MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file - Votre référence

Our file - Notre référence

NOTICE

The quality of this microform is heavily dependent upon the quality of the original thesis submitted for microfilming. Every effort has been made to ensure the highest quality of reproduction possible.

If pages are missing, contact the university which granted the degree.

Some pages may have indistinct print especially if the original pages were typed with a poor typewriter ribbon or if the university sent us an inferior photocopy.

Reproduction in full or in part of this microform is governed by the Canadian Copyright Act, R.S.C. 1970, c. C-30, and subsequent amendments.

AVIS

La qualité de cette microforme dépend grandement de la qualité de la thèse soumise au microfilmage. Nous avons tout fait pour assurer une qualité supérieure de reproduction.

S'il manque des pages, veuillez communiquer avec l'université qui a conféré le grade.

La qualité d'impression de certaines pages peut laisser à désirer, surtout si les pages originales ont été dactylographiées à l'aide d'un ruban usé ou si l'université nous a fait parvenir une photocopie de qualité inférieure.

La reproduction, même partielle, de cette microforme est soumise à la Loi canadienne sur le droit d'auteur, SRC 1970, c. C-30, et ses amendements subséquents.

**A MULTI-TECHNIQUE STRATEGY FOR STUDY OF SOME
MECHANISMS OF ATOM FORMATION AND DISSIPATION
IN
ELECTROTHERMAL ATOMIC ABSORPTION
SPECTROMETRY**

by

MARC MAURICE LAMOUREUX, B. Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of

Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

July 8, 1993

© copyright

1993, Marc Maurice Lamoureux

National Library
of Canada

Acquisitions and
Bibliographic Services Branch

395 Wellington Street
Ottawa, Ontario
K1A 0N4

Bibliothèque nationale
du Canada

Direction des acquisitions et
des services bibliographiques

395, rue Wellington
Ottawa (Ontario)
K1A 0N4

Your file Votre référence

Our file Notre référence

The author has granted an irrevocable non-exclusive licence allowing the National Library of Canada to reproduce, loan, distribute or sell copies of his/her thesis by any means and in any form or format, making this thesis available to interested persons.

L'auteur a accordé une licence irrévocable et non exclusive permettant à la Bibliothèque nationale du Canada de reproduire, prêter, distribuer ou vendre des copies de sa thèse de quelque manière et sous quelque forme que ce soit pour mettre des exemplaires de cette thèse à la disposition des personnes intéressées.

The author retains ownership of the copyright in his/her thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without his/her permission.

L'auteur conserve la propriété du droit d'auteur qui protège sa thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

ISBN 0-315-89783-X

Canada

Name MARC Maurice Lamoureux

Dissertation Abstracts International is arranged by broad, general subject categories. Please select the one subject which most nearly describes the content of your dissertation. Enter the corresponding four-digit code in the spaces provided.

Analytical Chemistry

SUBJECT TERM

0486

SUBJECT CODE

U·M·I

Subject Categories

THE HUMANITIES AND SOCIAL SCIENCES

COMMUNICATIONS AND THE ARTS

Architecture 0729
Art History 0377
Cinema 0900
Dance 0378
Fine Arts 0357
Information Science 0723
Journalism 0391
Library Science 0399
Mass Communications 0708
Music 0413
Speech Communication 0459
Theater 0465

EDUCATION

General 0515
Administration 0514
Adult and Continuing 0516
Agricultural 0517
Art 0273
Bilingual and Multicultural 0282
Business 0688
Community College 0275
Curriculum and Instruction 0727
Early Childhood 0518
Elementary 0524
Finance 0277
Guidance and Counseling 0519
Health 0680
Higher 0745
History of 0520
Home Economics 0278
Industrial 0521
Language and Literature 0279
Mathematics 0280
Music 0522
Philosophy of 0998
Physical 0523

Psychology 0525
Reading 0535
Religion 0527
Sciences 0714
Secondary 0533
Social Sciences 0534
Sociology of 0340
Special 0529
Teacher Training 0530
Technology 0710
Tests and Measurements 0288
Vocational 0747

LANGUAGE, LITERATURE AND LINGUISTICS

Language
 General 0679
 Ancient 0289
 Linguistics 0290
 Modern 0291
Literature
 General 0401
 Classical 0294
 Comparative 0295
 Medieval 0297
 Modern 0298
 African 0316
 American 0591
 Asian 0305
 Canadian (English) 0352
 Canadian (French) 0355
 English 0593
 Germanic 0311
 Latin American 0312
 Middle Eastern 0315
 Romance 0313
 Slavic and East European 0314

PHILOSOPHY, RELIGION AND THEOLOGY

Philosophy 0422
Religion
 General 0318
 Biblical Studies 0321
 Clergy 0319
 History of 0320
 Philosophy of 0322
Theology 0469

SOCIAL SCIENCES

American Studies 0323
Anthropology
 Archaeology 0324
 Cultural 0326
 Physical 0327
Business Administration
 General 0310
 Accounting 0272
 Banking 0770
 Management 0454
 Marketing 0338
Canadian Studies 0385
Economics
 General 0501
 Agricultural 0503
 Commerce-Business 0505
 Finance 0508
 History 0509
 Labor 0510
 Theory 0511
Folklore 0358
Geography 0366
Gerontology 0351
History
 General 0578

Ancient 0579
Medieval 0581
Modern 0582
Black 0328
African 0331
Asia, Australia and Oceania 0332
Canadian 0334
European 0335
Latin American 0336
Middle Eastern 0333
United States 0337
History of Science 0585
Law 0398
Political Science
 General 0615
 International Law and Relations 0616
 Public Administration 0617
Recreation 0814
Social Work 0452
Sociology
 General 0626
 Criminology and Penology 0627
 Demography 0938
 Ethnic and Racial Studies 0631
 Individual and Family Studies 0628
 Industrial and Labor Relations 0629
 Public and Social Welfare 0630
 Social Structure and Development 0700
 Theory and Methods 0344
Transportation 0709
Urban and Regional Planning 0999
Women's Studies 0453

THE SCIENCES AND ENGINEERING

BIOLOGICAL SCIENCES

Agriculture
 General 0473
 Agronomy 0285
 Animal Culture and Nutrition 0475
 Animal Pathology 0476
 Food Science and Technology 0359
 Forestry and Wildlife 0478
 Plant Culture 0479
 Plant Pathology 0480
 Plant Physiology 0817
 Range Management 0777
 Wood Technology 0746
Biology
 General 0306
 Anatomy 0287
 Biostatistics 0308
 Botany 0309
 Cell 0379
 Ecology 0329
 Entomology 0353
 Genetics 0369
 Limnology 0793
 Microbiology 0410
 Molecular 0307
 Neuroscience 0317
 Oceanography 0416
 Physiology 0433
 Radiation 0821
 Veterinary Science 0778
 Zoology 0472
Biophysics
 General 0786
 Medical 0760

EARTH SCIENCES

Biogeochemistry 0425
Geochemistry 0996

Geodesy 0370
Geology 0372
Geophysics 0373
Hydrology 0388
Mineralogy 0411
Paleobotany 0345
Paleoecology 0426
Paleontology 0418
Paleozoology 0985
Palynology 0427
Physical Geography 0368
Physical Oceanography 0415

HEALTH AND ENVIRONMENTAL SCIENCES

Environmental Sciences 0768
Health Sciences
 General 0566
 Audiology 0300
 Chemotherapy 0992
 Dentistry 0567
 Education 0350
 Hospital Management 0769
 Human Development 0758
 Immunology 0982
 Medicine and Surgery 0564
 Mental Health 0347
 Nursing 0569
 Nutrition 0570
 Obstetrics and Gynecology 0380
 Occupational Health and Therapy 0354
 Ophthalmology 0381
 Pathology 0571
 Pharmacology 0419
 Pharmacy 0572
 Physical Therapy 0382
 Public Health 0573
 Radiology 0574
 Recreation 0575

Speech Pathology 0460
Toxicology 0383
Home Economics 0386

PHYSICAL SCIENCES

Pure Sciences
Chemistry
 General 0485
 Agricultural 0749
 Analytical 0486
 Biochemistry 0487
 Inorganic 0488
 Nuclear 0738
 Organic 0490
 Pharmaceutical 0491
 Physical 0494
 Polymer 0495
 Radiation 0754
Mathematics 0405
Physics
 General 0605
 Acoustics 0986
 Astronomy and Astrophysics 0606
 Atmospheric Science 0608
 Atomic 0748
 Electronics and Electricity 0607
 Elementary Particles and High Energy 0798
 Fluid and Plasma 0759
 Molecular 0609
 Nuclear 0610
 Optics 0752
 Radiation 0756
 Solid State 0611
Statistics 0463
Applied Sciences
Applied Mechanics 0346
Computer Science 0984

Engineering
 General 0537
 Aerospace 0538
 Agricultural 0539
 Automotive 0540
 Biomedical 0541
 Chemical 0542
 Civil 0543
 Electronics and Electrical 0544
 Heat and Thermodynamics 0348
 Hydraulic 0545
 Industrial 0546
 Marine 0547
 Materials Science 0794
 Mechanical 0548
 Metallurgy 0743
 Mining 0551
 Nuclear 0552
 Packaging 0549
 Petroleum 0765
 Sanitary and Municipal 0554
 System Science 0790
Geotechnology 0428
Operations Research 0796
Plastics Technology 0795
Textile Technology 0994

PSYCHOLOGY

General 0621
Behavioral 0384
Clinical 0622
Developmental 0620
Experimental 0623
Industrial 0624
Personality 0625
Physiological 0989
Psychobiology 0349
Psychometrics 0632
Social 0451

The undersigned hereby recommend to
the Faculty of Graduate Studies and Research
acceptance of the thesis,

**"A MULTI-TECHNIQUE STRATEGY FOR STUDY OF SOME MECHANISMS
OF ATOM FORMATION AND DISSIPATION IN ELECTROTHERMAL ATOMIC
ABSORPTION SPECTROMETRY"**

submitted by
MARC MAURICE LAMOUREUX, B. Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

ABSTRACT

A multi-technique strategy was employed for study of some mechanisms of atom formation and dissipation in electrothermal atomization atomic absorption spectrometry (ETAAS).

The mechanism of interference by magnesium chloride matrix with the determination of manganese in ETAAS was studied using electrothermal vaporization inductively coupled plasma mass spectrometry (ETV-ICP-MS). At temperatures below 700°C, the suppression in the manganese atomic absorption signal is due to a vapour-phase interference caused by formation of manganese chloride during atomization. At temperatures above 700°C, manganese is lost during pyrolysis; this loss occurs as the magnesium chloride matrix undergoes hydrolytic decomposition, and the manganese is carried away from the graphite furnace with the hydrogen chloride gas generated by the hydrolysis reaction. The ascorbic acid chemical modifier removes the interference in both the lower and the higher pyrolysis temperature regions.

The interference by sodium chloride with the determination of manganese in ETAAS was also studied with chemical modification by ascorbic acid. The suppression in the manganese atomic absorption signal is due to a vapour-phase interference caused by formation of manganese chloride during atomization. The ascorbic acid chemical modifier removes the sodium chloride interference at all pyrolysis temperatures investigated (450-1100°C) by promoting an early release of chloride during the atomization cycle.

