

**DETERMINATION AND ASSESSMENT OF POTENTIAL
MOBILITY OF HEAVY METALS IN SOLID SAMPLES BY
SEQUENTIAL EXTRACTION PROCEDURES (SEP)**

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**THESIS SUBMITTED IN FULFILLMENT OF
THE REQUIREMENT FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY**

**DEPARTMENT OF CHEMISTRY
FACULTY OF SCIENCE
UNIVERSITY OF MALAYA
KUALA LUMPUR**

2011

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Determination and assessment of potential mobility of heavy metals in soil and sediments by Sequential Extraction Procedures (SEP)

Field of Study: **ENVIRONMENTAL ANALYTICAL CHEMISTRY**

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ABSTRAK

Penggunaan kaedah pengekstrakan berurutan bagi fraksinasi logam dalam substrat yang berbeza telah berkembang secara eksponen dalam masa lebih dua dekad yang lalu. Walaupun kaedah ini popular, namun ianya telah dikritik disebabkan pengagihan semula logam oleh reagen yang digunakan. Kerja-kerja dibentangkan di dalam disertasi ini adalah bertujuan untuk menangani masalah yang disebutkan itu melalui, (i) pengekstrakan berurutan Tessier (ii) kaedah pengekstrakan berurutan BCR dan kaedah BCR yang diubahsuai, (iii) perbandingan antara kaedah Tessier dan BCR untuk enapcemar akuakultur. Daripada pengekstrakan berurutan, kebanyakan Cd, Mn dan Pb ditemui dalam bentuk karbonat dan ini menunjukkan kecenderungannya untuk melarut lesap dengan mudah. Kebanyakan Cu dan Zn juga telah diekstrak dalam bentuk oksida. Semua logam (kecuali Cd, Zn dan Cu) telah diekstrak dengan kepekatan lebih tinggi daripada pecahan baki melalui kaedah ini. Dengan membandingkan peratus dapatan kembali, kaedah BCR adalah lebih baik daripada kaedah Tessier. Namun peratus dapatan kembali bagi kedua-dua kaedah boleh diterima. (iv) kajian perbandingan ke atas sistem pencernaan terbuka dibantu oleh kaedah pencernaan gelombang mikro untuk penentuan logam dalam kompos enapcemar udang. Kompos yang dihasilkan daripada enapcemar udang akuakultur bersama kompos bahan-bahan organik (gambut, kulit kayu hancur dan baja) banyak digunakan sebagai medium organik untuk tanaman. Sistem pencernaan terbuka dan pencernaan gelombang mikro telah digunakan dalam penyediaan sampel. Pelbagai kombinasi dan isipadu asid hidrofluorik, nitrik dan hidroklorik dinilai untuk melihat kecekapan kedua-dua kaedah. Dapatan kembali yang terbaik ditemui pada julat antara 95% dan 99% untuk pencernaan gelombang mikro dengan campuran 2 ml HF, 6 ml HNO₃ dan 2 ml HCl.

Kepekatan logam berat daripada stesyen dan kedalaman yang berlainan diperolehi dari Sungai Buloh dan sedimen daripada Selat Melaka di Selangor, Malaysia dengan kaedah

ubahsuai BCR. Keputusan sampel ini menunjukkan pencemaran yang tinggi di stesen 1, 2 dan 3. Kepekatan logam berat telah berkurang dari lapisan atas ke kelapisan yang lebih rendah. Perubahan kepekatan untuk setiap elemen dalam tujuh teras sampel adalah lebih kurang sama. Kita boleh melihat penurunan yang normal dari atas ke bawah.

Kaedah pengekstrakan perubahan urutan (PPT) telah diterima dengan meluas dan digunakan terhadap fraksinasi elemen dalam sampel alam sekitar yang berbeza. Penghad utama untuk prosedur pengekstrakan urutan ini adalah keperluan masa yang lama dan kurang digunakan untuk analisis rutin. Masalah ini telah dikenalpasti dan digantikan dengan prosedur yang konvensional seperti pemanasan gelombang mikro (MV) dengan goncangan ultrasonik (US).

Keputusan pencernaan ultrasonik menunjukkan pada pecahan 1, Cu, Pb dan Zn memberikan dapatan yang tertinggi dalam masa 40 minit, sementara Cd, Cr dan Ni telah didapati masing-masing dalam masa 50, 50 dan 30 minit. Pecahan 2 menunjukkan dapatan paling tinggi bagi Cd, Cr, Pb dan Zn dalam masa 50 minit tetapi Cu dalam masa 40 minit dan Ni 30 minit. Dalam pecahan 3, dapatan yang tertinggi telah didapati untuk Cu, Pb dan Zn dalam masa 50 minit sementara, Cd dan Cr dalam masa 40 minit dan Ni dalam masa 30 minit. Keputusan dari kaedah pencernaan gelombang mikro untuk CRM BCR 701 menunjukkan dapatan sebanyak 98% diperolehi kecuali Zn yang memberikan 96%. Dalam pecahan 2, dapatan yang tertinggi melebihi 95% untuk semua logam telah diperolehi kecuali Pb yang memberikan 94%. Dalam keadaan ini, dapatan yang tertinggi melebihi 97% diperolehi untuk BCR yang diubahsuai. Dalam pecahan 3, dapatan terendah diperolehi untuk Pb dan Zn sama seperti pecahan 2.

