## Trace Element Analysis of Food and Diet



Namk K. Aras and O. Yavuz Ataman

RSCPublishing

## **Preface**

The researchers who choose to work in the field of trace element determinations are not necessarily experienced analytical chemists. However, once involved in this sort of research, they either should acquire the necessary instrumentation in their laboratory or should be able to communicate with their collaborating colleagues who will probably be analytical chemists. In any case, this type of reader will need to know more about analytical chemistry, its language, literature and basics. Some chapters of this book will address this class of reader who need a rather quick review of the field through easy reading.

The book should also be useful to readers who perform actual experiments for sampling, analysis and evaluation. Therefore, especially the last chapter will provide the reader with procedures, brief suggestions for methodology and current references. All chapters include illustrations. These are mostly adapted from original articles or literature developed by manufacturing companies. Therefore, our choice of this particular approach is intended to establish some useful linkages between theory and actual practices in the manufacturing world.

The language, style and appearance of the book have been designed carefully by the authors who both have over thirty years of teaching and research experience in the field of analytical chemistry that hopefully has contributed to the pedagogical aspect of the book. This book is expected to provide an easily comprehensible basic orientation for those new in the field while at the same time offering ample opportunities for experienced researches to acquire new perspectives.

Some parts of Chapter 9, Nuclear Activation Analysis, have been based on the lecture notes of N.K. Aras and D.L. Anderson, which were prepared while they were giving a short course at the University of Maryland. Namik Aras would like to thank to late Professor Glen E. Gordon who taught him the importance of trace elements during his years at MIT and University of Maryland and to Robert Parr from IAEA for many years of fruitful discussions on trace elements in diet. Thanks are also due to R. Lindstrom from NIST and M. Yukawa from National Institute of Radiological Sciences, Japan for providing gamma ray and PIXE spectra of diet samples, and Özge Hacıfazlıoğlu for helping us in organizing the index of this book. Special thanks go to Peter Belton who encouraged us to write this book; and Annie Jacob, Janet Freshwater and Katrina Turner from the RSC for their organizational help. Finally we thank our wives Çiğdem Aras and Gülay Ataman for their moral support and patience throughout this endeavor.

## **Contents**

Abbreviation	ons		XV		
Chapter 1	Introduction				
_	1.1	Importance of Trace Elements in Food	1		
		1.1.1 Essential Trace Elements	1		
		1.1.2 Classification of Trace Elements	3		
		1.1.3 Discovery of Essential Trace Elements	3		
		1.1.4 Functions of Trace Elements	5		
	1.2	Trace Element Studies	5		
	Refe	erences	6		
Chapter 2	Statistical Evaluation of Data				
	2.1	Introduction	8		
	2.2	Analytical Errors	8		
		2.2.1 Accuracy and Precision	8		
		2.2.2 Determinate and Indeterminate Errors	9		
		2.2.3 Significant Figures	9		
	2.3	Mean, Median, Mode, Range and Mean Deviation	10		
		2.3.1 Mean	11		
		2.3.2 Median	11		
		2.3.3 Mode	11		
		2.3.4 Range	11		
		2.3.5 Mean Deviation	11		
	2.4	Normal Distribution of Random Variables:			
		Gaussian Distribution	12		
		2.4.1 Log-Normal Distribution	13		
		2.4.2 Standard Deviation	14		
	2.5	Confidence Limit, Confidence Interval and			
		Confidence Level	15		
	2.6	Student's t Distribution: Confidence Limit for			
		Small Number of Measurements	16		
	2.7	Testing for Statistical Hypothesis	17		
		2.7.1 Comparison of Experimental Means with			
		True Value or with Each Other: Student's			
		t Test	17		

viii

		2.7.2	Compari	son of Two Experimental Standard	
			_	ons: The F Test	18
	2.8	Rejec	ction of O	utliers	19
		2.8.	1 Dixon	n's Q Criterion	19
		2.8.	2 Stude:	nt's t Criterion	19
		2.8.	3 Gibbs	s's R Criterion	19
	2.9	Linea	ar Regress	sion Analysis	22
		2.9.	1 Multij	ple Linear Regression	25
	2.10		ptor Mode	els	26
••		2.10.		r Analysis	27
		2.10.		ical Mass Balance Method	29
			3 Enricl	hment Factors of the Elements	30
	Refe	erences			30
Chapter 3	Tra	ce Ana	lysis		32
	3.1	Scope	of Trace.	Analysis	32
	3.2	Metho	odology, T	erms and Definitions	33
		3.2.1	-	Analyte, Matrix and Blank	33
		3.2.2	Qualifica	ations for a Trace Analysis Laboratory	
			3.2.2.1	Water Purification	35
		3.2.3		n, Accuracy and Traceability	39
		3.2.4			40
		3.2.5	-	al Figures of Merit	41
			3.2.5.1	Detection Limit and Limit of	
				Quantitation	41
			3.2.5.2	Analytical Range	42
			3.2.5.3	3	43
			3.2.5.4	Signal to Noise Ratio	44
			3.2.5.5	,	
		226		Sensitivity, DL and S/N	44
		3.2.6		ity and Interference	45
		3.2.7	_	nportance of Results,	40
	<b>D</b> 6		Traceabi	ility and Other Related Concepts	49
	References				51
	Furt	her Rea	ding		52
Chapter 4	Sampling and Sample Pre-treatment				53
	4.1 General Guidelines in Collection and				
		_		Staple Foods and Diets	53
	4.2		_	ajor Staple Foods	54
		4.2.1	Wheat		54
			Wheat F	lour	55
		4.2.3	Bread		55

