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ABSTRACT

DETERMINATION OF TOXIC AND ESSENTIAL ELEMENTS IN SEA FOOD. Toxic elements, i.e. As,Cd,Cr,Hg,Pb,Sb and Se and essential elements, i.e. Zn and Cu in fish and shellfish had been determined using instrumental neutron activation analysis and atomic absorption spectrometry. Hg in activated samples were determined after radiochemical separation using Pb $(DDC)_2$ solution in chloroform. The results showed that concentration of the elements studied were still lower than the respective MPC's. The concentration of As,Cd,Cr, Cu,Hg and Se in the fish and shellfish samples were still in natural normal range.

ABSTRAK

PENENTUAN UNSUR-UNSUR LOGAM BERACUN DAN LOGAM ESENSIAL DALAM BAHAN MAKANAN HASIL LAUT. Penentuan logam beracun As,Cd,Cr,Hg,Pb,Sb dan Se, dan logam esensial Zn dan Cu dalam contoh ikan dan kerang telah dilakukan dengan menggunakan analisis aktivasi neutron instrumental dan spektrofotometer penyerapan atom. Hg dalam contoh yang telah diaktifkan ditentukan setelah dilakukan pemisahan secara radiokimia dengan menggunakan larutan Pb $(DDC)_2$ dalam kloroform. Hasil analisis menunjukkan bahwa kadar logam-logam tersebut dalam contoh ikan masih lebih rendah daripada kadar maksimum yang diizinkan. Kadar As,Cd,Cr,Cu,Hg.Pb dan Se masih dalam batas normal.

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INTRODUCTION

The main foodstuffs of Indonesian people are rice, bean, corn, wheat, vegetables, fruits, meat, fish, milk, tea and coffee.

In Jakarta, fish and other marine organisms sold in the market are cought from Jakarta bay and other Indonesian waters. The marine organism, i.e. fish and shellfish represent some of toxic elements pathway entering human body. The amount of toxic elements entered to human body from fishery products depend on the amount of fish consumed and toxic elements concentration in the fish flesh. The contaminated fish or shellfish would be hazardous to human health when it is consumed, such as in case of Minamata desease in Japan. In Indonesia, the control of toxic elements contaminating foodstuffs have not been carried out as in many other countries. Up to now, Indonesia has only a list of the maximum permissible concentration of toxic elements in water stated in a national regulation. Therefore, it is important to study the toxic elements content in fish and shellfish, because these marine organism, are good for biological indicators.

The interesting elements to be analyzed are toxic elements, i.e As, Cd, Cr, Hg, Pb, Sb and Se, and essential elements, i.e, Zn and Cu. As, Cr, Hg, Sb, Se and Zn can be determined by Neutron Activation Analysis (NAA), while Cd, Cu and Pb by Atomic Absorption Spectrophotometry (AAS). The determinations of such elements in other foodstuffs i.e. rice, corn, mung bean, wheat, vegetables, fruits, tea and coffee have been done previously (1). For determination of mercury (Hg), radiochemical separation was used, because the gamma ray energy of ^{203}Hg is very close to that of ^{75}Se. Previous investigators (4-6) had developed a method for determination of mercury in natural waters. The mercury was extracted using 8×10^{-4}M Pb(DDC)2 solution in chloroform, producing Hg(DDC)2. Such a method is now being adapted to

foodstuff matrix.This study was supported by the International Atomic Energy Agency as a Research Contract, during nine months period, i.e.November 1988 - August 1989.

The major purpose of this work is to know whether the concentration of toxic elements in marine organism is approaching or exceeding the maximum permissible concentration as stated by International legislation.

MATERIALS AND METHOD

Samples and Standard Preparation. The samples that were analyzed in this study were Mackerel (Rastrelliger sp), Pompret (Pampus thinausi), Kakap (Lates carferitus), Shrimp (Penaeus sp), Shellfish, i.e, Anadara granosa, Anadara indica, and Cardium unedo. All of these species are commonly consumed by the Indonesian.

