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SPECIATION OF MERCURY IN DIFFERENT ENVIRONMENTAL COMPARTMENTS. DESIGN, DEVELOPMENT AND OPTIMIZATION OF ANALYTICAL METHODS AND PROCEDURES.

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A dissertation submitted to the faculty of science, University of Witwatersrand, in fulfilment of the requirements for the degree of Master of Science.

Johannesburg 2008

Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

_____

(Signature of Candidate)

_____ Day of _____2009

Abstract

The widespread use of organometallic compounds and their subsequent release into the environment has created a great environmental concern about the toxicity and effects of these pollutants. Mercury pollution is a growing concern worldwide because its can reach high concentrations in various environmental media and thus adversely affect humans, wildlife and ecosystem functioning.

Mercury is present in the environment in different molecular forms with specific biogeochemical transformation and ecotoxicity. Inorganic Hg^{2+} is the main form in water and sediment samples. Concentration levels of organomercury species is very low (usually ng L-1) in aquatic environments but the toxic effect of these compounds can be significant due to their tendency for bioaccumulation and biomagnification in the food chain.

The development of a sensitive, reliable, simple, and cost effective procedure for speciation analysis of mercury in different environmental compartments is currently one of the principal research challenges in environmental analytical chemistry. To this end, this study aimed to develop and optimize analytical methods and procedures for the determination of total mercury and the speciation of inorganic and organic forms of mercury. The hyphenation of gas chromatography and inductively coupled plasma mass spectrometry (GC-ICP-MS) was achieved and used successfully.

Rapid and efficient sample preparation procedures based on microwave-assisted extraction for solid samples were developed. The optimized analytical methods and procedures were validated by the analysis of environmental certified reference materials (CRM 015-050 sediment for Hg_{TOT} and CRM 463 tuna fish for Hg_{TOT} and MeHg).

The developed methodologies were finally applied to real environmental samples, namely soil, sediment, water, fish and human hair, collected in some South African regions affected by environmental pollution due to reprocessing of old tailings dumps and chlor-alakali facilities. The study included collection of ancillary data (pH, redox potential) which are critically important for mercury monitoring program. Predictive models of mercury speciation in water samples based on thermodynamic solution equilibria were also established.

Dedication

To Mickel-Ange Lusilao

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TABLE OF CONTENTS

CONTENTS **Page**

DECLARATION …….. …….……ii
ABSTRACT …..……..……iii
DEDICATION……..v
ACKNOWLEDGEMENTS……vi
TABLE OF CONTENTS …….…….....vii
LIST OF FIGURES ……...…… xi
LIST OF TABLES ……xiii
LIST OF ABBREVIATIONS …….. ..xv

CHAPTER ONE – INTRODUCTION

1.1 General background …… 1
1.2 Problem statement ……...… 2

CHAPTER TWO – LITERATURE REVIEW

2.1 Chemistry of mercury …… 6
2.2 Mineralogy …….. 8
2.3 Abundance and distribution in the environment ……. 8
2.3.1 Rocks, soils and sediments ……..…… 8
2.3.2 Minable deposits ……...… 11
2.3.3 Fossil fuels …… 11
2.3.4 Natural water ……. 12
2.4 Sources …….. 14
2.4.1 Natural mercury emissions ……..... 14
2.4.2 Anthropogenic sources ……...…... 14
2.4.3 Mineral working …… 17
2.5 Pathways and behaviour of mercury in the environment ……..... 18
2.5.1 Mercury in the atmosphere ……..…….. 19
2.5.2 Terrestrial components …….. 22
2.5.3 Aquatic components ……..…. 24
2.5.4 Transport and exchange processes …… 27
2.6 Organomercury compounds in the environment ……... 28
2.6.1 Methylmercury in water …… 29
2.6.2 Methylated mercury in the atmosphere ……..… 32
2.6.3 Methylmercury production and decomposition …… 33
2.6.4 Bioaccumulation ……..……..…… 36
2.7 Health effects ……..... 40
2.8 Risk assessment and exposure pathways …….. 42
2.8.1 Exposure assessment ……..... 42
2.8.2 Risk characterization ……..... 42

2.8.3 Risk management ……... 43
2.8.4 Exposure pathways ……... 43
2.9 Legislation and guidelines ……..... 45
2.9.1 Water ……..... 45
2.9.2 Food …….. 46
2.9.3 Air ……. 46