Contents

		4.2.4	Pasta	56	
		4.2.5	5 Rice	56	
		4.2.6	6 Potato	56	
		4.2.7	<sup>7</sup> Meat	57	
		4.2.8	Vegetables and Fruits	58	
		4.2.9	) Milk	58	
		4.2.10	Fresh Eggs	59	
		4.2.11	Other Staple Foods	59	
	4.3	Collec	ction of Diet Samples	59	
		4.3.1	Collection and Preparation of Foods for		
			Composition of Representative Mixed		
			Total Daily Diets, Market Basket Method	60	
		4.3.2	r	62	
		4.3.3	<b>.</b>	62	
			Homogenization and Freeze Drying	62	
	4.4	_	le Dissolution and Decomposition	63	
		4.4.1	5 6	66	
		4.4.2	8	66	
			4.4.2.1 Open Wet Digestion	69	
	<b>T</b>		4.4.2.2 Closed Wet Digestion	70	
		erences		73	
	Furt	her Rea	iding	74	
Chapter 5	Spectrochemistry for Trace Analysis				
	5.1	Funda	mentals, Definitions and Terms	75	
	5.2	Atom	ic and Molecular Spectrometry	84	
		5.2.1	Molecular Spectrometry	85	
		5.2.2	Luminescence Spectrometry	86	
		5.2.3	Atomic Spectrometry	86	
	5.3		mentation	86	
		5.3.1	Basic Components for Spectrometric		
			Instrumentation	87	
			5.3.1.1 Some Important Optical Units	87	
			5.3.1.2 Wavelength Selectors	89	
			5.3.1.3 Sources	98	
			5.3.1.4 Detectors	101	
	Furt	her Rea	ding	104	
Chapter 6	Ato	mic Al	osorption Spectrometry	105	
	6.1	Introd	uction, History and Principles	105	
	6.2	Instru	mentation	107	
		6.2.1	Sources	107	
		6.2.2	Monochromators	109	

*Contents* 

	6.2.3	Atomiz	ers	109	
		6.2.3.1	Flame Atomizers	109	
		6.2.3.2	Furnace Atomizers	111	
		6.2.3.3	Cold Vapour Atomic Absorption		
			Spectrometry (CVAAS)	116	
		6.2.3.4	Hydride Generation Atomic		
			Absorption Spectrometry	117	
		6.2.3.5	Atom Traps for Flame Atomizers	118	
	6.3 Inter	ferences		119	
	6.3.1	Non-sp	ectral Interferences	120	
	6.3.2	2 Spectra	l Interferences	122	
	6.4 Anal	lysis of So	lid Samples	130	
	6.5 A G	eneral Eva	luation and Capabilities of		
	AAS	Systems		131	
	Reference	S		134	
	Further Re	eading		135	
Chapter 7	Atomic F	Emission	and Mass Spectrometry using		
Chapter 7	Plasma T			136	
	7.1 Introduction, History and Principles				
			on Spectrometry	136 138	
	7.2.1		Emission Spectrometry with		
		•	al Sources	138	
	7.2.2	2 Optical	Emission Spectrometry with		
		_	Sources	140	
		7.2.2.1	Power Supplies for RF Generation	n 142	
		7.2.2.2	Sample Introduction Systems	143	
		7.2.2.3	Detection Systems and Measuren	nent	
			Modes in ICP-OES	146	
		7.2.2.4	Interferences	148	
	7.3 Indu	ctively Co	upled Plasma–Mass Spectrometry	150	
	7.3.1	Instrum	entation	152	
		7.3.1.1	Mass Analyzers	152	
		7.3.1.2	Detectors	154	
	7.3.2	Interfere	nces	155	
		7.3.2.1	Spectral Interferences	155	
	•	7.3.2.2	Non-spectral Interferences	157	
		7.3.2.3	* *		
			Interferences	158	
	7.3.3	_	Dilution ICP-MS	160	
	7.3.4	Instrume	ents and Applications	162 163	
	References				
	Further Readings				