A commercial graphite furnace was modified and coupled to an ICP-MS. This

modified furnace allows simultaneous measurement of atomic absorption (AA), or molecular absorption (MA), and ICP-mass spectrometric signals of samples. The modified furnace was characterized and its performance was evaluated for 57 elements.

The modified furnace coupled to the ICP-MS and a charge-coupled device (CCD) imaging system were used to investigate the mechanism of formation and dissipation of aluminium spikes in ETAAS. This multi-technique strategy has allowed the acquisition of temporally and spatially resolved spectra of Al atoms and Al-containing molecules during an Al spike formation and dissipation. It is proposed that the Al spikes are formed from Al_2O as precursors of Al atoms and that this reaction is triggered by the formation of an Al_4C_3 melt.

REMERCIEMENTS/ACKNOWLEDGEMENTS

Beaucoup d'efforts furent dépensés afin d'amener à terme cet ouvrage, et autant de support et d'encouragement en a-t-ils nécessités. Je dois tout d'abord remercier du plus profond de mon coeur mon épouse, Micheline Millette, qui mérite sûrement un doctorat pour toute la patience, la compréhension, et l'amour qu'elle a su démontrer envers moi durant ces années d'études graduées.

Ils y a évidemment tous les amis(es) qui, au fil des ans, m'ont répété leur encouragement et fierté face à ce but qui était si cher à mes yeux. Merci particulièrement à Alfred Deschênes et Michelle Gélinas, à Lucie Gélinas et Richard Beaulieu, et à Gary Swindells et Nathalie Beaumont pour tout les bons moments que nous avons partagés ensemble. À mes meilleurs amis, Gilles Groulx et Françoise Racette, je dis merci pour tout l'amour que vous avez manifesté envers moi, et une partie de cette thèse contient l'inspiration et la motivation que vous m'avez apporté.

Je tiens à remercier tous les membres de ma famille, Alain, Linda, Johanne, Manon, et particulièrement mes parents et mes beau-parents que j'aime beaucoup, pour l'affection qu'ils m'ont toujours manifesté.

This thesis could not have been accomplished without the support of many people. My scientific development has been moulded by three great men, they moulded me like potters who work clay: First, Professor John Byrne from Australia, who virtually sculptured me and made me think like a scientist should think! Memories of our collaboration will always be a great source of motivation - Thank you John. Second, I

wish to express my sincere gratitude to Dr. Conrad Grégoire who helped refining my scientific abilities by carving my raw knowledge such that it became a mind with clear ideas. Third, but certainly not the least, Professor Chakrabarti; Chak let John and Conrad forge my raw scientific potential while he was taking care of my soul! He ask me to look deep inside myself to search where I was and where I wanted to go; and then he showed me that a straight line is the quickest route to get to my objectives and not by wandering around (Brownien motion), **THERE IS JUST NO TIME!** Your adoptive son is indebted to you for life Chak.

I have been fortunate to have the privilege of working and collaborating with great scientist. One of the great scientists that I had the opportunity to collaborate with was Professor Albert Gilmudinov from Kazan University, Russia, and I wish to thank him very much for his valuable discussion and support.

I wish to thank all the people in the lab (graduate students, visiting scholars, undergraduate students), and especially Doug Goltz, Glen Gilchrist, Kurt Headrick, Tam Ly, Shamil Cathum, Yanja Lu, Jianguo Cheng, Amina Sekali, Brian Dimock, Victor Pavski, Absalan, Victoria VanderNoot, Sabah Al-Maawali, Diane Hughes, who had to cope with my French accent for nearly five years but who always help me and supported me. In particular, I wish to thank Craig Hutton, a great friend who showed a lot of understanding.

Many thanks to all the supporting staff of the Department of Chemistry, especially the secretaries, Marilyn, Kim and Ms. Villeneuve, to Karl and Robert from the chemistry store, and to Michel and Jim from the electronic shop.

TABLE OF CONTENTS

ACCEPTANCE SHEET	ii
ABSTRACT	iii
REMERCIEMENTS/ACKNOWLEDGEMENTS	v
LIST OF TABLES	xiii
LIST OF FIGURES	xv
LIST OF ABBREVIATIONS	xxiii
INTRODUCTION	1
CHAPTER 1	
MECHANISM OF INTERFERENCES BY MAGNESIUM CHLORIDE MATRIX AND MECHANISM OF CHEMICAL MODIFICATION BY ASCORBIC ACID WITH THE ATOMIZATION OF MANGANESE IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY	5
INTRODUCTION	5

EXPERIMENTAL	10
Atomic Absorption Spectrometry	10
Apparatus	10
Gases	10
Standards and Reagents	11
Experimental and Operating Conditions	12
Determination of the Residual Magnesium Chloride	12
Apparatus	12
Standards and Reagents	14
Extraction Procedure	14
Electrothermal Vaporization Inductively-Coupled Plasma Mass	
Spectrometry	16
Apparatus	16
Standards and reagents	18
RESULTS AND DISCUSSION	21
ETAAS experiments	21
ETV-ICP-MS experiments	30
Mechanism of removal of the MgCl_2 matrix interference by	
ascorbic acid	45
SUMMARY	50

CHAPTER 2

MECHANISM OF INTERFERENCES BY SODIUM CHLORIDE MATRIX AND MECHANISM OF CHEMICAL MODIFICATION BY ASCORBIC ACID WITH THE ATOMIZATION OF MANGANESE IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY 52

INTRODUCTION 52

EXPERIMENTAL 55

Atomic Absorption Spectrometry 55

Apparatus 55

Gases 56

Standards and Reagents 56

Experimental and Operating Conditions 57

Determination of the Residual Sodium Chloride 58

Apparatus 58

Standards and Reagents 58

Extraction Procedure 59

Electrothermal Vaporization Inductively-Coupled Plasma Mass

Spectrometry 60

Apparatus 60

Standards and reagents 61

RESULTS AND DISCUSSION 61

ETAAS experiments 61

ETV-ICP-MS experiments	70
Gas-phase chemical modification	80
Mechanism of removal of chloride interference by ascorbic acid . .	83
SUMMARY	90

CHAPTER 3

CHARACTERIZATION AND PERFORMANCE EVALUATION OF A MODIFIED ELECTROTHERMAL VAPORIZER FOR AN INDUCTIVELY COUPLED PLASMA

MASS SPECTROMETER	92
INTRODUCTION	92
EXPERIMENTAL	96
Apparatus	96
Standards and Reagents	102
RESULTS AND DISCUSSION	104
Parametric evaluation	104
Internal flow	104
Total flow	110
Vaporization temperature	112
Analytical calibration curve	114
Comparison of signal characteristics of ETAAS and ICP-MS . . .	120
Qualitative evaluation of the carrier gas flow	120
Appearance time	121

Peak broadening	124
Difference in the time scale	125
Interferences with Mn determination by the $MgCl_2$ matrix (revisited)	128
Quantitative determination	132
Limits of detection and sensitivity	132
Determination of silver in Geostandards	157
SUMMARY	161

CHAPTER 4

MECHANISM OF ALUMINIUM SPIKE FORMATION AND DISSIPATION IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY	164
INTRODUCTION	164
EXPERIMENTAL	169
Apparatus	169
Simultaneous measurement of ETAAS and ETV-ICP-MS signals	169
Graphite and tungsten strip ETV-ICP-MS	171
The imaging system	173
Standards and Reagents	176
RESULTS AND DISCUSSION	177
Determination of impurities in the aluminium test solution	177

ETV-ICP-MS signals for vaporization from the graphite or the tungsten strip	178
Simultaneous measurement of atomic or molecular absorption and ICP-MS signals	187
CCD imaging	195
Vaporization from the tube surface	196
Vaporization from a graphite platform surface	209
Mechanism of Al spikes formation	223
SUMMARY	226
REFERENCES	228

LIST OF TABLES

Table 1.	Experimental and operating conditions of the graphite furnace used for atomization of manganese.	13
Table 2.	Experimental and operating conditions for the determination of the residual magnesium chloride.	15
Table 3.	Experimental and operating conditions for the ETV-ICP-MS. . . .	20
Table 4.	Experimental and operating conditions of the ETV-ICP-MS for the parametric evaluation of the modified furnace and for the determination of silver.	105
Table 5.	Experimental and operating conditions of the ETV-ICP-MS for the evaluation of the difference in the time scale.	126
Table 6.	Experimental and operating conditions of the ETV-ICP-MS for determination of the limits of detection of the modified electrothermal vaporizer.	133
Table 7.	Limits of detection in parts-per-trillion (ppt) for the modified electrothermal vaporizer and other literature values.	135
Table 8.	Effect of NASS-1, vaporization temperature, and vaporization surface on the sensitivity (counts pg^{-1}) of the elements determined using the modified electrothermal vaporizer.	141
Table 9.	Determination of Ag in geological reference material using the isotope dilution technique.	159
Table 10.	Experimental and operating conditions of the ETV-ICP-MS and the	

	ETAAS for the investigation of Al spikes formation.	172
Table 11.	Experimental and operating conditions of the graphite strip and the tungsten strip ETV-ICP-MS.	174

LIST OF FIGURES

Figure 1.	Schematic diagram of the laboratory-made electrothermal vaporizer (ETV).	17
Figure 2.	Schematic diagram of the electrothermal vaporizer (ETV) coupled to the inductively-coupled plasma mass spectrometer (ICP-MS).	19
Figure 3.	Pyrolysis curve (A) and atomization curve (B) for 400 pg Mn + 200 μ g MgCl ₂ in 1% v/v HCl.	23
Figure 4.	Pyrolysis curves in ETAAS.	24
Figure 5.	Typical absorbance profiles in ETAAS at a pyrolysis temperature of 900°C.	25
Figure 6.	Pyrolysis curves in ETAAS.	28
Figure 7.	Temporal behaviour of ⁵⁵ Mn ⁺ in ETV-ICP-MS in various matrices as a function of the pyrolysis temperature of the graphite strip. . .	32
Figure 8.	Temporal behaviour of ⁵⁵ Mn ⁺ in ETV-ICP-MS in various matrices at a pyrolysis temperature 700-900°C of the graphite strip.	33
Figure 9.	Temporal behaviour of ⁵⁵ Mn ⁺ in ETV-ICP-MS at a pyrolysis temperature 500-600°C of the graphite strip.	36
Figure 10.	Absorbance profiles of Mn in ETAAS at a pyrolysis temperature of 600°C.	37
Figure 11.	Temporal behaviour of ³⁷ Cl ⁺ in ETV-ICP-MS in various matrices at different pyrolysis temperatures of the graphite strip.	38

