TRACE ELEMENTS IN SQUID DETERMINED BY COUPLED PLASMA MASS SPECTROMETRY

CÁC NGUYÊN TỐ VẾT TRONG CON MỰC ĐƯỢC XÁC ĐỊNH BẰNG KHỐI PHỔ KẾ PLASMA

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ABSTRACT

Trace elements in the edible parts, and in the internal organs of squid collected from Binh Thuan Sea were analyzed, using inductively coupled plasma mass spectrometry (ICP-MS). The analyzed data on squid samples show the difference in the concentrations of trace elements in the edible parts and internal organs of squid. The distribution of trace elements including bio-essential elements such as Cu, Zn, Se, Cr and Fe and non-essential elements such as Cd, Ag, Th, U and rare earth elements (REE) in squid samples provided the evidence on the role of the squid on the ocean bioaccumulation and detoxification processes. The accuracy of the method was checked by the analysis of standard samples and the analyzed results obtained were in good agreement with those in the certified materials. From results obtained, it could be concluded that squid can be used as a bio-indicator for monitoring the marine environment.

Keywords: *Trace elements, Squid, Sea environment, Bio-indicator, ICP-MS analysis*

TÓM TẮT

Các nguyên tố vết trong phần ăn được và trong cơ quan nội tạng của con mực đánh bắt ở vùng biển Bình Thuận được phân tích bằng khối phổ kế plasma (ICP-MS). Các số liệu phân tích thể hiện sự khác biệt về nồng độ các nguyên tố vết trong phần nội tạng và phần ăn được của con mực. Sự phân bố các nguyên tố vết bao gồm những nguyên tố có chức năng sinh học như Cu, Zn, Se, Cr và Fe và những nguyên tố không có chức năng sinh học như Cd, Ag, Th, U và các nguyên tố đất hiếm (REE) trong con mực đã cung cấp bằng chứng vai trò của con mực trong quá trình tự đào thải và tích lũy sinh học của đại dương. Độ chính xác của phương pháp phân tích đã được kiểm tra bằng cách phân tích các mẫu chuẩn và kết quả phân tích thu được rất phù hợp với các giá trị đã được công nhận trong các mẫu chuẩn. Từ kết quả thu được, có thể kết luận rằng con mực là một chỉ thị sinh học cho quan trắc môi trường biển.

Từ khóa: *Các nguyên tố vết, Con mực, Môi trường biển, Chỉ thị sinh học, Phân tích ICP-MS*

1. INTRODUCTION

The accumulation of organic and inorganic pollutants in oceanic organisms is a fairly well known and often used as a bio-indicator for monitoring the quality of the marine environment. For example, the accumulation of contaminants in bivalves such as mussels, oysters, and animals as dolphins, whales via their filtering – feeding and / or ingestion has been reported, providing better understanding on the distribution of contaminants in sediments and seawater [1, 2].

Squid, *Cephalopoda*, is one of the important organisms in marine food chains. Squid has been studied as seawater bio-indicator for several characteristics in its life cycle [3]. The concentration of a certain trace element in squid, if known, would provide a useful annual record in the sea environment [4]. However, one of the challenges when analyzing samples for trace

elements from squid is that the concentration is often at very low levels, ranging from ppb to ppm depending on elements [5]. Thus, it requires an analytical method with high sensitivity and accuracy, such as Atomic Absorption Spectrometry (AAS), X-ray Fluorescence Spectrometry (XFS), Neutron Activation Analysis (NAA), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Among these, ICP-MS with its wide dynamic range and multi-element capability is considered as the most valuable instrument method for trace element analysis [6]. this report presents the analysis using ICP-MS and the concentrations of multiple metal elements including V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Ag, Cd, Cs, Ba, Th, U and Rare Earth Element (REE) in the internal organs and edible parts of squid collected from Binh Thuan Sea during 2013 - 2014. These data would provide valuable information for monitoring the sea environment in this region.

2. MATERIALS AND METHOD

2.1. Sample pretreatment

Annual squid season from Binh Thuan Sea is normally from February to the end of April. The fresh squid samples, approximately 2.0 - 3.0 kg each, were purchased in May, 2013 and May, 2014 in the local market and delivered to laboratory within two days. Squid samples were stored in a plastic container containing ice until used to prevent sample degradation. The internal organs (such as intestine and liver) of the fresh squid were taken and ashed at 450°C. The edible parts of squid samples were dried at 105°C. The ashed internal organs samples and the dried edible part samples were pulverized and homogenized, then stored in the closed containers. Four samples were prepared. Two are from the edible parts, labelled as TS-2 and TS-4; and two are from the internal organs, labelled as TS-1 and TS-3.

