Determination of the Heavy Metal Content of Sea-Foods by Atomic-Absorption Spectrophotometry

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Crustacea and mollusca, such as oysters, are able to accumulate metal ions from the ambient sea-water and high metal concentrations are often recorded (1). Recently, we have found levels of copper and zinc as high as 8,000 and 28,000 p.p.m. (dry weight), respectively, in oysters from non-commercial beds contaminated by mining wastes. Atomic-absorption spectrophotometry provides a rapid and sensitive technique for the analysis of trace metals in foodstuffs once the sample is in solution (2). To oxidize the sample, dry-ashing is preferable to wet-digestion for the latter method is time-consuming and requires large volumes of acids which may contain traces of heavy metals. It is necessary, however, with dry-ashing to guard against losses by volatilization and container retention (3).

We have determined the effectiveness of dry-ashing for the atomic-absorption analysis of some 8 metals in a number of typical sea-food samples.

Experimental

Sample preparation. The procedure was an adaptation

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of that of Joseph et al. (4). Samples (500 g) of the sea-foods were macerated in a Waring Blendor, water being added as required, then 25 g of the slurry was weighed into nitric acid-washed beakers and dried for 4 hours at 100°C in an oven and overnight at 450°C in a muffle furnace. The temperature of the furnace was raised slowly from 200°C to prevent ignition of the samples. The ash was dissolved in 2 ml concentrated nitric acid, diluted with 25 ml water and heated to boiling. The solutions were filtered (Whatman no.42) and made up to 100 ml. Approximately 2 g of the sea-food slurry was heated in aluminum dishes for determination of dry weight (5).

Atomic-absorption. Solutions of the samples were nebulized in a Perkin-Elmer Model 303 atomic-absorption spectrophotometer equipped with a Boling burner and a null recorder read-out accessory. The operating parameters are given in Table 1, the instrument settings correspond to the manufacturer's arbitrary scales. A multi-element standard solution of the 8 metals was prepared: Cu 1.0 µg/ml, Zn 0.2 µg/ml, Ni 0.2 µg/ml, Cr 0.2 µg/ml, Mn 0.05 µg/ml, Pb 0.5 µg/ml, Cd 0.05 µg/ml, and Co 0.2 µg/ml. The acidity of this solution was adjusted to 5% (v/v) with nitric acid.

TABLE 1

Operating parameters

	Cd	Co	Cr	Cu	Ni	Pb	Zn	Mn
Wavelength, Å	2288	2407	3579	3247	2320	2170	2138	2795
Slit width, mm	1	0.3	0.3	1	0.3	1	3	1
Source, ma	6	30	20	20	30	12	15	20
Air flow	8	9.7	9	9.2	9	9	9.2	9
Acetylene flow	9	8.0	9	8	9	9	8	9
Gain	6.3	6.1	5.8	5.7	6.2	6.3	5.4	5.4

Results and Discussion

To check dry-ashing technique 1,2, and 3 ml of the multi-element standard solution was added to duplicate 25 g samples of the sea-food slurry and the percentage recoveries, based on direct analysis of aqueous standards, are given in Table 2. The 6 typical commercial sea-foods were chosen to represent a range of canned sea-food. Table 2 shows that except for nickel in clam chowder satisfactory recovery of the metals was obtained for all the foods examined.

TABLE 2

Percentage recovery of added metals from sea-foods (average of 6 determinations)

	Cd	Co	Cr	Cu	Ni	Pb	Zn	Mn
Salmon	93	103	91	98	95	100	98	93
Clam chowder	100	101	86	92	72	93	103	105
Tuna	106	105	103	91	94	96	101	96
Oyster	95	106	92	100	98	98	-	-
Sardine	96	105	93	105	92	104	-	102
Crab Meat	96	105	97	105	90	106	-	103

The metal content of the sea-foods was determined by two methods: the method of addition and direct comparison of unknown with that of a standard metal solution. The results (Table 3) show that the latter, simpler, technique (i.e. method B) is satisfactory for all elements except nickel when the matrix interferes with absorption. Nickel, therefore, must be determined by the method of addition.

The high levels of copper and zinc in sea-food shown in Table 3 have been reported by many earlier workers (e.g. 1,6,7), however the levels of manganese and lead in clam and oyster, and of cadmium in oyster are worthy of note. Schroeder and Balassa (8,9) have also found

TABLE 3

The heavy metal content (p.p.m. dry weight) of six sea-foods

	Cd		Co		Cr		Cu		Mn		Ni		Pb		Zn	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Salmon	0.21	0.19	1.1	1.0	0.47	0.46	4.0	3.8	1.2	1.1	0.61	0.66	1.3	1.3	25	23
Clam chowder	0.12	0.12	1.4	1.2	0.85	0.71	3.5	3.8	9.4	9.1	2.6	2.4	2.2	2.1	37	33
Tuna	0.09	0.09	0.45	0.44	0.13	0.13	2.1	1.7	0.61	0.53	0.68	0.80	1.2	0.93	18	16
Oyster	2.6	2.2	0.45	0.46	0.58	0.58	61	60	*	42	0.77	1.2	4.3	3.9	*	1430
Sardine	0.24	0.22	0.69	0.72	0.37	0.35	3.2	3.2	3.4	3.2	1.3	1.9	1.3	1.1	*	46
Crab Meat	0.41	0.41	1.1	1.1	0.57	0.57	23	23	2.2	2.4	1.9	2.5	0.85	1.0	*	658

A : method of addition

B : direct comparison of unknown absorption with standard of metal in 5% nitric acid

* Concentration too high for method of addition

significant amounts of cadmium and lead in some samples of crustacea and mollusca and in view of the established toxic hazard of these metals further investigation of this problem is required.

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