Figure 12.	Temporal behaviour of $^{25}\text{Mg}^+$ in ETV-ICP-MS in various matrices at different pyrolysis temperatures of the graphite strip.	41
Figure 13.	Percentage of residual magnesium and chloride as a function of the pyrolysis temperature.	46
Figure 14.	Mole ratio of magnesium to chloride remaining after pyrolysis as a function of the pyrolysis temperature.	49
Figure 15.	Pyrolysis curve (A) and atomization curve (B) for 400 pg Mn in 1% v/v HNO_3 (●) and 400 pg Mn in 1% v/v HCl (■) for atomization from the graphite tube wall.	63
Figure 16.	Pyrolysis curve (A) and atomization curve (B) for 400 pg Mn + 100 μg NaCl in 1% v/v HCl	65
Figure 17.	Typical absorbance profiles in GFAAS for Mn after pyrolysis at 550°C.	67
Figure 18.	Pyrolysis curves in GFAAS for Mn in various matrices.	69
Figure 19.	Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS for various matrices at pyrolysis temperature 550°C.	73
Figure 20.	Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS for A: 200 pg of Mn + 50 μg NaCl in 0.04% v/v HCl ; pyrolysis temperature, 900°C.	74
Figure 21.	Temporal behaviour of (a) $^{23}\text{Na}^+$ and (b) $^{37}\text{Cl}^+$ in ETV-ICP-MS at a pyrolysis temperature 900°C.	76
Figure 22.	Temporal behaviour of $^{23}\text{Na}^+$ in ETV-ICP-MS for 200 pg Mn +	

	50 μg NaCl in 0.04% v/v HCl for two different pyrolysis temperatures.	79
Figure 23.	Pyrolysis curves in GFAAS for 400 pg Mn + 1% v/v HCl in argon gas (A); in argon gas containing 5% v/v H ₂ gas (B); for 400 pg Mn + 100 μg NaCl + 1% v/v HCl in argon gas (C); in argon gas containing 5% v/v H ₂ gas (D).	81
Figure 24.	Percentage of residual sodium and chloride as a function of the pyrolysis temperature.	84
Figure 25.	Mole ratio of sodium to chloride remaining after pyrolysis as a function of the pyrolysis temperature.	85
Figure 26.	Temporal behaviour of $^{37}\text{Cl}^+$ and $^{55}\text{Mn}^+$ in ETV-ICP-MS for various matrices at a pyrolysis temperature 550°C.	88
Figure 27.	Schematic diagram of the modified Perkin-Elmer HGA 76B graphite furnace.	97
Figure 28.	Photographs of the modified Perkin-Elmer HGA 76B graphite furnace.	98
Figure 29.	Block diagram of the ETAAS-ICP-MS simultaneous measurement apparatus.	101
Figure 30.	Block diagram of the flowmeter set-up with its equivalent electric circuit diagram.	106
Figure 31.	The effect of internal Ar flow on the integrated ion intensity of 50 ng ml ⁻¹ of Ag vaporized from the tube surface.	108

Figure 32.	The effect of the total Ar flow on the integrated ion intensity of 50 ng ml ⁻¹ of Ag vaporized from the tube surface.	111
Figure 33.	The effect of the vaporization temperature on the integrated ion intensity of 20 ng ml ⁻¹ of Ag vaporized from the tube surface. . .	113
Figure 34.	Analytical calibration curves for Ag.	116
Figure 35.	Ag transient in ICP-MS with the modified furnace ETV.	118
Figure 36.	Photograph showing the smoke plume from a piece of plastic vaporized at 2200°C.	122
Figure 37.	Temporal behaviour of 250 pg of Ag with simultaneous measurement of the ETAAS and ICP-MS signals.	123
Figure 38.	Temporal behaviour of 2 µg of Al with simultaneous measurement of the ETAAS and ICP-MS signals.	127
Figure 39.	Temporal behaviour of 100 pg of Mn in 1% HCl plus 200 pg of MgCl ₂ with simultaneous measurement of the ETAAS and ICP-MS signals.	130
Figure 40.	Temporal behaviour of some analytes in ICP-MS with vaporization from the platform surface at 2500°C.	146
Figure 41.	Temporal behaviour of some analytes in ICP-MS with vaporization from the platform surface at 2500°C.	148
Figure 42.	Temporal behaviour of some analytes in ICP-MS with vaporization from the platform surface at 2500°C.	150
Figure 43.	Temporal behaviour in ICP-MS of Ag, Cu, and Ni in the presence	

	of 350 ng of NASS-1 with vaporization from the graphite tube surface.	153
Figure 44.	Temporal behaviour in ICP-MS of Pt (solid line) and Te (broken line) in the presence of 350 ng of NASS-1 with vaporization from the platform surface.	154
Figure 45.	Temporal behaviour in ICP-MS of Eu (solid line) and Yb (broken line) in the presence of 350 ng of NASS-1 with vaporization temperature of 2650°C.	156
Figure 46.	Temporal distribution in ICP-MS of ^{109}Ag (solid line) and ^{107}Ag (broken line) from enriched ^{109}Ag added to geostandard materials.	160
Figure 47.	Temporal behaviour in the graphite strip ETV-ICP-MS of Al (broken line), AlO ($\diamond$), Al_2O (Δ), and AlC_2 ($\square$).	180
Figure 48.	Temporal behaviour of Al in ICP-MS (dotted line), C (dash-dotted line), and $m/z = 51$ (solid line).	184
Figure 49.	Temporal behaviour of Al (broken line); AlO (solid line) in the graphite strip ETV-ICP-MS.	186
Figure 50.	Simultaneous measurement of AAS and ICP-MS signals.	188
Figure 51.	Simultaneous measurement of MAS and ICP-MS signals.	190
Figure 52.	Simultaneous measurement of AAS and ICP-MS signals.	192
Figure 53.	Temporal behaviour in ETV-ICP-MS of Al (broken line) and m/z 28 (solid line).	193

Figure 54.	Sequence of atomic absorption images for the atomization of aluminium from the tube surface under Ar gas stop- flow conditions.	197
Figure 55.	Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the tube surface under Ar gas stop-flow conditions.	198
Figure 56.	Sequence of molecular absorption images for the vaporization of Al_2O from the tube surface under Ar gas stop-flow conditions. .	200
Figure 57.	Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O from the tube surface under Ar gas stop-flow conditions.	201
Figure 58.	Sequence of atomic absorption images for the atomization of aluminium from the tube surface under a convective flow of Ar purge gas.	204
Figure 59.	Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the tube surface under a convective flow of Ar purge gas.	205
Figure 60.	Sequence of molecular absorption images for the vaporization of Al_2O from the tube surface under a convective flow of Ar purge gas.	207
Figure 61.	Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O from the tube surface under	

	a convective flow of Ar purge gas.	208
Figure 62.	Sequence of atomic absorption images for the atomization of aluminium from the platform surface under stop-flow conditions.	211
Figure 63.	Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the platform surface under stop-flow conditions.	212
Figure 64.	Sequence of molecular absorption images for the vaporization of Al_2O from the tube surface under the gas stop-flow conditions.	215
Figure 65.	Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O from the tube surface under the gas stop-flow conditions.	216
Figure 66.	Sequence of atomic absorption images for the atomization of aluminium from the platform surface under the convective flow of Ar purge gas.	217
Figure 67.	Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the platform surface under the convective flow of Ar gas.	218
Figure 68.	Sequence of molecular absorption images for the vaporization of Al_2O from the tube surface under the convective flow of Ar gas.	220
Figure 69.	Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O from the tube surface under the convective flow of Ar gas.	221

Figure 70. Sequence of molecular absorption images for the vaporization of Al_2O_3 from the tube surface under the gas stop-flow conditions. . 222

LIST OF ABBREVIATIONS

ETAAS:	Electrothermal atomization atomic absorption spectrometry
ETV-ICP-MS:	Electrothermal vaporization inductively coupled plasma mass spectrometry
AA(S)	Atomic absorption (spectrometry)
MA(S)	Molecular absorption (spectrometry)
CCD	Charge coupled device
GFAAS	Graphite furnace atomic absorption spectrometry
ppt	part-per-trillion
m/z	mass-to-charge ratio
STPF	Stabilized temperature platform furnace
SSF	Spectral shadow filming
SN-ICP-MS	Solution nebulization inductively coupled mass spectrometry
RSD	Relative standard deviation
ROC	Reduction of oxides by carbides
FWHM	Full width at half maximum

INTRODUCTION

Determination of analyte elements in various samples at the trace level (parts-per-million) can be routinely done by electrothermal atomization atomic absorption spectrometry (ETAAS). This technique has been the object of many reviews and has been described by Welz¹. The development of ETAAS over the last few years has been intimately linked with the understanding of the fundamental processes of atom formation and dissipation^{2,3}. Mechanistic studies have permitted the development of the stabilized temperature platform furnace (STPF) technique which allows the elimination of many of the previously reported interferences^{4,5}.

Investigation of fundamental processes that are occurring in ETAAS are slow and sporadic because of the complex nature of the processes involved. Knowledge about mechanisms of atom formation and dissipation for a simple sample matrix is not complete and is even less complete for a complex sample matrix. Various approaches have been used to study mechanisms of atom formation and dissipation in ETAAS. The following approaches have been relatively successful: (1) evaluation of the chemical composition within the graphite furnace using thermodynamic equilibrium calculations^{6,7}, (2) study of atomization mechanisms by determining the activation energy, E_a , which characterizes the rate-determining step^{8,9}, (3) use of decomposition-atomization curves to understand the relationship between the appearance of analyte atoms and the presence of analyte containing molecules^{10,11}, and (4) the utilization of external techniques such as mass spectrometry^{12,13}, Rutherford backscattering spectroscopy (RBS)¹⁴, scanning electron microscopy (SEM)¹⁵, and imaging of the interior of an electrothermal atomizer by

spectral shadow filming (SSF) technique^{16,17}.

This thesis presents new investigative ways for studying mechanisms of atom formation and dissipation in ETAAS. Electrothermal vaporization with inductively coupled plasma mass spectrometry (ETV-ICP-MS) combined with measurements of the AAS signals obtained with a graphite furnace atomizer and a conventional spectrophotometer were used to elucidate the mechanisms of chloride interferences and the mechanisms of chemical modification by ascorbic acid. A commercial graphite furnace was modified in order to be used with the ICP-MS. This modified graphite furnace was designed to possess two important features: (1) to be an efficient sample introduction device for ICP-MS, and (2) to allow simultaneous measurement of the atomic absorption, or molecular absorption, and ICP-mass spectrometric signals.

Chapters 1 and 2 deal with investigation of chloride matrix interferences with the determination of manganese. It has been reported that the determination of manganese suffers from an interference from chloride matrices such as magnesium chloride and sodium chloride^{18,19}. The mechanisms by which these chloride matrices interfere with the determination of manganese are not fully known. To alleviate the interferences due to the chloride matrices, chemical agents, called chemical modifiers, are added to the sample in order to allow selective volatilization of the sample matrix without loss of analyte during the pyrolysis step. The mechanisms by which these chemical modifiers remove the chloride interferences are also not fully known. Chapter 1 deals with the mechanism of magnesium chloride interferences with the determination of manganese and the mechanism of chemical modification by ascorbic acid with the magnesium chloride

matrix as the interferent. Chapter 2 deals with the mechanisms of sodium chloride interferences with the determination of manganese and the mechanisms of chemical modification by ascorbic acid with sodium chloride matrix as the interferent. Both Chapters 1 and 2 present for the first time experimental evidence obtained by using ETV-ICP-MS as an investigative tool for studying fundamental processes occurring in ETAAS. Based on the new evidence obtained by ETV-ICP-MS, new mechanisms for chloride matrix interferences and for ascorbic acid chemical modification with the determination of manganese are proposed and discussed.

