

 **DETERMINATION OF TRACES OF HEAVY  
ELEMENTS (Pb, Zn, Cu, Cd, Ca and Mg) IN  
HUMAN TEETH FROM KLANG VALLEY AND  
MALACCA USING ICP-AES AND XRF  
TECHNIQUES**

by  
LEE CHEA BENG  
DEPARTMENT OF PHYSICS  
FACULTY OF SCIENCE  
UNIVERSITI MALAYA

DISSERTATION PRESENTED  
FOR  
THE DEGREE OF  
MASTER OF SCIENCE  
UNIVERSITI MALAYA  
KUALA LUMPUR  
(2002)

Perpustakaan Universiti Malaya



A510730784

*To my beloved parents*

## *Acknowledgements*

I am greatly indebted to my supervisors, Associate Professor Dr. Yussof M. Amin and Dr. Jamil Maah, for their continual supports, guidance and encouragement throughout the entire research of this project and the writing of this thesis. I am grateful to them for their valuable advice, inspiration and criticism on all phases of this research work. From them I have gained priceless insight into this research work.

My gratitude also goes to Dr. David Bradley and Mr. L.T.Chew, for their help and valuable advice.

I would like to acknowledge Mr. Suhaimi, Mr. Y.A. Abdulla, Mr. Nordin Ayob, Mr. S.H. Ong, Dr. B.C. Quek, Mr. Y.K. Low, Mr. W.S. Liew, Mr. S.P. Chew and Mr. H.C. Woo, for their support and help.

I would like to express my special gratitude to Dr. Sun and her colleagues in Klinik Pergigian Puchong, for their help to collect the teeth samples. My gratitude also goes to the dentists in Klinik Pergigian Melaka, for their assistance in collecting the teeth samples from Malacca area.

I wish to express my gratefulness to Mr. Eugene Koh, Miss H.Y. Leong, Miss C.Y. Kuek and Mr. C.S. Kuek, for their spiritual supports and concerns.

I would like to dedicate my love and gratitude to my parents, brothers and sisters for their supports and warmest concerns.

Lastly, I thank to Physics Department and the Volt-F grant, for the facilities and fund support to complete this research.

Lee Chea Beng (Jan 2002)

## *Abstract*

X-ray Fluorescence (XRF) and Inductively Coupled Plasma—Atomic Emission Spectrometry (ICP-AES) have been used to study the concentration of heavy metals in human teeth.

XRF technique has been used to determine Pb concentration in human teeth with the excitation source of Tc-99m combined with an XR-100T-CZT detector. The sensitivity of this system to determine the concentration of Pb lower than 800 ppm was constrained by Tc-99m's  $\gamma$ -ray energy of 140.5 keV. High percentage errors in the calculation of average mean of differences for each concentration (from 100 ppm to 800 ppm) were found if compared with the respective background measurements which caused the failure of setting up a standard calibration for this system.

To further determine the expected experimental counts measured by this XRF technique, a simple theoretical model has been developed to calculate the total count for the peak of Pb  $K_{\alpha 1}$ .

ICP-AES was used to determine Pb, Zn, Cd, Cu, Ca and Mg levels in 199 exfoliated human teeth (all of which required extraction for orthodontic reasons) from Klang Valley and Malacca areas. Lead concentrations for these groups were found to range from  $0.713 \pm 0.039 \mu\text{g (g of tooth mass)}^{-1}$  to  $55.512 \pm 8.945 \mu\text{g (g of tooth mass)}^{-1}$ , while for other toxic elements, Cd ranged in between of  $0.0181 \pm$

0.002  $\mu\text{g (g of tooth mass)}^{-1}$  to  $3.9110 \pm 0.072 \mu\text{g (g of tooth mass)}^{-1}$ . Zn and Cu showed the concentration levels from  $26.470 \pm 1.252 \mu\text{g (g of tooth mass)}^{-1}$  to  $296.630 \pm 2.762 \mu\text{g (g of tooth mass)}^{-1}$  and  $0.346 \pm 0.121 \mu\text{g (g of tooth mass)}^{-1}$  to  $54.754 \pm 1.537 \mu\text{g (g of tooth mass)}^{-1}$  respectively. The concentration levels for Ca and Mg were found higher if compared with others, which in between  $8828 \pm 40.551 \mu\text{g (g of tooth mass)}^{-1}$  to  $37238.024 \pm 131.961 \mu\text{g (g of tooth mass)}^{-1}$  and  $1655.792 \pm 4.108 \mu\text{g (g of tooth mass)}^{-1}$  to  $5889.979 \pm 18.851 \mu\text{g (g of tooth mass)}^{-1}$  respectively.

