

Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author.

**TRACE ELEMENTS IN NEW ZEALAND OILS  
THEIR SIGNIFICANCE FOR ANALYTICAL CHEMISTRY,  
GEOCHEMISTRY AND OIL CLASSIFICATION**

A thesis presented in partial fulfilment of  
the requirements for the degree of Doctor of  
Philosophy at Massey University

**MASSEY UNIVERSITY  
NEW ZEALAND**

**Anita Frankenberg**

**1994**

## ABSTRACT

This work is a study of trace elements in New Zealand and some overseas oils. Trace elements have been successfully used in previous studies to distinguish marine oils of different origins, to identify groups of related oils in individual regional areas and to establish migration patterns.

This is the first study of trace element concentrations and variations in New Zealand crude oils. A wide range of oil samples of different origins and geographical regions was analysed and the obtained trace element concentrations enabled a comprehensive comparison of trace element contents in terrestrial, lacustrine and marine oils. Over 120 oil samples of various marine and terrestrial origins were analysed for 42 elements and the resulting trace element concentrations were subjected to correlation and principal components analysis.

The trace element concentrations in New Zealand oils are very similar to those in other terrestrial-derived crude oils. Elements, associated with clay minerals had a high mutual correlation and were present in concentrations, comparable with, or exceeding those in marine oils. The origin of these elements and their implications to the classification of Taranaki Basin oils are discussed.

Trace elements in the asphaltene fractions of some New Zealand and overseas oils, in extracts of coal from the Pakawau Group and in ashed coal samples were determined to obtain additional information about the origin of Taranaki Basin oils.

In this study, 42 trace elements were determined by instrumental neutron activation analysis, graphite furnace atomic absorption and inductively coupled plasma emission spectrometry. Instrumental NAA was used to quantify a wide range of elements in undiluted and untreated crude oils. Graphite furnace AAS is a more sensitive method for some elements and was used to determine trace elements that were not detectable by INAA.

The analysis of organic oil solutions was difficult due to the complex organic oil

matrix. Various ashing, low temperature ashing, acid oxidation and extraction techniques were investigated and were considered to be unsuitable for the quantification of low amounts of elements in crude oils. A mixed-solvent system, using toluene and isopropanol, enabled the use of ready available aqueous standards and allowed the quantification of trace elements other than those present in the standard oil solutions. The close matching of standard and sample solutions was essential for the accuracy of the trace element results. Various analytical techniques, their use and suitability for the analysis of crude oils are discussed in detail.

## ACKNOWLEDGMENTS

I would like to thank my supervisors for their continuous assistance, support and suggestions throughout the project. My special thanks to Prof. Robert Brooks for enabling me to study in New Zealand and to Dr. John Collen for getting this study started in the first place and always arranging to have time if I needed to talk.

I am grateful to the Ministry of Commerce for financing this work and to the Institute of Geological and Nuclear Sciences for supplying many of the samples.

I would also like to thank Dr. Roy Filby, Cathy Grimm and Scot Fitzgerald at the Nuclear Research Center, Washington State University, Washington State, USA. Without their help, a large part of the work would have not been possible, as they analysed many samples. I enjoyed my stay at Washington State University, as they made me feel welcome and allowed me to gain valuable hands-on experience with INAA at the Nuclear Research Center.

I am especially grateful to my husband Mattias for his continuous encouragement, moral support and the occasional pep talk during difficult periods.

Ganz besonders möchte ich meinen Eltern danken, ohne deren Verständnis, Unterstützung und Hilfe ich es niemals soweit geschafft hätte.