2.2. Standard solutions of trace elements

The SPEX multi-element and single element solutions were used as stock standard solutions for the preparation of diluted standard solutions used in this analysis. For calibration, each standard solution (1ppt, 5ppt, 100ppt, 1ppb, 10ppb, 100ppb) was prepared by diluting the stock standard solutions with 1M HNO_3. The SPEX standard solutions at a concentration of 25 ppb were used for the measurement of REE elements. Certified Reference Materials (DOLT-2 (Dogfish liver), DORM-2 (Dogfish Muscle), TORT-2 (Lobster Hepatopancreas) and GBW 07605 (tea leaf) were used for revalidating the accuracy of the ICP-ICP-MS system.

2.3. Microwave digestion of the liquid samples (the internal organs and the edible parts)

Approximately 0.5 gram of each squid sample was digested with 10 ml super high purity (TAMAPURE-AA-100) HNO_3 and 0.5ml H_2O_2 using Milestone MLS-1200 MEGA microwave digestion system. Digested sample solution was diluted to an appropriate volume with 1M HNO_3. Two Quadruple ICP-MS systems, PMS2000 and PMS4500 (YOKOGAWA, Japan) are used for measurement.

3. RESULTS AND DISCUSSION

3.1. Trace elements

The analyzed data for trace elements including U, Th, Cu, Cd, Zn, Mn, Co, Ni, Sr, V, Cr and Ag in the edible and internal organs of squid are presented in Table 1. As shown in Table 1, the internal organs contain high concentration of Cr, Fe, Cu, Zn, Ag and Cd; while the edible parts contain high concentration of Fe, Cu, Zn, Sr, and Ba. Ba and Sr are the two elements found to have much higher concentration in the edible parts than in the internal organs. Furthermore, the high accumulation of Sr in squid should be concerned since it could relate to the contamination of the ^{90}Sr, a radio-nuclide released from nuclear explosions. Elements such as Cs, Th, U, Se, Co and V are relatively at low concentration in both internal organs and edible parts samples. The concentrations of Th in the internal organs of squid are quite low, at 0.0002 ppm; but the concentration of

U, at 0.02ppm, is significant enough to raise some alert for environmental monitoring. These metals were found only in the internal organs of squid. This suggests that U and Th were taken from the surrounding sea water by the feeding process. Based on biological activity, the elements analyzed in this study can be divided into three groups: *(i)* the first group is bio-essential metals such as Cu, Zn, Se, Cr and Fe, normally with highest concentrations; *(ii)* the second group is non-essential metals including Cd, Ag, Th and U; and *(iii)* the last group is rare earth elements. The remaining other metals such as Ba and Sr are not listed because their unknown roles in the biological process for squid. Grouping the elements by this way would provide more insight into the overall distribution of their concentrations as well as the related quality of the surrounding water in the squid environment. As noted that these two sets of samples were taken in consecutive years, 2013 and 2014, no significant variation was identified. Although there were only samples from two years, the analysis effort employed in this study would provide a set of continuing data, useful for environmental monitoring purpose.

3.2. Rare earth elements

The results of REE in the edible parts and internal organs of squid are shown in Table 2. In both types of samples, the internal organs and edible parts of squid, the concentrations of Light REE (LREE) (from La to Sm in the periodic table) are higher than the Heavy REE (HREE) (from Dy to Lu in the periodic table). Figures 1 and 2 show the REE distribution in the internal organs and the edible parts of squid, respectively. In general, these distributions are relatively similar regarding the maximum level of elements which has the even atomic number and the minimum level of those which has the odd atomic number. It is noted that the negative anomaly of Ce and Eu in the REE pattern is observed for all analyzed samples. These observations suggest that REE was taken passively by squid from the surrounding seawater.

Table 1. *Results of trace elements in the edible parts (TS-2 and TS-4) and internal organs (TS-1 and TS-3) of squid*

Element	TS-1 (ppm)	TS-2 (ppm)	TS-3 (ppm)	TS-4 (ppm)
V	0.06 ± 0.01	0.039 ± 0.01	0.07 ± 0.01	0.037 ± 0.01?
Cr	1.11 ± 0.15	1.34 ± 0.07	1.25 ± 0.03	0.071 ± 0.023
Mn	0.72 ± 0.07	1.08 ± 0.11	0.82 ± 0.03	1.17 ± 0.16
Fe	37.6 ± 1.8	1.44 ± 0.12	36.8 ± 1.9	1.38 ± 0.02
Co	0.08 ± 0.01	0.019 ± 0.002	0.08 ± 0.02	0.017 ± 0.013
Ni	0.13 ± 0.03	0.22 ± 0.02	0.13 ± 0.02	0.20 ± 0.05
Cu	107 ± 2.4	12.3 ± 1.2	106 ± 2.1	12.3 ± 1.4
Zn	32.8 ±1.2	60.7 ± 3.5	31.7 ± 1.1	62.4 ± 3.8
Ga		0.375 ± 0.041		0.354 ± 0.051
Rb	1.15 ± 0.27	6.09 ± 0.57	1.24 ± 0.19	6.32 ± 0.38
Sr	0.82 ± 0.08	9.91 ± 1.25	0.86 ± 0.07	10.2 ± 0.9
Ag	1.10 ± 0.04	0.041 ± 0.01	1.29 ± 0.03	0.03 ± 0.01
Cd	6.98 ± 0.73	0.28 ± 0.05	7.36 ± 0.80	0.21 ± 0.04
Cs	0.003 ± 0.010	0.04 ± 0.01	0.004 ± 0.001	0.03 ± 0.01
Ba	0.005 ± 0.001	3.69 ± 0.73	0.04 ± 0.010	3.67 ± 0.62
Se	0.034 ± 0.001			
Th	0.0002 ± 0.0001		0.042 ± 0.01	
U	0.019 ± 0.003		0.020 ± 0.004	

