SPECIATION OF TRACE METALS IN SEDIMENT: MODIFIED TESSIER SEQUENTIAL EXTRACTION SCHEME VERSUS BCR SCHEME

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ABSTRACT

Modified Tessier sequential chemical extraction scheme connected with ICP-MS was compared with the European Community Bureau of Reference (BCR) procedure for extraction of As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V and Zn for sediment samples collected from the coast of Sabah

and Sarawak, Malaysia. Reliability of the obtained data was achieved by calculating the recovery of the fractions results for the two sequential extraction methods. The distribution of the concentration of the elements through the chemical fractions showed that no significant differences between the two procedures for all elements under study with an exception of Zn element. According to the recovery calculation, both techniques are an equally competitive procedure for extraction of As, Cu, V, Se, Co and Pb. BCR is a superior technique for Mn and Fe over the modified Tessier procedure, while for Cr, Ni and Zn element the later one is the preferable method.

Key Words: Sequential extraction, Trace elements, Sediment

1. Introduction

Total metal concentration is a poor indicator of metal bioavailability, mobility and toxicity, because these properties depend on the chemical association of the different species of the sample (Hullebusch, Utomo et al. 2005). In fact, to predict the fate and bioavailability of trace metals during chemical digestion, there is a need to understand metals speciation. The speciation of heavy metals can be determined with the selective sequential chemical extraction analysis, consisting of several extraction steps depend on the use of different chemical reagents and conditions (Naji, Ismail et al. 2010), (Cuong and Obbard 2006). Therefore, sequential extraction provides information about the identification of the main binding sites, i.e. the strength of metal binding to the particulates and the phase associations of trace elements in sediment(Yuan, Shi et al. 2004). This contributes for a better understanding of the geochemical processes governing heavy metal mobilization and their potential risks. However, no selective extractants as well the

possible redistribution of heavy metals among extraction phases are the main disadvantages in using sequential extraction (Naji, Ismail et al. 2010). Despite these disadvantages, sequential extraction procedures are still widely used for the evaluation of availability and mobility of trace metals in solid matrixes.

Various sequential extraction schemes have been established and largely applied to determine which chemical forms of the trace metals are present (Tessier et al., 1979; Conesa et al., 2008; Saffari et al., 2009). The main differences between them are the number of fractions obtained using different reagents and extraction conditions, based on the purpose of the extraction ((Fanfani et al., 1997; Go´mez-Ariza et al., 1999; Li and Thornton, 2001) . These schemes have been criticized due to many reasons including; lack of consistency in the procedure; time needed to move from one step to the other; lack of selectivity of extracting reagents and lack of quality control. Moreover, the significant influence of operational parameters such as pH, temperature, the concentration of reagents, time of extraction, the ratio of solid mass to volume of extractants and stirring system are also factors stand as weaknesses of these schemes. However, these procedures are still used in the assessment of sediment and soil-associated metals in environmental studies and ultimately suggest information about their geochemical association help to predict the mobility and bioavailability of metals to living organisms (Kartal, AydIn et al. 2006), (Ngiam and Lim 2001).

There have been many sequential extraction schemes developed in the last four decades (Leleyter and Probst, 1999; Outola et al., 2009; Schultz et al., 1998; Tessier et al., 1979). Tessier scheme (Tessier et al., 1979) and modified Tessier scheme (Osuna et al., 2004) are among the most famous sequential extraction schemes applied to fractionate various environmental samples. The original Tessier method is based on three fractions, i.e. exchangeable, carbonates,

and organic matter. Another popular sequential extraction scheme is Schultz et. al. (1998), and it is based on five fractions, exchangeable, bound to organic matter, carbonates, associated with Fe/Mn oxides and residual. In 1987, the Commission of the European Communities Bureau of Reference (BCR), now the Standards, Measurement and Testing Program, initiated a programme to match the methodology used in different schemes (Ure et al., 1993). The BCR scheme extracts metals into three fractions, i.e. exchangeable, Fe and Mn oxides, organic matter and sulfides fraction.

These include, for example those developed by Tessier and BCR methods(Tessier, Campbell et al. 1979, Salomons and FÃ¶rstner 1984), (Nemati, Bakar et al. 2011).