## TABLE OF CONTENTS

<b><u>I. INTRODUCTION</u></b>	14
<b>1.1 PREVIOUS WORK</b>	14
<b>1.2 AIM OF THE STUDY</b>	18
<b><u>II. PETROLEUM GEOLOGY AND GEOCHEMISTRY</u></b>	21
<b>2.1. OIL FORMATION AND ACCUMULATION</b>	21
<b>2.1.1 DIAGENESIS, CATAGENESIS, METAGENESIS</b>	21
<b>A. Diagenesis</b>	21
<b>B. Catagenesis</b>	23
<b>C. Metagenesis</b>	24
<b>2.1.2 KEROGEN</b>	24
<b>2.1.3 TRACE ELEMENTS IN CRUDE OILS</b>	27
<b>2.1.4 ORIGIN OF TRACE ELEMENTS IN OILS</b>	29
<b>2.2 NEW ZEALAND OILS</b>	30
<b>2.2.1 GEOLOGY OF TARANAKI BASIN</b>	30
<b>2.2.2 ORGANIC GEOCHEMISTRY</b>	32
<b>2.2.3 SAMPLES</b>	35
<b>A. Taranaki Basin</b>	36
* McKee Field	42
* Kapuni Field	43
* Maui Field	43
* Kaimiro Field	43
* Moki Discovery	44
* Tariki and Ahuroa Discovery	44
* Kupe South Discovery	44
* Stratford Discovery	45
* Moturoa Field	45
* Kora Discovery	45
* Other samples	46

<b>B. East Coast Basin</b>	46
<b>C. Canterbury Basin</b>	48
<b>D. Westland Basin</b>	49
<b>2.3 OVERSEAS OIL SAMPLES</b>	51
2.3.1 CHINA	51
* Jiuxi Basin	51
* Minhe Basin	51
* Turpan Basin	51
2.3.2 AUSTRALIA	53
* Cooper/Eromanga Basin	53
* Timor Sea	53
2.3.3 U.S.A.	56
* San Juan Basin	56
* Los Angeles Basin	56
* Williston Basin	56
* Uinta Basin	57
* Gulf of Mexico	56
* Alaska	57
2.3.4 NORTH SEA	57
* Norwegian oils	57
2.3.5 CANADA	58
* Alberta Basin	58
2.3.6 MIDDLE EAST	58
2.3.7 NIGERIA	59
<b>2.4 POTENTIAL SOURCE ROCKS</b>	59
2.4.1 NEW ZEALAND	59
2.4.2 OVERSEAS SAMPLES	60
<b>2.5 FORMATION WATER SAMPLES</b>	60

<b><u>III. ANALYTICAL METHODS AND SAMPLE TREATMENT</u></b>	61
<b>3.1 SAMPLE TREATMENT</b>	61
3.1.1 REAGENTS AND EQUIPMENT	61
<b>A. Reagents and equipment</b>	61
<b>B. Glassware</b>	62
3.1.2 OIL SAMPLES	62
<b>A. Filtering</b>	62
<b>B. Ashing</b>	64
<b>C. Acid oxidation</b>	67
<b>D. Extraction</b>	73
<b>E. Solvents</b>	74
<b>F. Mixed solvent system</b>	75
<b>G. Nickel and vanadium determination</b>	79
3.1.3 OIL FRACTIONS	86
<b>A. Thin layer chromatography</b>	86
<b>B. Asphaltenes</b>	87
3.1.4 COAL AND POTENTIAL SOURCE ROCKS	91
<b>A. Ashing and HF/HNO<sub>3</sub> treatment</b>	91
<b>B. Bitumen extraction</b>	93
<b>C. Pyrolysis</b>	96
<b>D. Kerogen</b>	97
<b>3.2 NEUTRON ACTIVATION ANALYSIS</b>	98
3.2.1 PREVIOUS WORK	98
3.2.2 THEORY	99
3.2.3 ADVANTAGES, ERRORS AND PRECISION	99
3.2.4 INSTRUMENTATION	100
3.2.5 SAMPLES AND ANALYTICAL METHOD	100
<b>3.3 INDUCTIVELY COUPLED EMISSION SPECTROMETRY</b>	102
3.3.1 PREVIOUS WORK	102

3.3.2 THEORY	103
3.3.3 ADVANTAGES, ERRORS AND PRECISION	103
3.3.4 INSTRUMENTATION	104
3.3.5 SAMPLES AND ANALYTICAL METHOD	106
<b>3.4 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY</b>	<b>106</b>
3.4.1 PREVIOUS WORK	107
3.4.2 THEORY	108
3.4.3 ADVANTAGES, ERRORS AND PRECISION	109
3.4.4 INSTRUMENTATION	110
3.4.5 STANDARDS	112
<b>A. Organic standards</b>	112
<b>B. Aqueous standards</b>	113
3.4.6 SAMPLES AND ANALYTICAL METHODS	114
<b>A. Oil samples</b>	114
<b>B. Heating programs and wavelengths</b>	118
<b>C. Vanadium determination</b>	122
<b><u>IV. RESULTS AND DISCUSSION</u></b>	<b>124</b>
<b>4.1 TRACE ELEMENTS AND INTER-ELEMENTAL CORRELATIONS     IN NEW ZEALAND OILS</b>	<b>124</b>
4.1.1 NICKEL AND VANADIUM	126
4.1.2 BROMINE AND CHLORINE	132
4.1.3 ALUMINIUM	132
4.1.4 CHALCOPHILE ELEMENTS	133
4.1.5 SIDEROPHILE ELEMENTS	134