Chapter 3 describes the modification of a commercial graphite furnace that has been used with the ICP-MS as a sample introduction device and as an investigative tool for studying mechanisms of atom formation and dissipation in ETAAS. The redesigning of the commercial graphite furnace has allowed the development of a new analytical apparatus: the ETAA-ICP-mass spectrometer that allows the simultaneous measurement of the atomic absorption (AA), or molecular absorption (MA), and the ICP-mass spectrometric signals. The modified furnace was characterized and its performance was evaluated. The potential of the modified graphite furnace as a valuable complementary tool for investigating fundamental processes is assessed by revisiting the problem of the magnesium chloride interference with the determination of manganese.

Chapter 4 deals with formation of aluminium spikes in graphite furnace AAS - a phenomenon that has remained virtually unexplainable for the last ten years. L'vov and Savin^{20,21} have reported that when large quantities (microgram amounts) of aluminium (taken as the nitrate) are slowly heated under argon atmosphere in a graphite

furnace, a series of rapid bursts of atomic absorption signal appeared on top of a smoothly increasing Al atomic absorption signal. L'vov *et al.*²² have proposed to explain the occurrence of Al spikes by suggesting that condensed-phase aluminium oxides are reduced by gaseous aluminium carbides. This mechanism has failed to gain a general acceptance and other mechanisms have now been proposed¹⁷. Significant progress in the understanding the Al spike phenomenon has been made by Holcombe *et al.*¹², Styris and Redfield¹³, and Gilmutdinov *et al.*^{16,17}. However, the work by Holcombe *et al.*¹² was done by atomization of the aluminium sample under a vacuum, and the work by Styris and Redfield¹³ was done under nitrogen atmosphere. Hence, their results may not be applicable to the Al-spike formation under argon atmosphere in normal graphite furnace AAS. The pioneering work by Gilmutdinov *et al.*^{16,17}, the spectral shadow filming (SSF) technique, lacks sensitivity and quantitative information. In order to understand the mechanism of Al-spikes formation and dissipation in ETAAS, a multi-technique strategy has been used in this thesis research. By measuring simultaneously the atomic absorption (AA), or the molecular absorption (MA), and the ICP-mass spectrometric signals, new evidence about the temporal distribution of various Al atoms and Al-containing species have been obtained. In addition, the graphite furnace interior has been studied using a charge-coupled device (CCD) imaging system²³. These results combined with those of AA/MA-ICP-mass spectrometry have allowed a better understanding of the occurrence of Al spikes. A new mechanism for aluminium spikes formation and dissipation in graphite furnace AAS is proposed and discussed.

CHAPTER 1
MECHANISM OF INTERFERENCES BY MAGNESIUM CHLORIDE MATRIX
AND MECHANISM OF CHEMICAL MODIFICATION BY ASCORBIC ACID
WITH THE ATOMIZATION OF MANGANESE IN ELECTROTHERMAL
ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Chloride matrices interfere with determination of many elements by electrothermal atomic absorption spectrometry (ETAAS). Although the addition of nitric acid to aqueous solution of samples to make the aqueous solution pH 1.5 completely removes the interference of chloride matrix with determination of some elements (Zn, Mn, Fe)²⁴, for solid sampling it is necessary to know the cause of the chloride matrix interference in order that remedial action can be taken in direct analysis (without sample dissolution) of solid samples containing chloride matrices. Of more fundamental importance is the fact that knowledge and understanding of reactions between various chloride species, various analyte species and various chemical modifiers in graphite furnaces are essential for systematic development of graphite furnace technology.

Various theories have been proposed to explain the cause of chloride matrix interferences. These include : (i) loss of analyte during the pyrolysis step^{25,26}; (ii) occlusion of the analyte in microcrystals of the chloride matrix which are expelled from the furnace during atomization²⁷; (iii) expulsion of analyte from the furnace as a result of expansion of gaseous products released by the decomposition of matrix during

atomization^{26,28}; (iv) interferences caused by formation of stable gaseous molecular chloride species which are not completely dissociated during atomization^{29,30,31}. Using dual cavity platform atomization experiments Welz *et al.*²⁶ have shown that the mechanisms of chloride matrix interference may depend not only on the temperature of the pyrolysis cycle (thermal pretreatment step) but, more importantly, on the identity of the chloride matrix. His results show, for example, that the interference caused by hydrated nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, which hydrolyzes at elevated temperatures is different from that caused by sodium chloride which does not hydrolyze even on heating.

Although the mechanisms of some of these chloride interferences may not be known, and may, in fact, vary with different analytes and interfering species, various methods have been developed to control them. These include: use of inorganic chemical modifiers such as nitric acid^{24,25,32}; the constant temperature furnace³³; addition of hydrogen to the argon purge gas during pyrolysis and atomization³⁴; addition of sulphuric acid³²; phosphoric acid³⁵; and ammonium nitrate³⁶. Two of the most successful approaches to elimination of chloride interferences, particularly with high chloride concentrations, have been the use of the stabilized temperature platform furnace³⁷, in conjunction with suitable chemical modifiers^{35,38}, or in the case of tube wall atomization the addition of organic modifiers^{39,40}. Tominaga and Umezaki³⁹ showed that the addition of a 5% (m/v) solution of ascorbic acid to a solution containing manganese in 1% (m/v) sodium chloride gave 100% recovery of the analyte signal. Hydes⁴⁰ completely eliminated the effect of chloride interferences in direct analysis of manganese in seawater samples, adding 1% (m/v) aqueous solution of ascorbic acid,

although some small residual peak height depression was observed for cobalt and copper with the added ascorbic acid.

The mechanism by which ascorbic acid removes chloride matrix interferences at high chloride concentrations where the ratio of chloride to analyte is in excess of $10^5:1$ is not fully known. Regan and Warren⁴¹ proposed that pyrolysis of ascorbic acid leaves a carbon residue on the graphite tube surface, which enhances the reduction of metal oxides during atomization. However, Hydes⁴⁰ discounted this theory since oxalic acid which pyrolyses without leaving a residue was equally effective in removing chloride interferences with copper analyte in seawater samples.

Recently, Gilchrist *et al.*⁴² have elucidated the effect of ascorbic acid on the appearance temperatures, peak height and peak area of lead and five other elements⁴³. The effect on the lead absorbance profile was attributed to gas phase chemical modification caused by the release of hydrogen and carbon monoxide by pyrolysis of ascorbic acid during atomization. By coupling a gas chromatograph with a graphite furnace, these authors⁴² showed that hydrogen and carbon monoxide in excess of 1% v/v were released by ascorbic acid into the furnace during atomization. When argon purge gas was mixed with equivalent amounts of these gases the effect on the appearance temperature and the peak area for lead was the same as that obtained by the addition of ascorbic acid, confirming the gas phase chemical modification mechanism. Where atoms are formed by dissociation of gaseous oxide molecules, the oxygen levels are lowered by reaction with the released hydrogen and carbon monoxide, causing a shift in the peak appearance temperature to a lower temperature. However, in these experiments the

samples contained only 1% v/v nitric or hydrochloric acid as a matrix, so that the amount of interferent released during atomization was very small, originating only from the decomposition of the analyte compound itself, or from the small amounts of the acid retained by graphite tube after the sample was dried^{44,45}.

The objectives of this work were: (i) to distinguish between the chloride interference caused by loss of analyte in the pyrolysis cycle, and that caused by a gas phase interference mechanism during the atomization cycle; (ii) to determine if a gas phase chemical modification mechanism, similar to that proposed by Gilchrist *et al.*⁴³ can account for the removal of the chloride interference by ascorbic acid in samples which contain high concentrations of metal chloride interferents.

Electrothermal vaporization inductively-coupled plasma mass spectrometry (ETV-ICP-MS) was used in this work as a diagnostic technique for the following reason. The experimental evidence presented later would show that when manganese in a magnesium chloride matrix is determined by ETAAS, manganese is partially lost in the pyrolysis cycle (at $\sim 700^{\circ}\text{C}$). It is suspected that manganese is lost by being swept out of the furnace by the expanding HCl_g , generated by hydrolysis of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at temperature $\geq 700^{\circ}\text{C}$. However, the commercial (conventional) graphite furnace with its single atomizer (graphite tube) serving two separate functions, vaporization and atomization, used for this study cannot determine whether the lost manganese is atomic or molecular, or whether it is a condensed-phase or a vapour-phase species. This is because the temperature ($\sim 700^{\circ}\text{C}$) at which the manganese loss is observed in ETAAS is too low for the formation of Mn_g , and hence, too low for the Mn atomic absorption

signal to be observed. Diagnosis of this manganese loss in ETAAS would have been possible if, instead of the commercial (conventional) graphite furnace that has been used for this work, one were to employ a laboratory-made, two-step detachable graphite tube and cup furnace which employs two separate power supplies, one for heating the graphite cup (for vaporization) and the other for heating the graphite tube (for atomization). Such a furnace would permit spatial and temporal separation of two separate processes: vaporization and atomization^{46,47}. However, such a graphite furnace was not available for this work. The ETV-ICP-MS, with its spatial and temporal separation of vaporization process (at the ETV) and ionization process (at the ICP), coupled with mass-spectrometric detection (which gives extremely high sensitivity), offered a valuable diagnostic technique that can readily determine the manganese lost as free atoms or in chemically combined form in the pyrolysis cycle (during vaporization). Differentiation between free and combined Mn can be done by studying ETAAS data together with ETV-ICP-MS data. ETAAS is capable of detecting only atomic species whereas ICP-MS could detect ions produced from both atomic and molecular species. Also, the multi-element capability of ICP-MS would allow simultaneous determination of the analyte and the matrix ions of manganese, magnesium and chlorine, which is required for elucidating mechanisms of manganese loss during the pyrolysis cycle (vaporization).

To determine if a gas phase chemical modification mechanism was responsible for the effect of ascorbic acid addition, experiments, similar to those described by Gilchrist *et al*⁴³, were conducted in which the argon purge gas was mixed with hydrogen, in amounts similar to those produced by pyrolysis of the added ascorbic acid. In

addition, the amounts of magnesium and chlorine remaining in the furnace after pyrolysis, but prior to the atomization step, were determined. These experiments quantified the amount of matrix removed during the pyrolysis cycle and, in the case of the magnesium chloride matrix, determined the extent of hydrolysis during the pyrolysis step. The residual amounts of magnesium and chloride were determined by flame atomic absorption spectrometry (AAS), and ion-chromatography, respectively.

EXPERIMENTAL

Atomic Absorption Spectrometry

Apparatus. A Perkin-Elmer Model 5000 atomic absorption spectrometer equipped with a Zeeman Effect Background Corrector and a Heated Graphite Atomizer (HGA) Model 500 was used. Absorbance signals were recorded directly from the spectrometer. The absorbance versus time profiles were recorded with an IBM compatible computer using a software program TGP (Tech Graph Pad designed for scientists and engineers). The outputs were printed using a Hewlett-Packard Laser-Jet III printer. A Perkin-Elmer hollow-cathode lamp for manganese and pyrolytically-coated graphite tubes (Perkin-Elmer Part No. B009-1504) were used. The temperature of the graphite tube was monitored with an Ircon Model 300c automatic optical pyrometer. Test solutions of 20 μ l volumes were injected using a 20 μ l Eppendorf pipette.