In this study, modifications in Tessier sequential extraction scheme were carried out by using NH4CH3COO in the exchangeable fraction to minimize the matrix effect caused by $MgCl_2$ (Filgueiras, Lavilla et al. 2002).Moreover, The concentration of $NH_2OH\cdot HCl$ was raised up to 0.1M to increase the extractability in Fe-Mn oxide fraction. This new modified scheme was compared with BCR protocol developed by Commission of the Reference European Communities Bureau.

2. Materials and Methods

2.1 Samples Collection

Sediment samples were collected from the coast of Sabah and Sarawak, within the 1º45.93´-7º24.68´ N latitude and 109 º 49.20´- 119 º 03.78´ E longitudes. The most important economic activity in Sabah and Sarawak States which may cause pollution is oil and gas industry. 26 sampling sites were selected at various distances (between 0.7-113 m) from the coast. The stations were labelled as SB series for Sabah coast and as SR series for Sarawak coast. The

samples were stored in polyethylene containers at -4°C. Then the samples were dried in a thermal oven at 50°C and homogenized by powdering in an agate mortar. The homogenized samples were sieved through 0.2 mm nylon grid sieve and heated at 50°C until constant weight was established. The moisture content was measured for the prepared samples using AND MX-50 moisture analyzer and found to be $\leq 5\%$. The pH of the samples was also detected by dissolving the sediment samples in deionized water with a ratio of sediment to water of 1 to 5. The pH was measured after 10 minutes and found to be 6.5-7.5.

2.2 Sequential Extraction Procedures:

Accurately, 1.00g of the dry sample was weighed and then the BCR and modified Tessier schemes were followed as shown in Tables 1 and 2, the extraction was carried out using 100 ml centrifuge tube. At the end of each step the tube was centrifuged for 10 mints at 4000 rpm and then the solution was decanted into 50 ml polyethylene container, then 10 ml of deionized water was added to the residue and centrifuged for 5 mints and the solution decanted. The solution completed to 50 ml and then stored at -8∘C until analysis. The residue was taken to the next step. Blank samples were prepared following the above procedures.

Table 1: Operation Conditions in BCR sequential extraction procedure

Fraction	Extracting agent	Extraction conditions	
		Shaking time[a]	Temperature
F1. Exchangeable + water and acid soluble	40mLCH3COOH (0.11 M, pH = 7)	16 h	20 ∘C
F2. Iron and manganese oxides	40mL NH2OH–HCl (0.1 M, pH = 2)	16 h	20 ∘C
F3. Organic matter and sulfides	10mL H2O2 (30%, pH = 2) and then 50mL CH3COONH4 (1 M, pH = 2)	1, 2, 16 h	20, 85, 20 ∘C
F4. Residual	8ml HNO3+4ml HF (Conc)and then 10ml H2O2	16, 8 h	20, 250∘C

a Shaking was applied at 30 rpm.

Table 2: Operation conditions in the modified Tessier sequential extraction procedure

Fraction	Extracting agent	Extraction conditions Shaking time[a]	Temperature
F1. Exchangeable	10mL NH4CH3COO (1 M, pH = 7)	1 h	20 ∘C
F2. Carbonates	10mLCH3COOH(1M, pH = 5.5)	1h	20 ∘C
F3. Iron and manganese oxides	20mL NH2OH–HCl (0.1 M, pH = 2)	5 h	20 ∘C
F4. Organic matter and sulfides	5mL H2O2 (30%, pH = 2) and then 10mL CH3COONH4 (1 M)	3, 16 h	85, 20 ∘C
F5. Residual	8ml HNO3+4ml HF (Conc)and then 10ml H2O2	16, 8 h	20, 250∘C

a Shaking was applied at150 rpm.

2.3 Sample Analysis:

Concentrations of metal in the prepared extracts obtained after each step were determined using PE SCIEX ELAN 6000 inductively coupled plasma mass spectroscopy ICP/MS system atomic absorption spectrometer. Instrument settings were applied as recommended in the manufacturer's manual and all readings of the absorbance were made in triplicate.