Table 2. *Results of REE in the internal organs of squid*

Element	TS-1 (ppm) internal organs	TS-2 (ppm) Edible parts	TS-3 (ppm) Internal organs	TS-4 (ppm) Edible parts
La	2.14 ± 0.23	0.88 ± 0.05	2.22 ± 0.17	0.8 7± 0.06
Ce	1.62 ± 0.12	0.61 ± 0.04	1.63 ± 0.23	0.58 ± 0.04
Pr	0.18 ± 0.03	0.13 ± 0.12	0.19 ± 0.04	0.12 ± 0.02
Nd	1.50 ± 0.32	1.21 ± 0.45	1.49 ± 0.06	1.02 ± 0.03
Sm	0.32 ± 0.11	0.79 ± 0.06	0.32 ± 0.02	0.699 ± 0.04
Eu	0.05 ± 0.01	0.16 ± 0.02	0.07 ± 0.01	0.145 ± 0.012
Gd	0.51 ± 0.08	0.70 ± 0.06	0.42 ± 0.05	0.678 ± 0.035
Tb	0.05 ± 0.01	0.17 ± 0.04	0.05 ± 0.01	0.16 7± 0.013
Dy	0.41 ± 0.05	0.83 ± 0.07	0.31 ± 0.04	0.83 ± 0.04
Ho	0.08 ± 0.01	0.12 ± 0.01	0.07 ± 0.01	0.100 ± 0.011
Er	0.07 ± 0.01	0.48 ± 0.04	0.05 ± 0.01	0.43 ± 0.06
Tm	0.003 ± 0.001	0.12 ± 0.03	0.023 ± 0.005	0.111 ± 0.015
Yb	0.58 ± 0.02	0.71 ± 0.08	0.697 ± 0.04	0.70 ± 0.02
Lu	0.10 ± 0.01	0.25 ± 0.04	0.10 ± 0.06	0.200 ± 0.010