This study also showed the working environment especially for those donors involved in factory activities (welding metal, wire, automobile, refrigerator, aluminium) seemed to provide lead concentrations higher than the median level. This trend was noted especially from the Klang Valley samples.

Besides, the correlation coefficients had been calculated to investigate the two relationships, namely (1) the relationship between the element concentration and the age of donor, (2) the relationship between each element.

The correlation coefficients for Mg and Ca, and Zn and Cd, were calculated at 0.251 and 0.416 respectively. These coefficients were further determined by using a tow-tailed T-test to determine the significant of them at the 1% level. This statistical test showed there is some correlation between Zn and Cd, and Ca and Mg.

The findings also showed that the female samples indicated the concentration of Pb increased as the age of female donors increased.

## *Abstrak*

Kaedah 'X-ray fluorescent' (XRF) dan 'Inductively Coupled Plasma—Atomic Emission Spectrometer' (ICP-AES) telah digunakan untuk mengkaji kepekatan logam berat di dalam gigi manusia.

Teknik XRF telah digunakan untuk menentukur kepekatan plumbum di dalam gigi manusia dengan sumber radioaktif Tc-99m sebagai penguja, dan alat pengesan XR-100T-CZT. Kepekaan sistem ini untuk menentukan kepekatan Pb yang lebih rendah daripada 800 ppm telah dihadkan oleh tenaga sinaran gamma bagi Tc-99m, iaitu 140.5 keV. Peratusan ralat yang tinggi dalam pengiraan bagi "Average Mean of Differences" untuk setiap kepekatan dari 100 ppm ke 800 ppm akan didapati jika dibandingkan dengan pengukuran nilai latar belakang yang terlibat. Oleh kerana itu, eksperimen XRF ini tidak sesuai untuk mendapatkan satu piawai penentukuran bagi sistem ini.

Untuk penentuan kejituan eksperimen ini, satu model kiraan teori telah digunakan. Model kiraan ini telah digunakan untuk menentu jumlah bilangan bagi puncak  $K_{\alpha 1}$ , bagi Pb.

ICP-AES digunakan untuk menentukan kepekatan bagi Pb, Zn, Cd, Cu, Ca dan Mg di dalam gigi manusia, di mana sejumlah 199 sampel telah dikumpul dari kawasan Lembah Klang dan Melaka. Kepekatan Pb bagi dua kawasan ini berada di antara  $0.713 \pm 0.039 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> dan  $55.512 \pm 8.945 \mu\text{g}$  (seunit

jisim dalam gram)<sup>-1</sup>, di mana bagi unsur-unsur yang lain, seperti Cd, kepekataannya berada di antara  $0.0181 \pm 0.002 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> dan  $3.9110 \pm 0.072 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup>. Manakala Zn dan Cu menunjukkan kepekatan masing-masing berada di takat dari  $26.470 \pm 1.252 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> kepada  $296.630 \pm 2.762 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> dan dari  $0.346 \pm 0.121 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> kepada  $54.754 \pm 1.537 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup>. Kepekatan bagi Ca dan Mg telah didapati tinggi jika dibandingkan dengan yang lain, di mana kepekatan berada di takat antara  $8828 \pm 40.551 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> kepada  $37238.024 \pm 131.961 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> dan  $1655.792 \pm 4.108 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> kepada  $5889.979 \pm 18.851 \mu\text{g}$  (seunit jisim dalam gram)<sup>-1</sup> masing-masing.

Kajian ini juga memaparkan pengaruh kesan negatif alam sekitar terhadap penderma-penderma gigi sampel ini, terutamanya bagi mereka yang terlibat dalam aktiviti-aktiviti kilang (seperti di kilang besi, kilang wayar, kilang kereta, kilang peti sejuk, kilang aluminium). Kepekatan Pb bagi kumpulan sampel tersebut adalah lebih tinggi daripada paras median dan paling ketara bagi sampel dari Lembah Klang.

Di samping itu, 'correlation coefficient' telah dikira untuk mengkaji 2 jenis perhubungan, iaitu (1) kepekatan unsur-unsur dengan umur penderma-penderma sampel, dan (2) perhubungan di antara setiap unsur.



Didapati bahawa 'correlation coefficient' bagi Mg-Ca, dan Zn-Cd, adalah berada di 0.251 dan 0.416 masing-masing. 'Correlation coefficient' ini telah ditentusahkan selanjutnya dengan menggunakan kaedah statistik, iaitu "t-test" pada paras 1%. Ini telah menyahkan perhubungan di antara Mg-Ca dan Zn-Cd.