Gases. Argon gas of high-purity (99.995% pure, Matheson Gas Products, Canada) was used both as the purge gas and the sheath gas. The 5.0% v/v hydrogen gas in argon (supplied by Matheson Gas Products) was used to simulate the amount of H₂ gas released from pyrolysis of ascorbic acid. The H₂ gas was diluted to the appropriate composition

using a flowmeter regulator.

Standards and Reagents. Standards and reagents in ultrapure water were individually prepared as follows:

- (a) A stock solution of $1000 \mu\text{g ml}^{-1}$ manganese solution was prepared by dissolving 0.5026 g of Mn metal (99.94% pure, Fisher Scientific) in 10.00 ml of 1:1 HNO_3 (Ultrex, Baker) and diluting the solution to 500.00 ml with ultrapure water.
- (b) $5 \mu\text{g ml}^{-1}$ manganese solution was prepared by a serial dilution of the above $1000 \mu\text{g ml}^{-1}$ Mn stock solution with ultrapure water.
- (c) 5% m/v MgCl_2 solution was prepared by dissolving 10.6700 g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (99.4% pure, Baker Analyzed Reagent) in 100.00 ml ultrapure water.

Test solutions were prepared by serial dilution of the above solutions (b) and (c) with ultrapure water in 25.00 ml volumetric flasks immediately prior to determination. The following solutions were prepared in ultrapure water.

- (a) Solution A contained $0.02 \mu\text{g ml}^{-1}$ Mn + 1% v/v HCl solution.
- (b) Solution B contained $0.02 \mu\text{g ml}^{-1}$ Mn + 1% v/v HCl + 1% m/v MgCl_2 solution.
- (c) Solution C contained $0.02 \mu\text{g ml}^{-1}$ Mn + 1% v/v HCl + 1% m/v MgCl_2 + 1% m/v ascorbic acid.
- (d) Solution D contained $0.02 \mu\text{g ml}^{-1}$ Mn + 1% v/v HCl + 1% m/v MgCl_2 + 3% m/v ascorbic acid.

Solution C and D of ascorbic acid were prepared by dissolving 0.2500 g and 0.7500 g of L-ascorbic acid (99.5% pure, Baker Analyzed Reagent), respectively, in a minimum amount of ultrapure water. The solutions were then transferred quantitatively

to a 25.00 ml volumetric flask that contained appropriate amounts of solutions of the other three components of solution C or D. The solutions were then made up to the mark with ultrapure water.

- (e) Solution E contained $0.02 \mu\text{g ml}^{-1} \text{Mn} + 1\% \text{ v/v HNO}_3$.
- (f) Blanks for solutions A to D were prepared to contain only 1% v/v HCl (Ultrex, Baker) in ultrapure water. Blank for solution E was prepared to contain only 1% v/v HNO₃ (Ultrex, Baker) in ultrapure water.

Ultrapure water was obtained direct from a Millipore-Q™ water purification system (Millipore Corporation, Mississauga, ON., Canada) immediately prior to its use.

Experimental and Operating Conditions. The experimental and operating conditions used for the atomization of manganese are presented in Table 1. The Mn hollow cathode lamp was operated at a lamp current of 20 mA. The most sensitive line of Mn, 279.5 nm, a spectral bandpass of 0.2 nm (low slit), and an integration time of 7.0 seconds were used.

Determination of the Residual Magnesium Chloride.

Apparatus. A Perkin-Elmer Model 603 atomic absorption spectrometer equipped with an air-acetylene flame atomizer-burner and a Deuterium Arc Background Corrector, was used to determine the residual magnesium (as the chloride) that remained after the pyrolysis cycle. A Mg hollow-cathode lamp (Perkin-Elmer) was used. The most sensitive magnesium line, 285.2 nm, and at a lamp current of 18 mA were used. The absorbance signals were recorded from the digital read-out of the spectrometer and were then corrected for blanks.

The chloride that remained after the pyrolysis cycle was determined using a

Table 1. Experimental and operating conditions of the graphite furnace used for atomization of manganese.

Step	Drying*	Drying*	Pyrolysis	Cool	Atomize	Clean
Temp. (°C)	90	120	Variable	400	2500	2700
Hold Time (s)	40	20	40	3	7	3
Ramp Time (s)	10	5	10	2	1	1
Record (s)	-	-	-	-	-2	-
Read (s)	-	-	-	-	0	-
Baseline (s)	-	-	-	-	-1	-
Gas Flow Internal (ml min ⁻¹)	300	300	300	300	50	300

The 1% v/v H₂ gas was added separately using another gas inflow device.

*The two drying cycles were required in order to dry the sample completely in the graphite tube prior to the pyrolysis cycle.

DIONEX series 4000i ion chromatograph, equipped with an electrical-conductivity detector. The ion chromatography column was an AS4A analytical column (Dionex), equipped with a membrane ion suppressor (MPIC, Dionex). The eluent consisted of a 1.8mM Na_2CO_3 and 1.7 mM NaHCO_3 in ultrapure water. The membrane ion suppressor was regenerated with a 5mM H_2SO_4 in ultrapure water. The chromatograms were recorded with a SP4290 integrator. Aqueous solutions of the sample were loaded in a 50 μl sample loop with a 1 ml plastic syringe and were injected with an automatic injection device of the chromatograph.

Standards and Reagents. A stock solution of 100 $\mu\text{g ml}^{-1}$ Cl^- was prepared by dissolving 0.1648 g NaCl (Grade 1 Ultrapure, Johnson Matthey, England) in 1000.00 ml of ultrapure water.

A stock solution of 100 $\mu\text{g ml}^{-1}$ Mg was prepared by dissolving 0.1658 g of MgO (99.5% pure, Fisher Scientific) in 5.5 ml of concentrated HNO_3 (Ultrex, Baker) and diluting the solution to 1000.00 ml with ultrapure water.

Determination of the residual magnesium and chloride in the recovery experiments required daily preparations of analytical calibration curves using standard solutions of chloride (using NaCl) with the chloride concentrations in the range 0.1-15.0 $\mu\text{g ml}^{-1}$, and standard solutions of magnesium (using MgO) with magnesium concentrations in the range 0.2-5.0 $\mu\text{g ml}^{-1}$.

Table 2 presents the experimental and operating conditions used for the determination of the residual magnesium chloride.

Extraction Procedure. Recovery and clean-up experiments were performed to ensure that

Table 2. Experimental and operating conditions for the determination of the residual magnesium chloride.

Step	Drying*	Drying*	Pyrolysis
Temp. (°C)	90	120	Variable
Ramp Time (s)	10	10	10
Hold Time (s)	30	20	40

*The two drying cycles were required in order to dry the sample completely in the graphite tube prior to the pyrolysis cycle.

the extraction procedure gave ~100% recoveries of the residual magnesium (as the chloride) and to avoid possible contamination of the next sample by carry-over of measurable amounts of the magnesium or the chloride because of inadequate thermal treatment for clean-up of the graphite tube prior to its re-use.

Extractions of the magnesium chloride residue, with or without the added ascorbic acid, were performed in triplicate. The magnesium chloride matrix was pyrolyzed at various pyrolysis temperatures using the operating procedures shown in Table 2. The residues were extracted by inserting the graphite tube (containing the residue) in 15 ml polystyrene tubes (Fisher Scientific), equipped with snap caps, which contained 10.00 ml of dilute HNO_3 (pH ~ 3). Each polystyrene tube with its contents was heated for 15 minutes at 70°C and shaken for 5 minutes with a test tube mixer (Vortex-Genie, Fisher Scientific). Each of these extracts was analyzed for magnesium and chloride using flame AAS and ion chromatography, respectively.

Electrothermal Vaporization Inductively-Coupled Plasma Mass Spectrometry

Apparatus. The inductively coupled plasma mass spectrometer (ICP-MS) used for this work was a Perkin-Elmer/Sciex Elan Model 250. The ICP-MS was used in the positive ion detection mode. An extended quartz torch was used for all experiments. The electrothermal vaporization (ETV) device was constructed in the laboratory and was of a design similar to that reported by Park *et al.*^{48,49}. Figure 1 shows a schematic diagram of the electrothermal vaporization (ETV) device used in our experiments. Several modifications were made to this device including installation of an automatic optical pyrometer, Ircon Model 300c, to monitor the temperature of the vaporization

Figure 1. Schematic diagram of the laboratory-made electrothermal vaporizer (ETV).

surface of the electrothermal vaporizer (ETV), and use of specially designed graphite strips for the ETV. The loss in the radiance transmission through the quartz cover was compensated for by adjusting the emissivity dial on the Ircon Model 300c. There was an 8% loss that was measured by monitoring the temperature at $\sim 800^{\circ}\text{C}$ with and without the quartz cover. The ETV device consisted of a resistively-heated strip of graphite measuring 11 x 4 x 1 mm connected to an IL 55 power supply (Instrumentation Laboratory Inc., Mass., USA). The sample material vaporized from the graphite strip was transported to the plasma by a stream of argon whose flow was directed tangentially to the graphite support electrodes on which the graphite strip was mounted. A quartz cover resembling an inverted thistle tube was used to form an envelope above the vaporization surface. The tangential flow of Ar gas and the shape of the quartz cover served to minimize condensation of the sample material (analyte and matrix components) on the quartz surface, and thus to maximize sample transport to the plasma. Figure 2 shows a schematic diagram of the ETV device coupled to the ICP-MS. The interface between the ETV unit and the ICP-MS consisted of a Tygon tubing 1.0 m x 6.0 mm i.d. connected direct to the plasma torch.

Pyrolytically coated crystalline graphite (Ultra Carbon, Bay City, Michigan, USA) was used to fabricate the graphite strips. A small oval-shaped depression was machined onto the surface of each strip at its centre. The depression served to hold the liquid sample and to prevent spreading of the sample during the drying step.

The instrumental settings for the ETV-ICP-MS are given in Table 3.

Standards and reagents. Solutions of Mn, Mn plus MgCl_2 , and Mn plus MgCl_2 plus

Figure 2. Schematic diagram of the electrothermal vaporizer (ETV) coupled to the inductively-coupled plasma mass spectrometer (ICP-MS).

Table 3. Experimental and operating conditions for the ETV-ICP-MS.

Electrothermal vaporizer conditions and heating cycle

Step	Drying	Pyrolysis	Vaporization
Temp.(°C)	110	Variable	2500
Ramp Time (s)	10	20	2
Hold Time (s)	60	20	10

Carrier gas flow-rate 1.0 l min⁻¹

Sample volume 10 µl

Mass spectrometer interface

Sampler Nickel, 1.14 mm orifice

Skimmer Nickel, 0.89 mm orifice

Plasma conditions

R.F. power 0.9 kW

Reflected power 5 W

Auxiliary flow-rate 2.0 l min⁻¹Nebulizer flow-rate 0.7 l min⁻¹Plasma gas flow-rate 12.5 l min⁻¹

Sampling depth* 25 mm

*Distance in millimetres from the tip of the mass spectrometer sampling cone to the downstream turn of the load coil.

ascorbic acid, were identical to the solutions for the ETAAS experiments except these were prepared in 0.04% v/v HCl for the following reasons. The samples prepared in 1% v/v HCl occasionally spread toward the graphite electrode upon drying, which affected the repeatability of the results. This was avoided by making all solutions in 0.04% v/v HCl. The ETV-ICP-MS signal for Cl was excessively large for 1% v/v HCl solutions, but much smaller for 0.04% v/v HCl solutions and the ETV-ICP-MS signal for Mn and Mg were identical for both the 1% v/v and the 0.04% v/v HCl solutions. Test solutions of 10 μ l volumes were injected onto the graphite strip using a 10 μ l Eppendorf pipette.