4.1.6 RARE EARTH ELEMENTS	135
4.1.7 INTER-ELEMENTAL CORRELATIONS	135
<b>4.2 RELATIONSHIP OF NEW ZEALAND AND OVERSEAS OILS</b>	<b>148</b>
4.2.1 NICKEL AND VANADIUM	150
4.2.2 BROMINE AND CHLORINE	156
4.2.3 ALUMINIUM	157
4.2.4 CHALCOPHILE ELEMENTS	157
4.2.5 SIDEROPHILE ELEMENTS	158
4.2.6 RARE EARTH ELEMENTS	159
4.2.7 INTER-ELEMENTAL CORRELATION	159
<b>4.3 OILS AND SOURCE ROCKS</b>	<b>164</b>
<b>4.4 FORMATION WATERS</b>	<b>171</b>
<b>4.5 PRINCIPAL COMPONENTS ANALYSIS</b>	<b>172</b>
4.5.1 NEW ZEALAND OILS	172
4.5.2 NEW ZEALAND AND OVERSEAS OILS	179
4.5.3 NEW ZEALAND OILS AND BITUMEN	190
<b>4.6 ASPHALTENES</b>	<b>193</b>
<b><u>V. CONCLUSIONS</u></b>	<b>199</b>
<b>5.1 ANALYTICAL METHODS</b>	<b>199</b>
<b>5.2 TRACE ELEMENT RESULTS</b>	<b>200</b>
<b><u>REFERENCES</u></b>	<b>203</b>
<b><u>APPENDICES</u></b>	

## LIST OF FIGURES

<b>1</b>	Nickel and V content in oils from various origins	16
<b>2</b>	Formation of petroleum from sedimentary matter	25
<b>3</b>	Structural subdivision and structural cross-section for Taranaki Basin, New Zealand	31
<b>4</b>	Hydrocarbon accumulations under production or development	33
<b>5</b>	Main hydrocarbon-producing fields and wells in Taranaki Basin	40
<b>6</b>	Stratigraphic map of Taranaki Basin	41
<b>7</b>	East Coast hydrocarbon accumulations and stratigraphic map	47
<b>8</b>	Hydrocarbon occurrences in the Canterbury Basin	48
<b>9</b>	Hydrocarbon occurrences in the Westland area	49
<b>9a</b>	Stratigraphic column for the central Westland Basin	50
<b>9b</b>	Stratigraphic column for the Murchison Basin	50
<b>10</b>	Hydrocarbon occurrences in the Jiuxi Basin, China	52
<b>11</b>	Hydrocarbon occurrences in the Cooper/Eromanga Basin, Australia	54
<b>11a</b>	Stratigraphic column for the Cooper/Eromanga Basin, Australia	55
<b>12</b>	Nickel standard curves obtained with NBS oil and Maui-1 oil solutions	80
<b>13</b>	Peak shapes of of V in oil and aqueous solutions	83
<b>14</b>	Trace element concentrations in coals after ashing at different temperatures	92