3. Results and discussion:

3.1 Reliability of the results:

Reliability of the obtained data was achieved by calculating the recovery of the fractions results of the tow sequential extraction procedures by sum of the amounts of the metals removed M_s in each step of the procedures with the results of the pseudo-total digestion M_t as shown in the following equation (Hullebusch, Utomo et al. 2005) :

$$Recovery\ (\%) = \frac{\sum M_s}{M_t} \times 100 \tag{1}$$

Tables 3 and 4 show the reliability for BCR procedure and modified Tessier procedure respectively.

Table 3 The reliability for the BCR procedure

Elements	$\sum M_s$	M_t	Recovery (%)
As	17.44	18.80	92.74
Cd	1.89	1.40	134.72
Co	15.10	13.40	112.67
Cr	87.49	68.90	126.98
Cu	34.69	37.20	93.26
Fe	23157.33	26285.90	88.10
Mn	452.87	483.20	93.72
Ni	62.48	51.80	120.62
Pb	37.25	40.90	91.08
Se	3.44	3.60	95.55
V	107.57	125.20	85.92
Zn	252.10	320.40	78.68

Table 4 The reliability for the modified Tessier procedure

Elements	$\sum M_s$	M_t	Recovery (%)
As	18.10	18.80	96.28
Cd	0.90	1.40	64.29
Co	14.76	13.40	110.15
Cr	67.80	68.90	98.40
Cu	41.20	37.20	110.75
Fe	16929.00	26285.90	64.40
Mn	578.80	483.20	119.78
Ni	56.48	51.80	109.03
Pb	41.13	40.90	100.56
Se	3.19	3.60	88.56
V	136.30	125.20	108.87
Zn	335.80	320.40	104.81

From Tables 3 and 4 the following remarks can be shown. From Table 3, the BCR procedure shows acceptable recovery (between 90 - 110%) for all elements and to some extend Co, Fe and V (113, 88 and 86%), respectively. However, some elements indicate either over recovery value

Cd (134.7%) and Cr (127%) or poor recovery, Zn (78.8%). While for the modified Tessier procedure, as in Table 4, the elements As, Co, Cr, Cu, Ni, Pb, V and Zn show acceptable recovery (between 90 - 110%) and to some extend Mn and Se (119% and 88%), respectively. While elements Cd and Fe show poor recovery values (64%). These results indicate that, in both sequential extraction schemes, for most elements, the sums of the fractions are in good agreement with the total concentrations, and therefore the procedures are reliable and repeatable.

3.2 Distribution of elements in different chemical fractions:

To compare between modified Tessier and BCR schemes which were applied in this work, the tow side t-test was applied using equation (2) and (3). The result was tabulated in Table 5.

$$t_{cal} = \frac{(\bar{x}_1 - \bar{x}_2)}{\sqrt{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)}} \qquad (2)$$

Where:

$\bar{x}_1$ = mean of the first method.

$\bar{x}_2$ = mean of the second method.

s_1^2 and s_2^2 = respective variances.

n_1 and n_2 = respective number of measurements.

$$df = \frac{\left(\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}\right)^2}{\frac{(s_1^2/n_1)^2}{(n_1 - 1)} + \frac{(s_2^2/n_2)^2}{(n_2 - 1)}} \qquad (3)$$

When the $t_{cal} > t_{\alpha/2}$, it can be concluded that the difference between the means obtained by the two methods is statistically significant. If the $t_{cal} \leq t_{\alpha/2}$, it can be concluded that there is no significant difference between the two methods.

Table 5 Comparison between modified Tessier and BCR sequential extraction schemes

Elements	Modifide Tessier		BCR		t (cal)	df
	Mean	SD	Mean	SD		
As						
	18.10	481.80	17.44	47.6	0.01	60.15
Cd						
	0.90	6.70	1.89	3.5	-1.01	88.97
Co						
	14.76	30.40	15.10	18	-0.07	95.84
Cr						
	67.80	178.10	87.49	322.2	-0.41	91.98
Cu						
	41.20	215.40	34.69	40.6	0.23	63.19
Fe						
	16.93	35.65	23.16	15.8791	-1.24	81.52
Mn						
	578.80	1405.50	452.87	392.7	0.67	68.16
Ni						
	56.48	132.50	62.48	90	-0.29	103.89
Pb						
	41.13	90.40	37.25	59.4	0.28	101.94
Se						
	3.19	15.00	3.44	6.8	-0.12	82.27
V						
	136.30	149.00	107.57	138.8	1.09	117.41
Zn						
	335.80	317.10	252.10	208.5	1.71	101.98

From Table 5 and the table of values for the two-sided t-distribution, it can be observed that in all elements concentrations there is no significant difference between the two procedures except for Zn.