Kajian ini juga menunjukkan bahawa kepekatan Pb untuk sampel bagi kumpulan wanita meningkat secara langsung dengan umur mereka.

# Contents

		Page
Acknowledgement		iii
Abstract		iv
Abstrak		vii
Contents		x
Chapter 1	<b>Introduction</b>	1
	References	4
Chapter 2	<b>Human Teeth as an Indicator for Heavy Elements in Body</b>	7
	Introduction	7
	2.1 The Effects of Pb on Human Health	8
	2.2 The Effects of Cadmium	9
	2.3 The Significance of Calcium (Ca) to Human Health	11
	2.4 The Significance of Magnesium (Mg) in Human Body	12
	2.5 Zinc Important Element in Adolescent Growth of Teeth	13
	2.6 Copper in the Role of Normal Development and Bone Maintenance	13
	References	14
Chapter 3	<b>The Basic Theory of X-ray Fluorescence and Inductively Coupled Argon Plasma</b>	16
	3.1 The History of X-ray Fluorescence Spectroscopy	16
	3.2 The Principle of XRF	19
	3.3 The Auger Process: Fluorescent Yield	22
	3.4 Bremsstrahlung Effect	23
	3.5 Photoelectric Effect	25
	3.6 Compton Scattering	26
	3.7 Pair Production	29
	3.8 Theoretical Model	29
	3.8.1 Simple Theory of the Model	29
	3.9 The Basic Principle of ICP-AES	33
	3.10 ICP Main Components	36
	3.11 Advantages and Disadvantages	37
	3.12 Combining ICP with Atomic Emission Spectroscopy	38
	References	39
Chapter 4	<b>Materials and Methodology</b>	41
	Introduction	41
	4.1 XRF: Instrumentation	41

	4.2.1 The Detector	44
	4.2.2 Multi-Channel Analyzer (MCA)	46
	4.2.3 A Measurement on Standard Radiation Sources of Ba-133, Am-241 and Cs-137	48
	4.3 Technetium-99m (99m-Tc)	54
	4.4 Materials Preparation for XRF Experiment	58
	4.4.1 The Preparation of Standard Lead Solutions	59
	4.5 Experimental Set-up	60
	4.6 System Calibration	63
	4.7 Experimental Procedure	65
	4.8 The Experimental Preparation for Induced Coupled of Plasma-Atomic Emission Spectroscopy (ICP-AES)	66
	4.9 Treatment for Teeth Samples from Adult Donors: Preparing Teeth Samples	67
	4.10 ICP-AES Calibration	68
	4.11 The Summarized Procedure of ICP Operation	69
	4.12 Experimental Procedure	70
	References	73
<b>Chapter 5</b>	<b>Determination of Pb Concentration Using XRF Method</b>	<b>74</b>
	Introduction	74
	5.1 Results and Discussion	75
	5.1.1 Comparison the Measurement of Background and Pure Pb Spectrum	75
	5.1.2 Spectrum of Pb XRF K-lines from the Concentration of 1000 ppm to 100 ppm	77
	5.1.3 Average Mean of Difference—Used to Maximize the Spectral Information	82
	5.2 Theoretical Model	86
	5.2.1 Calculation of the Total Count for the Line $K\alpha_1$	86
	5.2.2 Geometrical Set-up of the Experiment	87
	5.2.3 Assumptions in Theoretical Calculation	91
	5.3 Conclusion	91
	References	92
<b>Chapter 6</b>	<b>Determination of Trace Elements Using ICP-AES Technique</b>	<b>94</b>
	Introduction	94
	6.1 The Calibration of ICP-AES	95
	6.1.2 Distribution of the Concentrations of Earth Element in Klang Valley and Malacca Samples	97
	6.2 Concentration of Pb	98
	6.3 Concentration of Zn	101
	6.4 Concentration of Cu	103
	6.5 Concentration of Cd	105

	6.6 Concentration of Ca	108
	6.7 Concentration of Mg	110
	6.8 Results of Comparison of Average Concentration for Each Element between Male and Female from the samples of Klang Valley and Malacca	111
	6.9 The Distribution of Concentrations for Each Element in Different Types of Tooth	116
	6.10 Comparison of the Average Concentration of Each Element for the Different Age Groups and Ethnicity	120
	6.11 Conclusion	126
	References	127
<b>Chapter 7</b>	<b>Analysis of Correlation Coefficient</b>	
	7.1 Relationship between the Elements' Concentration and the Age of Donors	129
	7.2 Relationships between Each Element	138
	7.3 Conclusion	140
	References	141
<b>Chapter 8</b>	<b>Conclusion</b>	142
	References	145
<b>Appendix</b>		146
<b>List of Publications</b>		147