CHAPTER THREE – AN OVERVIEW OF ANALYTICAL METHODS USED IN MERCURY SPECIATION

3.1 Sampling and storage …… 49
3.1.1 Water samples ……... 50
3.1.2 Solid sample …….. 51
3.1.3 Biological samples …… 51
3.2 Preparation of solid samples ……. 52
3.3 Methods for mercury species determination ……. 54
3.3.1 Comparison of modification techniques applied in CE, LC and GC … 55
3.3.2 LC and GC in mercury speciation ……..... 58
3.3.3 Detection of mercury species …… 60
3.3.4 Coupling of GC with ICP-MS ……..…... 60
3.4 Methods validation ……..... 60

CHAPTER FOUR – OBJECTIVES OF THE STUDY…… 68

CHAPTER FIVE – DEVELOPMENT OF INSTRUMENTAL METHODS FOR MERCURY SPECIES ANALYSIS

5.1 Optimization of ICP-MS ……..... 70
5.1.1 Chemicals ……..……...….. 70
5.1.2 Sample preparation ……...……...… 71
5.1.3 ICP-MS analysis ……..…..…..…… 72
5.1.4 Results and discussion …….. 73
5.1.5 Conclusion ……..…..…… 76
5.2 Coupling of GC with ICP-MS …….. 76
5.2.1 Design, development and optimization of hyphenated GC-ICP-MS …77
5.2.1.1 Instrumental design ……...……...…. 77
5.2.1.2 Method development and optimization ……..... 79
5.2.2 Material and reagents …… 81
5.2.3 Sample preparation ……...…... 82
5.2.4 Analysis ……..…… 83
5.2.5 Results and discussion …….. 84
5.2.5.1 Analytical instrument …… 84
5.2.5.2 Linearity …… 85

5.2.5.3 Repeatability and detection limit 87
5.2.5.4 Analysis of the certified reference material 88
5.2.6 Conclusion 90
5.2.7 Recommendations 91

CHAPTER SIX – APPLICATION OF DEVELOPED METHODS

6.1 Introduction 92
6.2 Mercury determination in a dismantled chlor-alkali plant 93
6.2.1 Material and reagents 96
6.2.2 Sampling and sample preparation 96
6.2.2.1 Soil samples 96
6.2.2.2 Water samples 97
6.2.2.3 Sample preparation 98
6.2.3 Analysis 100
6.2.3.1 Total mercury 100
6.2.3.2 Mercury speciation 101
6.2.4 Results and discussion 101
6.2.4.1 Standard calibration 101
6.2.4.2 Soil samples 105
6.2.4.3 Water samples 119
6.2.5 Conclusion 122
6.3 Ecotoxicology assessment in three villages affected by mercury pollution 123
6.3.1 Sample preparation 125
6.3.1.1 Hair samples 125
6.3.1.2 Fish samples 126
6.3.2 Results and discussion 127
6.3.2.1 Speciation calibration 128
6.3.2.2 Hair samples 128
6.3.2.3 Fish samples 136
6.3.3 Conclusion 140
6.4 Mercury from gold tailings 140
6.4.1 Sampling area 141
6.4.2 Sampling and sample preparation 144
6.4.3 Results and discussion 145
6.4.3.1 Mercury in water samples 150
6.4.3.2 Mercury in sediment samples 151
6.4.4 Conclusion 155

CHAPTER SEVEN – GENERAL CONCLUSION 157

REFERENCES 161

APPENDIX 1ICP-MS Calibration Graph.....…….. 191

APPENDIX 2 GC-ICP-MS Chromatograms…..…….……...192

APPENDIX 3 Photographs of features in the study area (Klip River, Johannesburg). ……...……194