15	Trace element concentrations in bitumen extracted from shale with toluene, chloroform, toluene/methanol and toluene/dichloromethane	94
16	Trace element concentrations in bitumen extracted from New Zealand coal with different solvents	95
17	Nickel and Fe concentrations in bitumen obtained after 6, 12, 24, 48 and 72 hours extraction of coal with chloroform/methanol	95
18	Diagram of a plasma torch	105
19	GBC system 1000 with AAS 902 and graphite furnace head	111
20	Nickel and Fe standard curves obtained with fuel oil and aqueous standard solutions	116
21	Nickel peaks in new and worn graphite furnace tube	117
22	Nickel absorption peak with recorded background absorption	119
23	Absorption peak heights for Ni in oil solutions at different ashing temperatures	120
24	Vanadium standard curve (GBC system 2000/3000)	123
25	Tailing of V absorption peaks at high concentration compared to a absorption peak at low concentration	123
26	Range of trace element concentrations in New Zealand oils (log values and standard deviations)	125
27	Nickel ( $\mu\text{g/g}$ ) versus V ( $\text{ng/g}$ ) for New Zealand oils	128
27a	Nickel/V for oils from the McKee Field	128
28	API gravity versus Ni+V concentration ( $\mu\text{g/g}$ )	131
29	Sulphur (wt %) versus V ( $\text{ng/g}$ ) for New Zealand oils	131
30	Correlation matrix for New Zealand oils	137

31	Aluminium ( $\mu\text{g/g}$ ) versus V ( $\text{ng/g}$ ) for New Zealand oils	138
31a	Aluminium/V for oils from the McKee Field	138
32	Cobalt ( $\text{ng/g}$ ) versus Mn ( $\text{ng/g}$ ) for New Zealand oils	141
32a	Co/Mn for oils from the McKee Field	141
33	Co/Mn (normal concentration scale), New Zealand oils	142
34	Iron ( $\mu\text{g/g}$ ) versus Sc ( $\text{ng/g}$ ), New Zealand oils	143
34a	Iron ( $\mu\text{g/g}$ ) versus Sc ( $\text{ng/g}$ ) for oils from the McKee Field	143
35	Cobalt ( $\text{ng/g}$ ) versus As ( $\text{ng/g}$ ) for New Zealand oils	144
36	Nickel ( $\mu\text{g/g}$ ) versus As ( $\text{ng/g}$ ) for New Zealand oils	145
37	Nickel ( $\mu\text{g/g}$ ) versus Zn ( $\mu\text{g/g}$ ) for New Zealand oils	146
38	Arsenic ( $\text{ng/g}$ ) versus Br ( $\text{ng/g}$ ) for New Zealand oils	147
39	Range of trace element concentrations in New Zealand and overseas oils (log values and standard deviation)	148
40	Nickel ( $\mu\text{g/g}$ ) versus V ( $\text{ng/g}$ ) for New Zealand and other terrestrial-derived oils	152
41	Nickel ( $\mu\text{g/g}$ ) versus V ( $\text{ng/g}$ ) for oils from the Cooper/Eromanga Basin, Australia	153
42	Nickel ( $\mu\text{g/g}$ ) versus V ( $\mu\text{g/g}$ ), New Zealand and overseas oils	154
42a	Nickel/V, New Zealand and overseas oils (log values)	155
43	Correlation matrix for terrestrial-derived oils	160

44	Correlation matrix for lacustrine-derived oils	161
45	Correlation matrix for marine oils	161
46	Aluminium ( $\mu\text{g/g}$ ) versus V ( $\mu\text{g/g}$ ) for New Zealand and overseas oils	162
47	Cobalt ( $\text{ng/g}$ ) versus Mn ( $\text{ng/g}$ ) for New Zealand and overseas oils	163
48	Correlation matrix for New Zealand bitumen	167
49	Arsenic ( $\text{ng/g}$ ) versus Br ( $\text{ng/g}$ ) for New Zealand bitumen	168
50	Cobalt ( $\text{ng/g}$ ) versus Ni ( $\mu\text{g/g}$ ) for New Zealand bitumen	169
51	Nickel ( $\mu\text{g/g}$ ) versus V ( $\text{ng/g}$ ) for New Zealand and overseas bitumen	170
52	Principal component 2/pc1 for New Zealand oils	173
53	PC3/PC1 for New Zealand oils	174
54	PC3/PC2 for New Zealand oils	175
55	Three dimensional graph of principal components for New Zealand oils	177
55a	Three dimensional graph of principal components for New Zealand oils (individual groups)	178
56	PC2/PC1 for New Zealand and overseas oils	180
57	PC3/PC1 for New Zealand and overseas oils	181
58	PC3/PC2 for New Zealand and overseas oils	182
59	PC2/PC1 for all oil samples (6 trace elements)	183
60	PC3/PC1 for all oil samples (6 trace elements)	184
61	PC3/PC2 for all oil samples (6 trace elements)	185