Abstract

The use of sequential extraction schemes for fractionation of metals in different substrates has grown exponentially over the past two decades. Despite the popularity of these schemes, they have been criticized for metal redistribution and the reagents used. The work presented in this dissertation is aimed at addressing these problems by, (i) a Tessier sequential extraction (ii) a BCR sequential extraction schemes and modified BCR method, (iii) a comparison between Tessier and BCR method for shrimp aquaculture sludge.

From the sequential extraction, Cd, Mn and Pb were mostly found in exchangeable/carbonate form, showed its susceptibility to be leached easily. Also Cu and Zn were extracted predominantly in oxidizable form. All metal concentrations (except Cd, Zn and Cu) were extracted to be higher in residual fraction in this method. By comparing the percentage of recovery, the BCR method was better than Tessier method. Nevertheless, for both methods the percent of their recoveries were acceptable. (iv) a comparative study on open system digestion and microwave assisted digestion methods for metal determination in shrimp sludge composts was done. The compost made from shrimp aquaculture sludge co-composted with organic materials (peat, crushed bark and manure) was used as an organic growing medium for crop. Open system digestion and microwave assisted digestion procedures were employed in sample preparation. Various combinations and volumes of hydrofluoric, nitric and hydrochloric acids were evaluated for the efficiency of both methods. The best recoveries were found in the range between 95% and 99% for microwave assisted digestion with a mixture of 2 ml of HF, 6 ml of HNO₃ and 2 ml of HCl.

The concentration of heavy metals in different stations and different depths obtained for Sungai Buloh and the straits of Melaka sediments in Selangor, Malaysia by modified BCR method.

The results of these samples showed high contamination in stations 1, 2 and 3. Also the concentration of heavy metals has been decreased from top to lower layers. Variation trends of concentration for each element in the seven sample cores were approximately similar. We can see a normal decreasing from top to down.

Modified sequential extraction method (MSE) is broadly accepted and applied to elemental fractionation in different environmental samples. The main limitations of sequential extraction procedures are that, they are extremely time-consuming, and are less used for routine analysis. This problem has also been noted and is replacing the conventional procedure by other alternatives, such as microwave (MW) heating and ultrasonic (US) shaking.

The results of ultrasound digestion showed in fraction 1, Cu, Pb and Zn showed highest recoveries in 40 min, while, for Cd, Cr and Ni it was obtained in 50, 50 and 30 min respectively. Fraction 2 showed highest recoveries for Cd, Cr, Pb and Zn in 50 min but Cu was found in 40 min and Ni in 30 min. In fraction 3, the highest recoveries have been found for Cu, Pb and Zn in 50 min while, for Cd and Cr found in 40 min and Ni in 30 min.

The results of microwave assisted digestion method for CRM BCR 701 showed all recoveries have been obtained more than 98% except Zn that is about 96 %. In fraction 2, the highest recovery has been found for all metals more than 95 % except Pb about 94 %. In this case highest recoveries have been obtained for modified BCR more than 97 %. In fraction 3 lowest recoveries have been obtained for Pb and Zn same as Fraction 2.

Acknowledgement

First and foremost, I would like to thank my supervisors, Dr. Nor Kartini Abu Bakar and Prof. Mhd. Radzi Bin Abas for their support during the course of this research project. I am especially grateful to them for encouraging, showing great patience and letting me make mistakes. Also I have to thank Dr. Nor Kartini Abu Bakar for supporting me financially as a research assistant. My studies were generously supported by a PhD student fellowship and two postgraduate studies grants (PS189/2008 and PS234/2009) funded by the University of Malaya. I would also like to thank all the staff of Faculty of Science and Department of Chemistry for their patient, encouragement and help. I am also thankful to all my labmates, technical staffs and my friends in Department of Chemistry for their help.

I would like to express my gratitude to everyone who makes it possible for me to complete this thesis.

Last but not least, my warmest thanks and loves to my wife Elham Sobhanzadeh, for her prayers, encouragement and taking care me during this project. She kept me going, and I will forever be grateful for that. My children Armia and Ilia were patient and gracious to let me spend extra hours in the lab. I thank them for the sweet and warm welcome I received each time I got home after a long and tiring day.

Keivan Nemati

December 2011

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List of Abbreviation:

SEP	Sequential Extraction Procedure
BCR	The Community Bureau of Reference
FAAS	Flame Atomic Absorption spectrometry
AAS	Atomic Absorption Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
CRM	Certified Reference Materials
MW	Microwave heating
US	Ultrasonic shaking
GFAAS	Graphite Furnace Atomic Absorption Spectrometry
ETAAS	Electrothermal Atomic Absorption Spectrometry
AES	Atomic Emission Spectrometry
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
IRMM	Institute for Reference Materials and Measurements
U-SEP	Ultrasonic Sequential Extraction Procedure
MAD	Microwave Assisted Digestion
MAD-SEP	Microwave Assisted Sequential Extraction Procedure
SE	Sequential Extraction

HMs	Heavy Metals
MAS	Microwave Assisted System
OD	Open (conventional) Digestion
SEM	Sequential Extraction Modified
C_f	Contamination Factor
RAC	Risk Assessment Code
MSE	Microwave Sequential Extraction
USE	Ultrasonic Sequential Extraction