List of Figures

Figure 2.1:	A comparison of the mercury concentrations measured in the South Atlantic with those measured in 2002 in the North Pacific ……..…….……	13
Figure 2.2:	Spatially distributed inventory of global anthropogenic emissions of mercury to the atmosphere, 2000…….	17
Figure 2.3:	TGM in the atmosphere at several locations…….	21
Figure 2.4:	Summary of some of the important physical and chemical transformations of mercury in the atmosphere …….	21
Figure 2.5:	Proposed mechanism for elemental oxidation in the marine boundary layer, or in other regimes where there is the presence of halogen-containing aerosol ……	22
Figure 2.6:	Generalised view of mercury biogeochemistry in the aquatic environment……	26
Figure 3.1:	Schematic representation of an ICP-MS instrument……..	61
Figure 3.2:	GC-ICP-MS hyphenated technique……	64
Figure 5.1:	ICP-MS calibration for different mercury isotopes……	74
Figure 5.2:	schematic representation of the used hyphenated technique….	77
Figure 5.3:	GC-ICP-MS coupled with the transfer line on top of the GC…	78
Figure 5.4:	"T-piece" glass used for the connection of the transfer line and the nebuliser to the plasma torch…….	78
Figure 5.5:	Example of Chromatogram of inorganic and organic mercury Standard…….	84
Figure 5.6:	Example of Chromatogram of Hg isotopes 202 and 199 without baseline correction……	85
Figure 5.7:	Chromatogram of a blank……..	85
Figure 5.8a, b and c:	Chromatograms of calibration standards……	86
Figure 5.9:	Calibration for inorganic and organic mercury species…….	87
Figure 5.10a and b:	Chromatograms of CRM 463 at different extraction conditions	89
Figure 6.1:	Sketch of the sampling site with indications where soil and water samples were collected…….	94
Figure 6.2:	Sample preparation chart for mercury determination in soil…..	99
Figure 6.3:	Sample preparation chart for mercury determination in water..	100
Figure 6.4:	ICP-MS calibration for ^{199}Hg isotope……	102
Figure 6.5:	ICP-MS calibration for ^{202}Hg isotope……	103
Figure 6.6:	Chromatograms of Hg standards……	103
Figure 6.7:	GC-ICP-MS calibration for ^{202}Hg isotope…….	104
Figure 6.8:	Example of soil chromatogram obtained with GC-ICP-MS….	105
Figure 6.9:	Example of water chromatogram obtained with GC-ICP-MS...	105
Figure 6.10:	Eh-pH diagram for some of the most important chloride and sulphur mercury species…….	107

Figure 6.11: Predominant Hg(II) species with pH…….. 108

Figure 6.12: Variation of pH with depth for the different profiles…… 109
Figure 6.13: Variation of redox potential in soil wit the depth…….. 109
Figure 6.14: Variation of the conductivity with the depth……. 110
Figure 6.15: Examples of metal concentrations with depth…… 113
Figure 6.16: Concentration of inorganic mercury with depth…… 115
Figure 6.17: Mercury concentrations in the sampling site……. 116
Figure 6.18: MeHg concentration at different profiles…….. 117
Figure 6.19: Chromatogram of sample 9C60-80…… 117
Figure 6.20: Variation of IHg, MeHg concentrations and redox potential with depth……... 118
Figure 6.21a: Water speciation by Geochemist's Workbench (-Log a Cl^- = 0.143)…….. 121
Figure 6.21b: Water speciation if Cl^- concentration is increased to - Log a = 0.8……... 121
Figure 6.22: Map of the sampling site…… 124
Figure 6.23: Sample preparation for the determination of mercury in hair… 126
Figure 6.24: Total mercury concentration in hair for each village……. 132
Figure 6.25: Example of chromatogram of hair sample (H74)……... 133
Figure 6.26: Example of chromatogram of fish sample (carp fish)…… 137
Figure 6.27: Eventual pathway of mercury contamination of vegetarians living in Madimeni……. 139
Figure 6.28: Map of the sampling site…… 144
Figure 6.29: Redox potential, pH and conductivity of sediment profiles….. 148
Figure 6.30: Examples of metals and anions concentrations with depth for the sediment profile B…… 149
Figure 6.31: Example of chromatogram obtained on a sediment sample….. 151
Figure 6.32: Speciation of mercury compounds in the sediment profile B… 154
Figure 6.33: % carbon in the sediment profile B…… 155