The samples were obtained from a Fish Auction Place at Muara Angke Jakarta. During this study, about 50 samples were collected, consisting of about 1-2 kg each. The samples were brought to the laboratory in plastic bags. The samples were cleaned and washed with demineralised water. The flesh were taken out from the body, or the shell. The samples were dried in an oven at 65^{o}C for 48 hours, discontinuously.The dried samples were ground and homogenized . About 200-500 mg of the dried samples were put in polyethylene vials.

The standard was prepared by dropping 5 ul aliquot of freshly prepared standard solution (1000 ppm) of each elements on a filter paper whatman 42 (2). The vials containing the samples, standard, and reference standard were put in an aluminum container. The reference standard used was NBS SRM-1571 obtained from the IAEA (Table 2) .

Instrumental Neutron Activation Analysis, Nuclear reaction of the elements that were analyzed using INAA, namely Antimon (Sb), Arsen (As), Chromium (Cr), Selenium (Se), and Zinc (Zn), can be seen in Table 1 (3).

The container containing the samples and the standards was irradiated for 36 hours in TRIGA-MARK II REACTOR, at flux 10^{11} n $cm^{-2}s^{-1}$. After irradiation, the container was cooled for 2 days for short half-life elements, and 2 weeks for long half-life elements.

The samples and the standard were counted using a 4096 channel Nuclear-Data 62 Multichannel Analyzer, provided with a high pure germanium (Ge-Hp) detector. The system has a resolution FWHM 3.75 keV for the 1332 keV peak of ^{60}Co gamma ray. The counting time was 900 seconds.

Radiochemical Separation. The irradiated samples (200-500 mg) were digested with HNO_3 and H_2SO_4 mixture (1:3 v/v) in a distilating flask, and heated until white fume were evolved. For complete digestion of organic materials, 30% of H_2O_2 was added. After cooling to room temperature, the solution was diluted to 20 ml. The pH of the solution was 2-4. The samples solution was added with 1 mg of Hg as carrier, 4 ml of $Pb(DDC)_2$ solution, and then shaked for 10 minutes. The organic phase containing $Hg(DDC)_2$ was separated and counted using Multichannel Analyzer, at gamma ray energy of 279 keV for ^{203}Hg.

The detection limit, defined as 3xstandard deviation of continuous background counting under the peak was 0.01 ug of Hg.

Determination by Atomic Absorption Spectrophotometry. About 5 to 10 g of dried samples were put in a distilating flask and digested with a mixture of concentrated sulfuric acid and nitric acid (1:3 v/v). A small amount of 30% H_2O_2 was added to elliminate nitrogen dioxides. The digestion process was continued until the solution became clear.

The samples were transferred into a volumetric flask and diluted to 50 ml with demineralized water. Lead, cadmium and copper were excited using oxygen acethylene flame. The absorption of the elements were compared with the standard absorption.

RESULTS AND DISCUSSION

The results of determination of As, Cd, Cr, Cu, Hg, Pb, Sb, Se, and Zn in all samples analyzed are shown in Table 3. The accuracy of the method of analysis used was compared to IAEA standard reference material SRM-1571 (Table 2).

The photopeaks of ^{51}Cr at 320 keV, ^{75}Se at 266 keV, ^{76}As at 559 keV, ^{122}Sb at 564 keV, and ^{65}Zn at 1115 keV, were able to determine the isotopes without any interference from other isotopes.

Mercury was determined without any interference after being separated from selenium by radiochemical separation. The photopeak of ^{203}Hg was determined at 279 keV.

Results of the analyses were compared with the maximum permissible concentration (MPC) recommended by REILLY (7).

All the elements determined were found in all samples. The concentrations of Zn and As, in all samples were higher than Cr, Cu, Hg, Pb, Sb and Se. The highest concentration of As, Sb, Zn, Cd and Cu was found in shellfish. It means that shellfish accumulated As, Sb, Zn, Cd and Cu more than the other elements. The concentrations of Cr, Hg, and Se were almost similar among the fish, shrimp and shellfish samples.

The results obtained showed that the concentrations of toxic elements and essential elements in the samples analyzed were lower than the maximum permissible concentration (MPC) of the elements in foods for human consumption. Other similar legislation exists in many countries also for baby foods, animal feed, feed, sewage, sludge for agricultural use, and air particulates.