62	Three dimensional graph of principal components for New Zealand and overseas oils	186
62a	Three dimensional graph of principal components for New Zealand and overseas oils (individual groups)	187
63	Three dimensional graph of principal components (6 trace elements) for all oil samples	188
63a	Three dimensional graph of principal components (6 trace elements) for all oil samples (individual groups)	189
64	PC2/PC1 for New Zealand oils and bitumen	191
65	PC3/PC2 for New Zealand oils and bitumen	192
66	Cobalt (ng/g) versus Ni ( $\mu\text{g/g}$ ) for New Zealand asphaltene samples	196
67	Manganese (ng/g) versus Fe ( $\mu\text{g/g}$ ) for New Zealand asphaltene samples	196
68	Cobalt (ng/g) in maltenes and asphaltenes for New Zealand oils	197
69	Nickel ( $\mu\text{g/g}$ ) in maltenes and asphaltenes for New Zealand oils	197
70	Cobalt (ng/g) versus Ni ( $\mu\text{g/g}$ ) for New Zealand and some overseas asphaltene samples	198

## LIST OF TABLES

2.1	Evolution of sedimentary matter	22
2.2	Complete sample list	37-39
2.3	Well cutting and coal samples	59
3.1	Trace element concentrations in filtered and unfiltered ToeToe-2B oil solutions	64
3.2	Trace element concentrations in untreated, ashed and acid-oxidised Tuhua-2 oil	71
3.3	Trace element concentrations in aqueous standard BEC1, before and after acid-oxidation	71
3.4	Nickel values in standard oil and some New Zealand oils, determined in a mixed-solvent system	77
3.5	Zinc concentrations ( $\mu\text{g/g}$ ) in some New Zealand oils, determined by INAA and GFAAS	78
3.6	Nickel concentrations ( $\mu\text{g/g}$ ) in some New Zealand oils, determined by INAA and GFAAS	81
3.7	Asphaltene content of oil samples	89
3.8	Asphaltene content in New Zealand oils, compared with results from other studies	90
3.9	Comparison of Ni, Co and Fe concentrations in asphaltenes, determined by INAA and GFAAS	90
3.10	List of coal samples and ash content	91
3.11	Bitumen content (wt %) of rock and coal samples	96
3.12	Irradiation, decay and counting times for INAA	102
3.13	Trace element content of NBS standard oils	112
3.14	Instrumental NAA analysis of a Venezuelan standard oil	113
3.15	Wavelengths used for the determination of trace elements by GFAAS	118

3.16	Drying, ashing and atomizing temperatures used in the determination of trace elements by GFAAS	121
4.1	Variations in trace element concentrations in Waitangi Seep oil sample	125
4.2	Trace element concentrations of oils stored in glass and metal containers	126
4.3	Vanadium/Ni and Ni/V ratios for oils from the McKee Field	130

## APPENDICES

<b>A</b>	Trace elements concentrations in New Zealand oils	230
<b>B</b>	Trace elements concentrations (17) in overseas oils	231
<b>C</b>	Trace elements concentrations (6) in overseas oils	232
<b>D</b>	Nickel/V and V/Ni ratios for New Zealand oils	233
<b>E</b>	Cadmium, Cu and Pb concentrations determined in a mixed-solvent system	234
<b>F</b>	Trace element concentrations in bitumen	235
<b>G</b>	Trace element concentrations in coal, determined by ICP-ES and GFAAS	236
<b>H</b>	Trace element concentrations in asphaltenes	237
<b>I</b>	Trace element concentrations in kerogen	238
<b>J</b>	Trace elements in formation water	239
<b>K</b>	Original correlation matrix for New Zealand oils	240
<b>L</b>	Original correlation matrix for overseas oils	241
<b>M</b>	Original correlation matrix for overseas oils (6 elements)	242
<b>N</b>	Original correlation matrix for New Zealand oils and bitumen	243
<b>O</b>	Principal components analysis, New Zealand oils	244
<b>P</b>	Principal components analysis, New Zealand and overseas oils	245
<b>Q</b>	Principal components analysis, New Zealand and overseas oils (6 elements)	246
<b>R</b>	Principal components analysis, New Zealand oils and bitumen	247