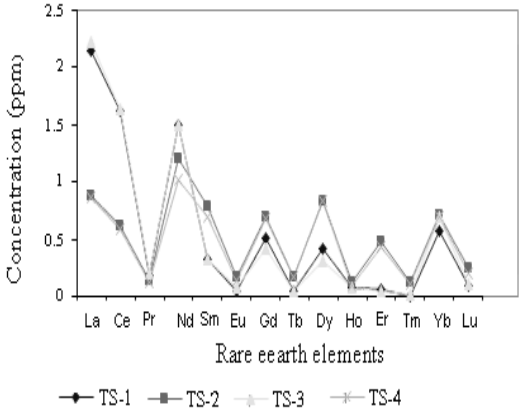

Fig.1*. Distribution of rare earth elements in the squid samples*

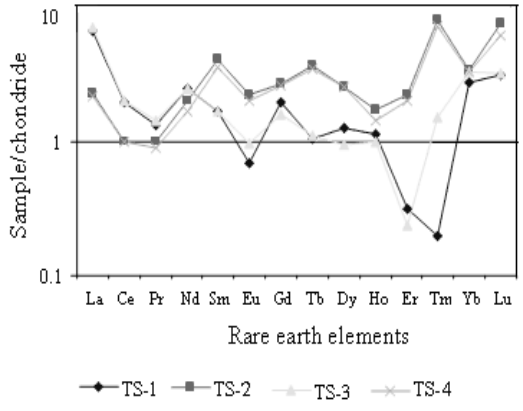

Fig.2. *REE pattern in the edible part and internal organs of squid*

3.3. Accuracy of the method

The accuracy of the ICP-MS method used in this study was evaluated by using the certified reference materials: NRC DOLT-2 (Dogfish liver), NRC TORT-2 (Lodster Hepeatopancreas), NRC DORM-2 (Dogfish Muscle) for trace metals and GBW 07605 for REE concentration only. The contents of trace elements and REE in these three certified materials are presented in the Tables 3, 4, and 5 respectively. Figure 3 shows the deviation (%) of analytical data of trace elements obtained by ICP-MS and the certified values in the referent materials. It indicates that the ICP-MS method, in general, provided data in good agreement with those in the certified materials. Percentage deviation (%) of the ICP-MS results for the trace elements in all referent samples is within 2 - 10 % of the provided data. There are two exceptions, namely silver (Ag) in sample DOLT-2 at 186% and selenium (Se) in TORT-2 at - 65.2 %. The values of Se obtained in this study were lower than the certified values, probably because of the process of the sample decomposition. It is noted that, the percentage deviation also varies from samples to samples. For example, Cu, Co, Mn in DOLT-2 sample is at -8.3,

-2.1, -18.8 % deviation, respectively; and this level in TOLT-2 sample is at -8.3, -1.6, -5.8, respectively. The results obtained of REE in GBW- 07605 are shown in Table 4. There are only several elements having certified values such as La, Ce, Sm, Eu and Yb that can be compared with ICP-MS results.

Table 3. *Results of trace elements in DORM-2 sample determined*

Element	Our results (ppm)	Reference value (ppm)	Deviation (%)
V	35.8	34.7	3.0
Cr	4.16	3.66	13.6
Mn	0.159	0.18	-4.2
Fe	136	142	16.6
Co	0.21	0.20	1.0
Ni	19.6	19.4	14.1
Cu	2.67	2.34	4.6
Zn	26.8	25.6	-4.8
Ag	0.039	0.041	-4.8
Cd	0.039	ND	
Ga	0.24	ND	
Sr	2.36	ND	
Cs	0.29	ND	
Ba	2.51	ND	

Table 4. *Results of trace elements in TORT-2 and DOLT-2 samples (ND: Non determination)*

Element	TORT-2 (ppm)			DOLT-2 (ppm)		
	Our result	Certified value	Deviation (%)	Our result	Certified value	Deviation (%)
V	1.66	1.64	1.2	0.32	0.37	-13.5
Cr	0.67	0.77	-12.9	0.32	0.37	-13.5
Mn	12.8	13.6	-5.8	5.58	6.88	-18.8
Fe	110	105	4.7	986	1103	-10.6
Co	0.49	0.51	-3.9	0.22	0.24	-8.3
Ni	2.21	2.50	-11.6	0.20	0.20	0
Cu	104	106	-1.6	84.0	85.8	-2.1
Zn	177	180	-1.16	84.0	85.5	-2.1
Se	1.94	5.63	-65.5	1.60	6.06	-73.6
Sr	44.5	45.2	-1.5	1.72	ND	
Ag		ND		19.7	0.60	186
Cd	26.2	26.7	-1.8	12.5	20.8	-4.0

Table 5. *Results of REE in GBW sample determined by ICP-MS (The values in bracket are non-certified value)*

Element	Our result (ppm)	Reference value (ppm)	Deviation (%)
La	0.63	0.60	3.0
Ce	1.0	1.0	
Pr	0.12	(0.12)	
Nd	0.46	(0.44)	
Sm	0.084	0.085	-1.1
Eu	0.020	0.018	11
Gd	0.073	(0.093)	
Tb	0.011	0.011	
Dy	0.066	(0.074)	
Ho	0.012	(0.019)	
Er	0.035		
Tm	0.005		
Yb	0.039	0.044	-10
Lu	0.005	(0.007)	

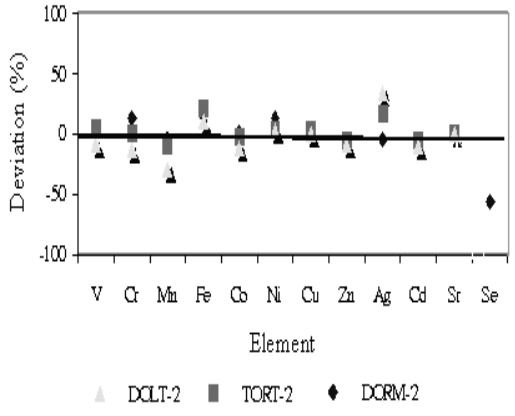

Fig. 3. *Deviation between values of trace elements and certified values of referent materials*

4. CONCLUSION

From the comparison analysis in this work, it can be concluded that the data of trace and rare earth elements in the internal organs and the edible parts of squid obtained by ICP-MS technique are reliable. This provides important information on the distribution of the trace metal elements and REE in squid which can be used as a bio-indicator for the marine environment. This study demonstrates that a powerful analytical tool like ICP-MS can be used to analyze the very low level of trace elements in species such as squid. The data as such could significantly contribute to a better understanding of the yearly fluctuation of trace metals in the seawater environment.

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