List of tables

Table 2.1:	Physical/ Chemical properties of mercury and some of its compounds……..	7
Table 2.2:	Mercury-bearing minerals……..	9
Table 2.3:	Distribution of mercury in the Earth's crust……..	10
Table 2.4:	Statistical data of analytical results from FOREGS……	10
Table 2.5:	Range of mean concentrations of Hg and MeHg in subsurface water at different stations of the world ocean…..	13
Table 2.6:	Major classes of anthropogenic emissions of mercury to the atmosphere in 1995……	15
Table 2.7:	Percent of mercury present as MeHg in tissues of invertebrae Aquatic..…….	39
Table 2.8:	Levels of Total Mercury in Seafood……..	41
Table 2.9:	Pathways of exposure to various species of mercury…….	44
Table 2.10:	Absorption of mercury species by routes……	45
Table 3.1:	Comparison of the speciation analysis using analyte modification by CE, LC and GC……	56
Table 3.2:	Most frequently used methods or quantification of Hg and their relative detection limit……	65
Table 5.1:	Microwave programme for sample extraction……	72
Table 5.2:	ICP-MS parameters…….	73
Table 5.3:	ICP-MS calibration parameters……...	74
Table 5.4:	Total Hg concentrations on CRM015-050 measured with ICP-MS and % recovery determined from the certified value	75
Table 5.5:	ICP-MS and GC operating conditions……	80
Table 5.6:	Optimized digestion parameter for the determination of Hg_{TOT} in CRM 463 tuna fish……..	82
Table 5.7:	RSD (%) of 0.5 µg ml^{-1} IHg and 0.2 µg ml^{-1} MeHg……	88
Table 5.8:	MeHg concentration determined in CRM 463 Tuna fish by GC-ICP-MS…….	90
Table 6.1:	Description of collected samples…….	95
Table 6.2:	Microwave program for soil digestion……	98
Table 6.3:	ICP-MS Standard calibration parameters……	102

Table 6.4: Samples measurement results obtained with ICP-MS (Hg_{TOT}) and GC- ICP-MS (IHg and MeHg)…… 106

Table 6.5: Mercury and total ions concentrations in water and soil samples…… 112

Table 6.6: Optimized digestion parameters for the determination of Hg_{TOT} in hair…… 125

Tables 6.7.: Determination of Hg_{TOT} in hair samples collected from a non- exposed area …… 129

Table 6.8: Hg_{TOT} in samples collected in Mshazi …… 129

Table 6.9: Hg_{TOT} in samples collected in Nqetho ……..… 130

Table 6.10: Hg_{TOT} in samples collected in Madimeni …… 131

Table 6.11: Inorganic and mono-methylmercury concentrations in hair samples ……. 133

Table 6.12: comparison between total analysis and speciation result on 3 hair samples ……. 134

Table 6.13: Summary of total Hg concentration in hair from inhabitants of the 3 villages..…… 134

Table 6.14: Fish mercury levels, Inanda dam, KwaZulu-Natal, South Africa……. 136

Table 6.15: Sampling GPS data……. 145

Table 6.16: Field parameters and mercury concentrations in water samples and sediment profiles…… 147

Table 6.17: Ions concentrations and % carbon on the sediment profile B. 147

ABBREVIATIONS

AAS: atomic absorption spectrometry

AFS: atomic fluorescence spectrometry

BCR: Community Bureau of Reference

CE: Capillary electrophoresis

CNRS: Centre national de recherché scientifique

CRM: certified reference material

CV: cold vapor

CVG: chemical vapor generation

CVT: cold vapor technique

CZE: capillary zone electrophoresis

Eth: Ethylation

FOREGS: Forum of the European Geological Surveys

GC: gas chromatography

GC-ICP-MS: gas chromatography- inductively coupled plasma-mass Spectrometry

GPS: Global Positioning System

HG: hydride generation

$HgEt_2$: Diethylmercury

Hg-P: particulate-bound mercury

HPLC: high-performance liquid chromatography

ICP-MS: inductively coupled plasma-mass spectrometry

IDMS: isotope dilution mass spectrometry

IHg: inorganic mercury

IPCS: International Programme on Chemical Safety

LC: liquid chromatography

LCABIE: Laboratoire de chimie analytique bio-inorganique et environment

LOAEL: lowest-adverse-affect-effect-level

LOD: Limit of detection

LOQ: Limit of quantitation

MAE: microwave-assisted extraction

MCL: maximum contaminant level

MeHg: monomethylmercury

MeHgEt: Methylethylmercury

MIP-AES: microwave-induced plasma atomic emission spectrometry

MRC SA: Medical Research Council South Africa

MS: mass spectrometry

$NaBEt_4$: sodium tetraethylborate

NOAEL: no-adverse-affect-effect-level

QC: quality control

RfD: reference dose

RGHg: reactive gaseous mercury

RSD: Relative standard deviation

SA: South Africa

SABS: South African Bureau of Standards

SAWQG: South African Water Quality Guidelines

SEM: secondary electron multiplier

SFE: supercritical fluid chromatography

TDI: tolerable daily intake

TMAH: Tetramethylammonium hydroxide

USEPA: United States Environmental Protection Agency

WHO: World Health Organization