Figures 3 and 4 showed the distribution of the elements under study over different chemical fractions for BCR and modified Tessier scheme, respectively.

From these figures, the following remarks can be conducted: As most of the element concentration associate with a residual fraction (74% and 58%) for BCR and modified Tessier

schemes respectively. Also, Cu and V show similar behaviour in the tow procedures (67% and 59% for Cu and 51% and 71% for V) in the tow procedures respectively. The chemistry of Cu shows that the element predominately bound as sulphide and more strongly bounded with sediment crystals. A significant amount of Cu in modified Tessier procedure associated with the organic fraction (21%), in contrast only (13%) of Cu associated with this fraction in BCR procedure. This can be a point of difference between the two procedures. The differences are in the extraction conditions used in the two procedures, etc the ability of chemical reagents used in each procedure to affect elements more or less. (Kot and Namiesnik 2000). Fe show 71% and 58% associated with Fe-Mn oxide fraction for BCR and modified Tessier procedures respectively, but 28% of the element extracted in Carbonate and water-soluble fraction with a negligible amount in the organic and residual fractions when BCR was applied. However, in the modified Tessier (18% and13%) of Fe were extracted in organic and residual fractions respectively, with only (9%) in the carbonate fraction. Most of Cd was extracted in the organic fraction (63%) with a significant amount in the residual fraction (36%) when BCR was applied, while (56%) of this element extracted in the residual fraction when modified Tessier procedure was applied with (21%) in Fe-Mn oxide fraction. However, normally Cd extracted in the first two fractions and may be due to the concentration of the extraction agents used in the first two fractions failed to extract Cd from the sediment latex. Mn bounded to the residual fraction (35%) in modified Tessier procedure. Nevertheless, significant amount of Mn appear in the organic fraction, Fe-Mn oxide fraction and Carbonate fraction (15% 25% and 20% respectively), while this element distributes in a different way when BCR procedure was applied, 55% and 42% in carbonate and acid soluble fraction and Fe-Mn oxide fraction respectively. Ni and Zn behave in the same manner 82% and 62% were extracted in the residual fraction for the tow elements