CONCLUSION

Radiochemical separation method for Hg determination showed a good result in analysing Hg content in foodstuff. The concentration of toxic elements and essential elements in fish and shellfish investigated were lower than the respective MPC's. Therefore, it can be concluded that the fish and shellfish analyzed are relatively not contaminated by the toxic and essential elements. The concentration of As, Cd, Cr, Cu, Hg, Pb, Sb, and Se in fish and shellfish are still in natural normal range.

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REFERENCES

1. SURTIPANTI, SUWIRMA, YUMIARTI, YUNE MELLAWATI, and SYAIFUDIN, S., Determination of toxic and essential elements concentrations in foodstuffs from local market, Atom Indonesia, 15, 1 (1989).

2. AHMAD, S.M., CHAUDHARY, M.S., MANNAN, A., and QURESHI, I.H., Determination of toxic elements in tea leaves by instrumental neutron activation analysis, Journal of Radiochemistry, 78, 2 (1983) 375.

3. CHAUDARY, M.S., AHMAD, S.M., and MANNAN, A., INAA of toxic elements in coal and their transfer into environments, Journal of Radioanalytical and Nuclear Chemistry 83, 2 (1984) 377.

4. CROUTHAMEL, C.E., Applied Gamma-Ray Spectrometry, Pergamon Press (1970) 733.

5. HANI, N.M. WAI, C.M., and WILLEMS, H., Dithiocarbamate extraction of trace amounts of selenium from biological samples for neutron activation analysis, Journal of Radioanalytical Nuclear Chemistry, 104, 1 (1986) 19.

6. LO, J.M., WEI, J.C., YANG, M.H., and YEH, S.J., Preconcentration of mercury with lead diethyldithiocarbamate for neutron activation analysis of biological and environmental samples, Journal of Radioanalytical Chemistry, 72,1-2 (1982) 57.

7. YUMIARTI, S., Determination of mercury in natural waters by preconcentration with lead diethyldithiocarbamate for neutron activation analysis, to be published.

8. REILLY, C., Metal Contamination of Food, Applied Science Publisher, London (1980).

Table 1. Nuclear data for the elements investigated.

Elements	Nuclear reaction	Energy (keV)	T1/2 (days)
Se	$^{74}Se(n,\gamma)^{75}Se$	224 & 279	128.4
Hg	$^{202}Hg(n,\gamma)^{203}Hg$	279.3	46
Cr	$^{50}Cr(n,\gamma)^{51}Cr$	320	27.8
As	$^{75}As(n,\gamma)^{76}As$	559	26.6
Sb	$^{121}Sb(n,\gamma)^{122}Sb$	564	2.76
Zn	$^{64}Zn(n,\gamma)^{65}Zn$	1115.4	245

Table 2. Results of the determination of test elements in biological sample NBS SRM-1571 (Orchad leaves) by INAA.

Elements	Certified value (SRM)	Results of experiments (Ug/g)
Se	0.080 ± 0.010	0.067 ± 0.015
Hg*	0.155 ± 0.015	0.135 ± 0.060
Cr	2.3	2.370 ± 0.340
As	14	11.97 ± 3.470
Sb	2.9	4.43 ± 0.840
Zn	25	24.11 ± 8.9

*: Determined by INAA and radiochemical separation

Table 3. Concentration range and x ± S.D of As, Cr, Hg, Sb, Se and Zn in seafood in Ug/g wet weight samples determined by Neutron Activation Analysis.

