantle Mantle	1 (10)	190 140	(130-280)	Murray (1981) Establier (1972)

Atlantic; NW Africa, 1981-82	Mantle		110		Hardisson (1984) (from Strancari & Lozano (1988))
۸ دامیند کیار مز رغطنه			120		Establier (1973)
Atlantic: NW Africa D 1980	Mantle	7	14	(11–35)	Gajewska & Nabrzyski
	Mantle	16	12	(10–20)	(1980)
	Muscle meat ⁴	10	14	(nd - 30)	
<i>llex argentinus</i> Atlantic; southeast, 1986	Mantle ^b	10	12 土 5	(6-27)	Falandysz (1988)
<i>llex coindetii</i> Atlantic; NW Africa Atlantic; Saharian Bank	Mantle Mantle	*	001		Establier (1973) Lozano & Cardell (1977)
llex illecebrosus Atlantic; northeast, 1971 Atlantic; northeast, 1977	Mantle ^b Mantle ^b	87 2	20-135 60	(nd-400)	Hall <i>et al.</i> (1978) Nabrzyski (1977)
Unspecified squid ? ?, p. 1974	Whole Mantle	1 7	81 70±20	(40-90)	Cappon & Smith (1982) Tanaka <i>et al.</i> (1974)

Number of samples and number of squid (in parentheses).
Skinless.
Tinned squid.
Processed squid.
not, not detected.

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Table 2 lists the available data on mercury levels for a different squid species—mostly in the mantle and a few in whole squid.

Our results of mercury determination in the mantle and whole L. opalescens squid are in the range of the low values reported for that species by Hall *et al.* (1978). As can be seen from the data gathered in Table 2, relatively low levels of mercury have been noted also in the skinless mantle of L. patagonica and Illex argentinus squid (Falandysz, 1988; 1989), and partly also for L. vulgaris squid (Gajewska & Nabrzyski, 1980). In a study by Stoeppler *et al.* (1979) some of ten L. vulgaris squid investigated contained mercury at a level close to the tolerance limit of $500 \,\mu g \, kg^{-1}$. In the case of the other results given in Table 2 all the mean values were below $200 \,\mu g \, kg^{-1}$.

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