respectively in modified Tessier procedure, and 70% for each extracted in Fe-Mn oxide fraction when BCR procedure was applied. This different in the fraction in which these elements extracted between the two procedures may be due to the extraction condition applied in the tow methods in Fe-Mn oxide fraction (16 h in BCR procedure and 5h in Tessier procedure). For Pb the different in the extracting agents used in the two procedures, CH3COO was used as extracting agent in the tow first fractions in modified Tessier procedure and the first fraction in BCR procedure, but 10 times less than in Tessier procedure) may cause the different appear during element extraction, were 38% of the element extracted in exchangeable fraction in modified Tessier procedure, while 39% of the element extracted in Fe-Mn oxide fraction when BCR procedure was applied. Se 72% of this element extracted in the residual fraction when BCR procedure was applied, with a significant amount in organic-sulphide fraction (29%). In contrary 29% of this element extracted in the exchangeable fraction when modified Tessier scheme was applied. However, a significant amount of the element distributes over all fractions. The behaviour of this element in the tow procedures gives evidence that this element is difficult to extract.
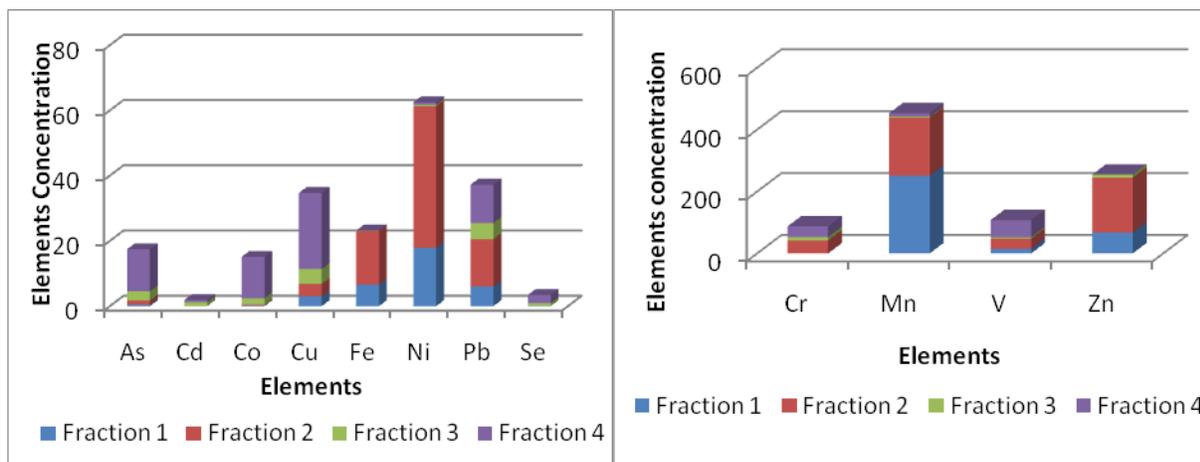
Figure 3 Distribution of the elements through the different chemical fractions using BCR scheme
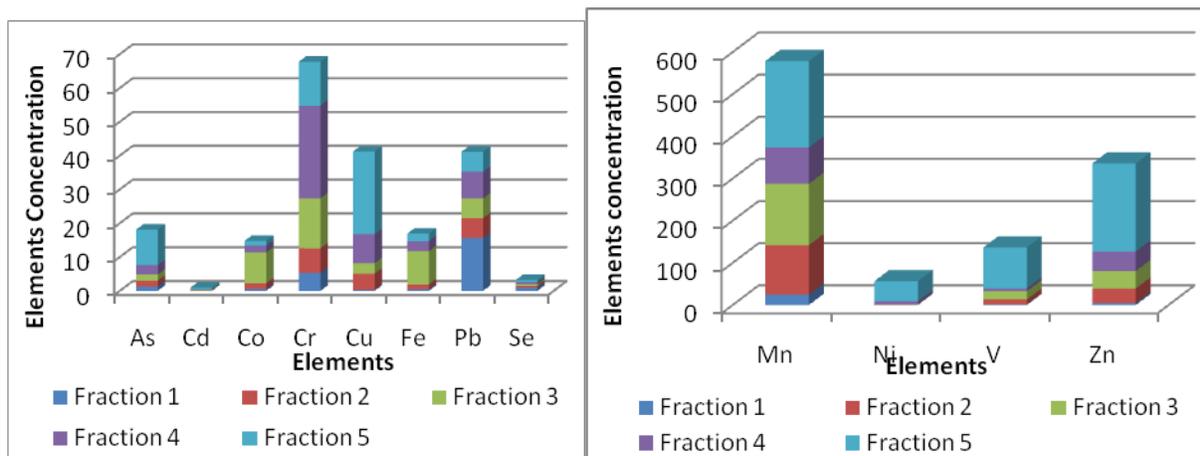
Figure 4 Distribution of the elements in the different chemical fractions using modified Tessier scheme

4. Conclusion:

Speciation analysis of metal in environmental samples particularly in sediment is important since it will give more information concerning of bioavailability, mobility and chemical form. For this purpose, sequential extraction technique is normally used. In this study, the modified Tessier scheme was compared with BCR protocol. The results indicated that the sum of metals concentrations within all fractions showed no significant different between the two procedures except for Zn. However, regarding the distribution of these metals through the chemical fractions, which depends on the strength of the chemicals used and the reaction condition in the fraction, it was found that the two protocols agree in the distribution of As, Cu, Fe and V but disagree in the distribution of the other elements.

The long steps and the more experimental works required are the limitations of Tessier scheme as compared to the BCR protocol. However, the long steps of Tessier are of advantage in that it

will give more information about the distribution of a particular element over the chemical fractions. Hence, if the aim of the study is to quantify the distribution of the particular element through chemical fractions, the BCR procedure is suitable for this purpose. However, if the aim of the study is to quantify the amount of the particular element in an individual fraction, Tessier scheme is recommended.

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