RESULTS AND DISCUSSION

ETAAS experiments.

The ETAAS was performed by atomization from the graphite tube wall of the HGA 500 graphite furnace in order to maximize the effects of the magnesium chloride matrix interference, providing more scope for study of interference mechanisms and their removal than would have been the case if these effects were minimized by the use of atomization from a graphite platform. Moreover, the use of a graphite platform for atomization would have made recovery studies of the residual amounts of magnesium chloride left in the furnace after the pyrolysis step more difficult because the matrix would then have been distributed between both the platform and the cooler parts of the tube wall after the pyrolysis cycle, making the washing out of the residue more difficult. The heating ramp time on the HGA 500 power supply was set at 1 s instead of the standard 0 s heating ramp time because the power supply of the Instrumentation Laboratory (IL) 555 for the graphite strip vaporizer used in the ETV-ICP-MS

experiments could provide a maximum heating ramp approximately equal to the 1 s ramp time of the HGA 500. The heating characteristics of both electrothermal atomizers used in this work were made to be similar in order that the results obtained using these two atomizers were comparable. It is emphasized here that the use of standard experimental procedures that would eliminate or minimize matrix interferences, e.g. atomization from a graphite platform in ETAAS, was deliberately avoided since the objectives were to maximize matrix interferences in order to investigate their mechanisms. Hence, the effects and mechanisms that are reported in this thesis may be different from those observed under standard (optimized) experimental conditions used in ETAAS.

Figure 3 shows the pyrolysis (A) and the atomization (B) curve for 400 pg of manganese plus 200 μg MgCl_2 in 1 % v/v HCl solution. Figure 4 shows pyrolysis curves for manganese alone (A), manganese plus MgCl_2 (B), manganese plus MgCl_2 plus various amounts of ascorbic acid (C and D). The pyrolysis curve for Mn in 1 % v/v HNO_3 (E) is shown as a reference curve. It shows the Mn AA signal without the chloride interferences. Typical absorbance profiles for these solutions at a pyrolysis temperature of 900°C are presented in Fig. 5. In Fig. 3 and 4, an unusual feature of the pyrolysis curve with the magnesium chloride matrix (A and B, respectively) is the pronounced maximum at a pyrolysis temperature of around 700°C. Figure 3 also shows that although manganese in the MgCl_2 matrix is lost at pyrolysis temperatures higher or lower than 700°C, the Mn atomic absorption signal is not observed until the furnace has attained a temperature of 1800°C (the appearance temperature for manganese in the MgCl_2 matrix). Since no Mn atomic absorption signal is observed below 1800°C, the

Figure 3. Pyrolysis curve (A) and atomization curve (B) for 400 pg Mn + 200 μ g MgCl_2 in 1% v/v HCl. The optimum atomization temperature for the pyrolysis curve (A) was 2400°C and the optimum pyrolysis temperature for the atomization curve (B) was 700°C.

Figure 4. Pyrolysis curves in ETAAS. A: 400 pg Mn in 1% v/v HCl. B: A + 200 μg MgCl_2 . C: B + 200 μg ascorbic acid. D: B + 600 μg ascorbic acid. E: 400 pg Mn in 1% v/v HNO_3 .

Figure 5. Typical absorbance profiles in ETAAS at a pyrolysis temperature of 900°C. A: 400 pg Mn in 1% v/v HCl. B: A + 200 μ g MgCl_2 . C: B + 200 μ g ascorbic acid.

manganese must have been lost as a molecular species. The thermal stability of the lost manganese molecular species is reflected in the 1100°C difference between the maximum in the pyrolysis curve (700°C) and the onset of the atomization curve (1800°C), and establishes the temperature range in which the manganese species is lost from the furnace. Figure 4, curve B, shows that the manganese absorbance values increase with increasing pyrolysis temperature, as might be expected, up to 700°C, but then drop dramatically as the pyrolysis temperature is increased beyond 700°C, even though this temperature is well below the normal appearance temperature (1480 K)⁸ of manganese alone. Pyrolysis curves showing similar maxima, in magnesium chloride matrices, have been reported for copper³² and lead⁵⁰. Figure 4 also shows that the effect of the ascorbic acid chemical modifier is different both above and below the pyrolysis temperature of 700°C. At concentrations of 1% m/v ascorbic acid (i.e. 200 µg ascorbic acid addition), ascorbic acid is effective in recovering 100% of the manganese absorbance at pyrolysis temperatures of 700°C or above; below this temperature the magnesium chloride interference is only partly removed. These results suggest that both the mechanism of the interference and its removal by ascorbic acid above 700°C is different from that below 700°C.

In order to establish if the effect of the ascorbic acid chemical modifier, in either of these pyrolysis temperature regions, could be attributed to a gas phase chemical modification mechanism, similar to that described by Gilchrist et al^{42,43}, the argon purge gas was mixed with 1% v/v hydrogen during the pyrolysis and atomization cycles. This hydrogen concentration is equivalent to that found to be released by pyrolysis of 100 µg

ascorbic acid in a graphite furnace, using similar pyrolysis temperatures and purge gas flow conditions⁴². The results of these gas phase modification experiments are given in Fig. 6. At pyrolysis temperatures below 700°C, the added hydrogen removes the magnesium chloride interference only partially. This result is similar to that observed in Fig. 4 when the ascorbic acid chemical modifier is added and suggests that the partial removal of the magnesium chloride interference at low pyrolysis temperatures is due to a gas phase chemical modification, in which some of the magnesium chloride remaining after the pyrolysis is removed during atomization via a gas phase reaction of the type:

Increasing the mass of ascorbic acid to 600 μg in the sample containing the manganese and the MgCl_2 matrix (Fig. 4, curve D) removes almost all the MgCl_2 matrix interference. Increasing the mass of ascorbic acid is equivalent to increasing the concentration of hydrogen in the argon purge gas, which then allows more chloride to be removed by the hydrogen gas via a gas phase chemical modification mechanism at pyrolysis temperatures below 700°C.

However, for pyrolysis temperatures above 700°C, the results of the hydrogen addition experiments (Fig. 6) in no way parallel the results of the ascorbic acid addition (Fig. 4). Whereas the ascorbic acid chemical modifier causes complete removal of the magnesium chloride interference in this higher pyrolysis temperature range, addition of hydrogen has, in fact, a slight depressive effect on the manganese peak area absorbance. This would indicate that, in this temperature range, the mechanism by which ascorbic

Figure 6. Pyrolysis curves in ETAAS. A: 400 pg Mn in 1% v/v HCl + 200 μ g MgCl_2 + argon containing 1% v/v H_2 gas. B: 400 pg Mn in 1% v/v HCl + 200 μ g MgCl_2 + argon gas.

acid eliminates the magnesium chloride interference is not a gas phase reaction, but one based on processes occurring in the condensed phase at the graphite surface during pyrolysis. Welz *et al.*²⁶ have differentiated chloride interferences arising from gas phase reactions and from condensed-phase reactions at the graphite surface using atomization from a dual-cavity graphite platform. They have studied the effect of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ interferences with lead atomization, at concentrations similar to those used in this paper, and have concluded that the interferences are caused by loss of analyte during pyrolysis. They have proposed that these losses result from the hydrolysis reaction of the hydrated nickel chloride matrix known to occur at temperatures around 600°C ⁵¹:

Welz *et al.* suggest that the above reaction results in covoatilisation of the analyte, and its expulsion from the furnace together with the hydrogen chloride gas generated by the hydrolysis reaction.

Hydrated magnesium chloride is also known to hydrolyze up to 600°C ^{52,53}. However, the mixed condensed phase (MgCl_2 , MgOHCl , MgO) which is present at 600°C ⁵² could hydrolyze at higher temperature releasing HCl gas. A mechanism similar to the one proposed by Welz⁵¹ that would involved hydrolysis of the magnesium chloride matrix and the loss of manganese by being carried away with the $\text{HCl}_{(g)}$ from the pyrolysis cycle hydrolysis reaction would explain the sharp decrease in the absorbance signal of manganese observed in the pyrolysis curve of Fig. 4 at temperatures above 700°C . Moreover, it would also explain why hydrogen, added to the argon purge gas,

is ineffective in restoring the manganese signal at pyrolysis temperatures above 700°C; if the analyte has been already lost from the furnace during pyrolysis, then no gas phase reaction during atomization could be expected to recover the manganese signal. The Mn atomic absorption signal is not observed when the MgCl_2 matrix is present until a temperature of at least 1800°C (Fig. 3) is attained. It is necessary to determine experimentally how this manganese is lost. As explained earlier, ETV-ICP-MS offers a promising diagnostic technique for investigation of the loss of manganese in the pyrolysis cycle.

ETV-ICP-MS experiments.

In these experiments, the manganese in the magnesium chloride matrix, with and without the ascorbic acid chemical modifier, was vaporized from a graphite strip electrothermal vaporizer (ETV), and the vapour generated, both during the pyrolysis and the atomization step, transported to the ICP-MS. Details of the experimental procedure are given in the Experimental Section. Any molecular chloride analyte species, produced either during the pyrolysis or the atomization step, were dissociated in the argon plasma to yield manganese atoms which were then ionised in the plasma and detected as manganese atomic ions by the mass spectrometer⁵⁴. This technique allows detection of analyte during both the pyrolysis and the atomization step as a function of temperature of the vaporizing graphite strip (ETV). For each sample tested, the ETV-ICP-MS signal for $^{55}\text{Mn}^+$, $^{37}\text{Cl}^+$, and $^{25}\text{Mg}^+$ were recorded simultaneously. No memory effect was detected for any of the above ions. The ETV-ICP-MS signals were corrected for blanks.

Figures 7 to 9 show $^{55}\text{Mn}^+$ ETV-ICP-MS signals for manganese in various

matrices and at different pyrolysis temperatures. The temperature of the graphite strip (ETV) surface during the pyrolysis and the vaporization step is also shown. The temperature of the graphite strip (ETV) increases after the end of the heating ramp during the pyrolysis cycle. Therefore, the temperature of the graphite strip (ETV) will be reported as a temperature range which covers the last 25 s of the pyrolysis cycle. The pyrolysis and the vaporization step for each figure are from 0 to 40 s and 40 to 50 s, respectively. Figure 7 shows the $^{55}\text{Mn}^+$ signal for 200 pg of manganese in 0.04% v/v HCl at pyrolysis temperatures of 500-600°C (Fig. 7a) and 700-900°C (Fig. 7b). The Mn peak, centred at around 42 seconds for both pyrolysis temperatures 500-600 and 700-900°C, appears in the vaporization step and has approximately the same peak area for both pyrolysis temperatures. The peak area sensitivity can be interpreted only qualitatively since the effects of the various matrices (specially Mg) on the mass transport efficiency and plasma properties, which affect the ion counts are not yet fully understood. During the pyrolysis step, no Mn peak is observed for any of the above pyrolysis temperatures, indicating that no manganese is evolved from the ETV before the vaporization step.