Contents хi

Chapter 8	Ator	nic Flu	iorescence Spectrometry	164		
_	8.1		action, History and Principles	164		
	8.2	Instrur	nentation	167		
		8.2.1	Excitation Sources	168		
		8.2.2	Atomizers	168		
	8.3	Interfe	rences	170		
	8.4	Instrur	nentation and Applications	170		
	Refe	rences		171		
	Furth	ner Read	ding	171		
Chapter 9	Nuclear Activation Analysis					
	9.1	Introd	uction	172		
	9.2	Basic	Principles	172		
		9.2.1	Radioactive Decay	173		
		9.2.2	Half-Life	173		
		9.2.3	Irradiation with Neutrons and			
			Charged Particles	174		
	9.3	Neutro	on Activation Analysis	176		
		9.3.1	Cross Section	177		
		9.3.2	Neutron Sources	177		
			9.3.2.1 Laboratory Neutron Sources	177		
			9.3.2.2 Research Reactors	178		
		9.3.3	Preparation of Samples for Irradiation	178		
		9.3.4	Short Irradiation	179		
		9.3.5	Intermediate and Long-Lived Isotopes,			
			Long Irradiation	180		
		9.3.6	Calculation of Activity Produced after			
			Neutron Irradiation	181		
		9.3.7	Measurement of Gamma Rays	184		
			9.3.7.1 Interaction of Gamma Rays with			
			Matter	184		
	9.4	Other	Nuclear Techniques	188		
	9.5	Deterr	nination of Trace Elements in Total Diet by			
		Neutro	on Activation Analysis	189		
	9.6	Preser	nt Status of Activation Analysis by			
	Comparison with Other Analytical Techniques					
	Refe	rences		1		
Chapter 10	<b>X</b> -	Ray M	[ethods			
	10.	1 Intr	oduction			
	10.	2 Bas	ic Principles			
	10.3 X-Ray Fluorescence Spectrometry					

10.3.1

Production of X-Rays

xii Contents

		10.3.2 Wavelength Dispersive X-Ray				
		Fluorescence Spectrometry	197			
		10.3.3 Energy Dispersive X-Ray Fluorescence	198			
		10.3.4 Total Reflection X-Ray Fluorescence				
		Spectrometry	199			
	10.4	Particle-Induced X-Ray Emission Spectrometry	201			
	10.5	Quantitative Determination in XRF Methods	202			
	Refer	rences	204			
Chapter 11	Spec	iation Analysis	205			
	11.1	Importance of Speciation Analysis and				
		Related Terms	205			
	11.2	Chromatography and Electrophoresis	207			
		11.2.1 Common Laws and Properties for				
		Chromatography and Electrophoresis	211			
		11.2.2 Instruments for Chromatography and				
		Electrophoresis	215			
		11.2.2.1 Columns	215			
		11.2.2.2 Detectors	216			
	11.3	Typical Instruments	219			
		rences	221			
	Furth	er Reading	221			
Chapter 12	Com	parison of Analytical Techniques	222			
_	12.1	General Approaches for Selecting a Technique	222			
	12.2	Criteria for Selecting an Analytical Technique	222			
		12.2.1 Considerations for Sample Preparation	223			
		12.2.2 Sensitivity	224			
		12.2.3 Speed	225			
		12.2.4 Ease of Use	226			
		12.2.5 Cost of Instrumentation and Analysis	228			
	12.3	Evaluation of Individual Analytical Techniques	232			
Chapter 13	<b>Essentiality and Toxicity of Some Trace Elements</b>					
_	and Their Determination 23					
	13.1	Introduction	233			
	13.2	Essential and Probably Essential				
		Trace Elements	233			
		13.2.1 Boron	233			
		13.2.2 Chromium	237			
		13.2.3 Cobalt	237			
		13.2.4 Copper	238			
		1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1				

xiii

	13.2.5	Iodine	239
	13.2.6	Iron	239
	13.2.7	Manganese	240
	13.2.8	Molybdenum	240
	13.2.9	Nickel	241
	13.2.10	Selenium	242
	13.2.11	Silicon	244
	13.2.12	Tin	245
	13.2.13	Vanadium	245
	13.2.14	Zinc	246
13.3	3 Potentia	lly Toxic Elements: Some Possibly	
	with Ess	sential Function	248
	13.3.1	Arsenic	248
	13.3.2	Fluorine	249
	13.3.3	Cadmium	250
	13.3.4	Lead	252
	13.2.5	Mercury	252
	13.3.6	Aluminium	253
13.4	4 Literatu	re on Determination of Trace	
	Element	s in Food Samples	254
Ref	erences		304
Subject Index			336