Name of sample		As*	Cr*	Hg**	Sb*	Se*	Zn*
Mackerel,	Range	0.13-0.71	0.03-0.07	0.05-0.10	<0.01	0.13-0.20	0.90-3.60
(Restrelliger sp)	Mean	0.42±0.29	0.05±0.02	0.07±0.02		0.17±0.04	2.25±1.35
Pompret	Range	0.12-0.39	0.02-0.09	0.01-0.10	<0.01	0.08-0.33	1.25-2.28
(Pampus chinansi)	Mean	0.24±0.13	0.05±0.02	0.05±0.04		0.20±0.12	1.76±0.51
Shrimp	Range	0.16-0.45	0.02-0.06	0.03-0.06	<0.01	0.04-0.13	1.04-3.45
(Penaeus sp)	Mean	0.30±0.13	0.04±0.02	0.04±0.01		0.09±0.05	2.28±1.26
Kakap	Range	0.31-0.77	0.09-0.18	0.03-0.11	<0.01	0.09-0.21	1.95-3.46
(Lates cafcarites)	Mean	0.53±0.23	0.12±0.06	0.07±0.04		0.16±0.70	2.73±0.75
Shellfish	Range	0.07-1.70	0.03-0.13	0.01-0.05	0.00-0.03	0.05-0.14	0.91-9.68
(Anadara indica)	Mean	1.03±0.77	0.08±0.04	0.02±0.01	0.02±0.01	0.09±0.03	3.74±3.09
Shellfish	Range	0.96-2.61	0.13-0.23	0.02-0.16	0.03-0.07	0.16-0.25	0.77-4.03
(Cardium unedo)	Mean	1.8 ±0.81	0.19±0.03	0.06±0.03	0.04±0.02	0.22±0.03	3.69±0.95
Shellfish	Range	0.05-1.70	0.03-0.13	0.01-0.08	0.01-0.03	0.12-0.18	0.91-14.1
(Anadara granosa)	Mean	0.96±0.60	0.08±0.04	0.03±0.01	0.02±0.01	0.12±0.02	7.18±3.61

* = Instrumental Neutron Activation Analysis (INAA)

** = Radiochemical Neutron Activation Analysis (RNAA)

Table 4. Concentration range and X ± S.D, of Cd, Cu, and Pb in seafood in Ug/g wet weigh samples determined by Atomic Absorption spectrophotometer

Name of sample		Cd	Cu	Pb
Mackerel (Rastrelliger sp)	Range	<0.01	0.05 - 0.11	0.01 - 0.07
	Mean		0.08 ± 0.02	0.03 ± 0.03
Pompret (Pampus chinansi)	Range	0.01 - 0.18	ud	0.01 - 0.08
	Mean	0.02 ± 0.004		0.04 ± 0.03
Shrimp (Penaeus sp)	Range	0.05 - 0.10	0.10 - 0.85	0.47 - 0.85
	Mean	0.08 ± 0.03	0.55 ± 0.33	0.61 ± 0.18
Kakap (Lates calcarites)	Range	0.01 - 0.10	0.05 - 0.18	0.50 - 0.71
	Mean	0.07 ± 0.06	0.11 ± 0.06	0.61 ± 0.11
Shellfish (Anadara indica)	Range	0.06 - 0.12	0.79 - 1.17	0.06 - 0.32
	Mean	0.09 ± 0.02	0.99 ± 0.16	0.17 ± 0.11
Shellfish (Cardium unedo)	Range	0.24 - 0.81	0.44 - 0.93	0.16 - 0.36
	Mean	0.40 ± 0.27	0.75 ± 0.22	0.24 ± 0.10
Shellfish (Anadara granosa)	Range	0.21 - 0.37	0.56 - 0.79	0.09 - 0.35
	Mean	0.28 ± 0.01	0.69 ± 0.12	0.24 ± 0.13

ud = undetectable

Tabel 5. The maximum permissible concentration (MPC) of As, Cd, Cr, Cu, Hg, Pb, Sb, Se, and Zn, food, rice, fish, vegetables, drinks, and drinking water, the units are mg/kg or mg/l.

Element	Food[1]	Rice[2]	Fish	Vegetables	Drinks[3]	Drinking Water
As	1		3	1	0.1-0.2	0.05
Cd	1	1	-	-	-	0.005-0.01
Cr	-		-	-	-	5.05
Hg	0.03		0.4-1.0	0.5	-	0.01
Pb	1-5		10	2-2.5	0.2-1	0.05
Se	2		-	-	-	0.01
Cu	20-50		50	50	2-5	0.1
Sb	1		-	-	0.15	-
Zn	40-50		-	40-50	5	0.05

The source mainly from REILLY, C.(8)

1. Food in general, excluding fish, vegetables and beverages.
2. Guideline for Cd in Japan (1 mg/kg for unpolished rice and 0.9 mg/kg for polished rice).
3. Drinks in general, excluding drinking water.