At pyrolysis temperature 700-900°C, the addition of 100 μg MgCl, (Fig. 8a) and 100 μg MgCl₂ plus 100 μg ascorbic acid (Fig. 8b) to 200 pg Mn in 0.04% v/v HCl shows significantly different Mn ETV-ICP-MS profiles. The sample without the ascorbic acid shows a manganese peak centred around 23 s during the pyrolysis cycle (Fig. 8a), indicating that the manganese is evolved from the sample during the pyrolysis cycle. The temperature that corresponds to the centre of the Mn peak at 23 s is 800°C. The Mn

Figure 7. Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS in various matrices as a function of the pyrolysis temperature of the graphite strip. A: 200 pg Mn in 0.04% v/v HCl. Pyrolysis temperature of the graphite strip: (a) 500-600°C; (b) 700-900°C. B: temperature profile of the graphite strip.

Figure 8. Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS in various matrices at a pyrolysis temperature 700-900 $^{\circ}\text{C}$ of the graphite strip. A: 200 pg Mn in 0.04% v/v HCl. (a) 100 μg MgCl_2 . (b) 100 μg MgCl_2 + 100 μg ascorbic acid. B: temperature profile of the graphite strip.

peak observed at 23 s in Fig. 8a provides convincing evidence that the chloride interference in ETAAS is caused by the manganese loss at 800°C during the pyrolysis cycle. Moreover, the above mechanism explains why, in the earlier ETAAS experiments, hydrogen gas was found to be ineffective in restoring the manganese signal at pyrolysis temperatures above 700°C. A gas phase reaction mechanism in ETAAS could only be expected to reduce interferences caused by formation of molecular chloride species in the gas phase, but would do nothing to prevent the manganese loss by expulsion during the preceding pyrolysis cycle. The manganese peak centred at 23 s in Fig. 8a (temperature of 800°C) accounts for approximately 39% of the total manganese signal, i.e. 39% Mn is lost in the pyrolysis cycle. In ETAAS, at a pyrolysis temperature of 800°C, the manganese AA signal for Mn with the MgCl_2 matrix (Fig. 4, curve B) was reduced to 58% of the manganese AA signal of Mn without MgCl_2 matrix, i.e. 42% Mn is lost in the pyrolysis cycle. The addition of ascorbic acid reduces the manganese loss during the pyrolysis cycle (Fig. 8b) and only a trace of Mn at 23 s can be observed. This result agrees with those shown in Fig. 4 where for pyrolysis temperatures above 700°C, the addition of ascorbic acid removes the matrix interference completely. Hence, it can be concluded that in ETAAS, in the above pyrolysis temperature range, the ascorbic acid removes the MgCl_2 matrix interference by preventing the manganese loss during the pyrolysis cycle; a mechanism to account for this will be proposed in the next section.

ETV-ICP-MS experiments were conducted at pyrolysis temperatures below 700°C to elucidate the interference mechanism in this low temperature pyrolysis region. The

results for a pyrolysis temperature of 500-600°C are given in Fig. 9. At this temperature, no loss of manganese in the MgCl_2 matrix was observed during pyrolysis periods of < 40 s (Fig. 9), which means that at this lower pyrolysis temperature the matrix interference did not follow the mechanism of manganese release from the graphite strip (ETV) during pyrolysis. Moreover, a comparison of Fig. 7a and 9 shows that the amount of manganese released during vaporization is similar both in the presence and in the absence of the magnesium chloride matrix. This result contrasts with the absorbance profiles obtained using graphite furnace atomization (Fig. 10), in which considerable suppression of the absorbance signal occurred in the presence of the magnesium chloride matrix (Fig. 10, curve B). The conclusion is inescapable that the suppression of the Mn absorbance signal observed in graphite furnace atomization (Fig. 10) is due to the formation of molecular manganese species (probably manganese chloride) which remains undissociated at a low temperature, producing no detectable Mn atomic absorption, since the ETV-ICP-MS results confirm that no loss of manganese occurs during the pyrolysis step. These same manganese molecular species formed during vaporization from the graphite strip in the ETV experiments but were subsequently dissociated in the high-temperature plasma, and detected as atomic manganese ions by the mass spectrometer, giving rise to the same signal obtained in the absence of the MgCl_2 matrix.

Figures 11a and 11b show the $^{37}\text{Cl}^+$ ETV-ICP-MS signals that correspond to Figs. 9 and 8 respectively. These figures were drawn using data corrected for blanks, and show only the net $^{37}\text{Cl}^+$ signal produced by the MgCl_2 matrix. Figures 12a and 12b show the corresponding $^{25}\text{Mg}^+$ ETV-ICP-MS signals for Figs. 9 and 8. At pyrolysis

Figure 9. Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS at a pyrolysis temperature 500-600°C of the graphite strip. A: 200 pg Mn + 100 μg MgCl_2 in 0.04% v/v HCl. B: temperature profile of the graphite strip.

Figure 10. Absorbance profiles of Mn in ETAAS at a pyrolysis temperature of 600°C. A: 400 pg in 1% v/v HCl. B: A + 200 μg MgCl_2 .

Figure 11. Temporal behaviour of $^{37}\text{Cl}^+$ in ETV-ICP-MS in various matrices at different pyrolysis temperatures of the graphite strip. (a) 500-600°C; (b) 700-900°C. A: 200 pg Mn in 0.04% v/v HCl + 100 μg MgCl_2 . B: A + 100 μg ascorbic acid.

temperatures between 500 and 600°C, (Fig. 12a), no Mg is observed during the pyrolysis period (20-40 s), which means that the chlorine observed in the corresponding region of Figure 11a must be due solely to the HCl produced by the onset of the matrix hydrolysis reaction. Figure 11a also shows that more chloride is released during pyrolysis (20-40s) when no ascorbic acid is present (curve A). This suggests that ascorbic acid inhibits the hydrolysis reaction of the magnesium chloride matrix. The Cl signal in the range of 4 to 14 s and the corresponding Mg signal of Fig. 12a is probably due to MgCl_2 crystals ejected during the temperature ramping at the beginning of the pyrolysis cycle (this has been observed several times). The most interesting feature of Fig. 11a is the sharp Cl peak, at approximately 42 s, during the vaporization cycle. This peak has an appearance time coincident with the Mn peak in Figure 9, and appears at a temperature of about 1500°C, some time during the temperature ramp after pyrolysis. Therefore, the above peak may be attributed to the residual MgCl_2 vaporized at its boiling point of 1480°C. This peak has an identical shape and ion intensity both in the presence and in the absence of the ascorbic acid chemical modifier. The identical peak areas would suggest that Mn in both solutions was subjected to the same amount of chloride interference during the vaporization of Mn, and that the interference with manganese by chloride is of the same magnitude in the MgCl_2 matrix, with or without the ascorbic acid chemical modifier. This is in agreement with the ETAAS results where the manganese integrated absorbance values are similar for the MgCl_2 matrix, with or without the ascorbic acid, for pyrolysis temperatures < 700°C (Fig.4, curve B and C), indicating that both solutions suffer the same degree of the chloride interference. The broader Cl peaks observed in the range

of 44-50 s occur at a higher temperature ($\sim 2400^{\circ}\text{C}$) and may be due to the release of Cl trapped in the MgO crystal.

The Cl signal from Fig. 11b exhibits a similar trend as in Fig. 11a in the range of 4 to 14 s. This is probably due to the same effect as described earlier. The Cl peak intensity at a pyrolysis temperature of $700\text{-}900^{\circ}\text{C}$ in the range of 16-30 s for the MgCl_2 matrix without the ascorbic acid (Fig. 11b, curve A) is about 1.7 times greater than that at a pyrolysis temperature of $500\text{-}600^{\circ}\text{C}$ (Fig. 11a, curve A), and for the MgCl_2 matrix with ascorbic acid (Fig. 11b, curve B) the Cl peak intensity is 2.3 times greater than that at a pyrolysis temperature of $500\text{-}600^{\circ}\text{C}$ (Fig. 11a, curve B). However, the Cl peak area in the absence of ascorbic acid is still larger, suggesting that the degree of hydrolysis of the MgCl_2 matrix is greater when no ascorbic acid is present. The Cl peaks at 42 s for the MgCl_2 matrix, with or without the ascorbic acid, have different intensities and both Cl peaks are smaller compared to the Cl peak in Figure 11a at 42 s. The Cl peak intensity is decreased about 9-fold in the MgCl_2 matrix with ascorbic acid, whereas the Cl peak intensity from the MgCl_2 matrix without ascorbic acid decreases only about 1.6-fold. This result suggests that ascorbic acid not only prevents Mn loss during pyrolysis cycle, but also reduces the amount of chloride present during the vaporization of manganese at 42 s.

Figures 12a and 12b show the $^{25}\text{Mg}^+$ ETV-ICP-MS signal corresponding to Figures 9 and 8, respectively. Because of the very high sensitivity of the ICP-MS technique for magnesium which produces the Mg signal near the upper limit of the linear dynamic range of the detector, the interpretation of Figs. 12a and 12b can only be done

Figure 12. Temporal behaviour of $^{25}\text{Mg}^+$ in ETV-ICP-MS in various matrices at different pyrolysis temperatures of the graphite strip. (a) 500-600°C; (b) 700-900°C. A: 200 pg Mn in 0.04% v/v HCl + 100 μg MgCl_2 . B: A + 100 μg ascorbic acid.

qualitatively. In both Figs. 12a and 12b, an off-scale Mg peak in the range of 40 to 50 s was observed and was due to the residual MgCl_2 remaining after the pyrolysis cycle which was vaporized early in the vaporization cycle and to the MgO (produced by the hydrolysis of MgCl_2) which vaporized at a much higher temperature. The Mg peaks observed in both Figs. 12a and 12b in the range of 0 to 14 s were due to the sample material ejected from the graphite strip during the temperature ramping in the pyrolysis cycle. The important distinction between Figs. 12a and 12b is the Mg peak centred at 24 s which appears in Fig. 12b. The Mg peak at 24 s appeared at the same time as the Mn peak in Fig. 8a. Experimental observations have confirmed that the hydrolytic decomposition of the MgCl_2 matrix without ascorbic acid is a violent reaction (like an explosion), which releases $\text{HCl}_{(g)}$. This explosive release of $\text{HCl}_{(g)}$ might have expelled the manganese and the matrix components from the ETV. Hence, the Mg peak at 24 s was probably due to the MgCl_2 carried away with the $\text{HCl}_{(g)}$ generated by the hydrolytic decomposition of the MgCl_2 matrix. The apparently high intensity of this Mg peak should be kept in perspective, considering the large amount of MgCl_2 matrix in the sample. If only 2% of the 100 μg sample of MgCl_2 is carried over during the hydrolysis reaction, this would correspond to 0.5 μg of Mg, sufficient to cause an off-scale peak, given the high sensitivity of Mg. However, this small amount of co-volatilised MgCl_2 would account for the shoulder at 24 s on the Cl peak (Fig. 11b, curve A). This shoulder, which coincides with the centre of the magnesium peak, could result from the small amount of MgCl_2 carried over, whereas the major part of this Cl peak, which precedes the release of Mg, probably comes from $\text{HCl}_{(g)}$ produced by the hydrolytic

decomposition of the MgCl_2 matrix. Except for the Mg peak observed in the range of 18 to 30 s, no other Mg peak originating from MgCl_2 vaporized during pyrolysis cycle could contribute to the Cl signal in Figs. 11a and 11b. Therefore, the Cl signals at times less than 18 s and greater than 30 s must be due to $\text{HCl}_{(g)}$, released by the hydrolytic decomposition of the MgCl_2 matrix, with or without the ascorbic acid, although in a smaller amount for the solution containing ascorbic acid.

A significant result of this research is that the $^{37}\text{Cl}^+$ and the $^{25}\text{Mg}^+$ ETV-ICP-MS signals in Figs. 11 and 12 provide us with experimental evidence for hydrolysis of the magnesium chloride matrix. Figure 12a, curve A, shows that at 500-600°C there is no Mg signal, and hence, MgCl_2 cannot be the source of the observed Cl signal in Fig. 11a, curve A. In Fig. 11a, curve A, the only other possible source of the Cl signal is $\text{HCl}_{(g)}$, which, at 500-600°C probably arises from the incipient hydrolysis of the MgCl_2 matrix, producing $\text{HCl}_{(g)}$ over a wide time interval (20-40 s); the width of the time interval is indicative of the slow hydrolysis of $\text{MgCl}_{2(s)}$ at this relatively low temperature. At 700-900°C, Fig. 11b, curve A, shows a greater Cl peak intensity in the 18-28 s range compared to the Cl signal in Fig. 11a, curve A, (500-600°C). In Fig. 11b, curve A, neglecting the Cl shoulder (24-28 s) that originates from the $\text{MgCl}_{2(s)}$ carried away by $\text{HCl}_{(g)}$ (Fig. 12b, curve A, 20-30 s, shows the corresponding $^{25}\text{Mg}^+$ peak), most of the Cl signal probably arises from vigorous hydrolysis of MgCl_2 at 700-900°C; also, the fact that the Cl signal is higher in intensity and covers a much smaller time interval (16-24 s) than the Cl signal (20-40 s) in Fig. 11a, curve A, suggests that the hydrolysis of $\text{MgCl}_{2(s)}$ is much more vigorous at 700-900°C than at 500-600°C. ETV-ICP-MS thus

presents valuable experimental evidence for hydrolysis of MgCl_2 , resulting in formation of $\text{HCl}_{(g)}$.

Use of the ETV-ICP-MS as a diagnostic technique permits experimental differentiation between the two different mechanisms for the chloride interference outlined by Welz *et al.*³, i.e. chemical interference caused by formation of molecular analyte species during atomization and chemical interference caused by the analyte loss during pyrolysis in the graphite furnace AAS. In addition, it explains the unusual shape of the pyrolysis curves of Fig. 4. In the $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ matrix, and presumably in many other hydrated chloride matrices, the interference mechanism is dependent on the pyrolysis temperature chosen. If the pyrolysis temperature is greater than the hydrolytic decomposition temperature of the metal chloride matrix, then extensive analyte loss caused by its expulsion with the gases produced by the hydrolytic decomposition of metal chloride matrix will occur. At pyrolysis temperatures below 700°C , the MgCl_2 matrix hydrolysis reaction does not occur, or occurs slowly, and hence, little analyte is lost. However, very little of the MgCl_2 matrix will be removed by pyrolysis at these lower temperatures, resulting in the release of relatively large amounts of the residual chloride from the MgCl_2 matrix during the atomization step and in consequent chemical interference by formation of molecular manganese chloride species during atomization. The optimum pyrolysis temperature of around 700°C for the manganese in the MgCl_2 matrix (Fig. 4) is the temperature at which maximum amount of the MgCl_2 matrix is removed from the furnace by vaporization prior to the onset of the matrix hydrolysis reaction.

Mechanism of removal of the MgCl_2 matrix interference by ascorbic acid.

Results of the ETV-ICP-MS experiments have shown that ascorbic acid chemical modifier inhibits the loss of manganese during pyrolysis at temperatures above 700°C . If the manganese is lost by being carried away with the products of the hydrolytic decomposition reaction of the MgCl_2 matrix, it is likely that ascorbic acid chemical modifier prevents such loss by inhibiting or retarding this hydrolysis reaction during the pyrolysis step. To test this hypothesis, the extent of hydrolysis of the MgCl_2 matrix after pyrolysis at various temperatures was determined, both in the presence and in the absence of ascorbic acid chemical modifier. To do this, the amounts of the magnesium and the chloride residue remaining in the graphite furnace tube immediately after the pyrolysis cycle (but prior to atomization cycle) were determined. The graphite furnace heating cycle was interrupted after the pyrolysis cycle, the furnace allowed to cool, and the residual matrix dissolved in 0.001 M nitric acid aqueous solution. This solution was then analyzed for magnesium by flame atomic absorption spectrometry, and for chloride by ion-chromatography.

Figure 13 shows how the residual amounts of magnesium and chloride, both in the presence and in the absence of ascorbic acid chemical modifier, change as a function of the pyrolysis temperature. The plotted data are the mean of three replicate determinations. The test solutions analyzed were identical to those used to obtain the pyrolysis curves of Fig. 4, i.e. 20 ml solutions containing $200\text{ }\mu\text{g}$ of MgCl_2 with or without $200\text{ }\mu\text{g}$ of ascorbic acid.

The effect of ascorbic acid on the hydrolysis reaction of the magnesium chloride

Figure 13. Percentage of residual magnesium and chloride as a function of the pyrolysis temperature. A, 200 μg MgCl_2 ; and B, 200 μg MgCl_2 + 200 μg ascorbic acid; Mg (closed symbols) and Cl (open symbols).

matrix during pyrolysis can be interpreted as follows. If the hydrolysis of the magnesium chloride matrix goes to completion via the reaction,

then all of the chloride would be removed from the furnace as $\text{HCl}_{(\text{g})}$ during pyrolysis, and almost all of the magnesium would remain in the furnace, since the vapour pressure of solid magnesium oxide would be expected to be extremely low at these relatively low pyrolysis temperatures. Hence, a large extent of hydrolysis would be indicated by low residual chloride, high residual magnesium and a high ratio of residual magnesium to residual chloride. If, on the other hand, the hydrolysis does not go to completion, or is retarded by the addition of ascorbic acid, then less hydrogen chloride would be released during pyrolysis, and the amount of chloride remaining in the furnace after the pyrolysis would be higher. Moreover, since the melting and the boiling point of $\text{MgCl}_{2(\text{s})}$ are much lower than those of $\text{MgO}_{(\text{s})}$, it would be expected that some of this unhydrolyzed $\text{MgCl}_{2(\text{s})}$ would be removed during the pyrolysis, resulting in a lower residual magnesium level when ascorbic acid chemical modifier is present. The results of Fig. 13 confirm this: when ascorbic acid chemical modifier is present at a pyrolysis temperature above that corresponding to the onset of the hydrolysis reaction i.e. around 600°C , the amount of residual chloride is higher, and the amount of residual magnesium lower. However, a better indicator of the extent of MgCl_2 hydrolysis during pyrolysis is the mole ratio of residual magnesium to residual chloride (Fig. 14). This ratio is 0.5 in unhydrolyzed magnesium chloride and will increase with increasing extent of hydrolysis, attaining very

high values as the hydrolysis reaction approaches completion. The retarding effect of ascorbic acid on the hydrolysis reaction is clearly illustrated by Fig. 14. At pyrolysis temperatures above 700°C, when no ascorbic acid is present, the mole ratio of Mg:Cl increases sharply, rising to about 250 at 1000°C. The addition of ascorbic acid by retarding the hydrolysis reaction reduces this ratio significantly, e.g. at 800°C, the mole ratio of Mg:Cl is reduced from 100 to 3 by the addition of ascorbic acid chemical modifier.

Kántor and Bezúr⁵³ have also investigated the effect of ascorbic acid on the hydrolytic decomposition of magnesium chloride, in the same temperature range, using a quartz furnace vaporizer coupled to a flame atomic absorption spectrometer. Samples were heated from 100 to 900°C at a slow heating rate (0.8 - 20 Ks⁻¹) and the magnesium atoms formed by the matrix decomposition were monitored by flame AA. Although these authors expected that addition of ascorbic acid should result in a "decrease in the adsorption hydrolysis of MgCl₂", they reported that "experience contradicted this expectation". This conclusion of Kántor and Bezúr⁵³ was based solely on the determination of the amount of magnesium atoms formed during the heating, rather than on determination of both magnesium and chloride, as has been done in this thesis. They concluded that less hydrolysis had occurred in the absence of ascorbic acid, since more magnesium was observed under these conditions. However, the above conclusion would be erroneous, if, during the vigorous hydrolysis reaction, some of the magnesium chloride matrix was carried away and expelled from the furnace by the hydrogen chloride gas formed, in the same manner as has been proposed in this thesis for the manganese

Figure 14. Mole ratio of magnesium to chloride remaining after pyrolysis as a function of the pyrolysis temperature. A: 200 μg MgCl_2 . B: 200 μg MgCl_2 + 200 μg ascorbic acid.

analyte (Fig 8a) and the MgCl_2 matrix (Fig. 12b). Expulsion of a small part of the MgCl_2 matrix in the ETV-ICP-MS experiments when no ascorbic acid chemical modifier was present was repeatedly observed.

The precise mechanism for the retardation of the hydrolysis of the MgCl_2 matrix by ascorbic acid is not known. However, observations of the manganese signal in the MgCl_2 matrix system during pyrolysis in the graphite furnace, and especially from the ETV graphite strip are as follows. When no ascorbic acid chemical modifier was present, the matrix dried to a white crystalline material and decomposed violently during pyrolysis, presumably as the hydrolysis reaction occurred. In the presence of ascorbic acid, the sample matrix formed a melt (in the drying step), which partially evaporated, in a much more controlled manner, during pyrolysis. Probably, ascorbic acid, a known bidentate ligand, forms a complex with the magnesium ions in this melt, facilitating the removal of water of hydration during the drying stage, and thereby retarding the hydrolysis reaction during pyrolysis.

SUMMARY

The interferences of magnesium chloride in the determination of manganese by ETAAS occur by two different mechanisms, depending on the pyrolysis temperature. If the pyrolysis temperature exceeds the temperature required for the hydrolytic decomposition of the MgCl_2 matrix then $\text{HCl}_{(g)}$ is formed. Manganese is lost during pyrolysis by expulsion with rapidly expanding $\text{HCl}_{(g)}$. At pyrolysis temperatures below 700°C , where minimal decomposition of the magnesium chloride matrix occurs, no manganese is lost during pyrolysis, but the manganese atomic absorption signal is

suppressed because large amounts of residual magnesium chloride is released into the vapour phase, resulting in formation of undissociated gaseous manganese chloride in the atomization cycle. This interference is reduced as the pyrolysis temperature is increased up to 700°C, presumably because more of the unhydrolyzed magnesium chloride matrix is removed from the graphite furnace by vaporization as the pyrolysis temperature is increased. The same mechanism should apply also to other hydrated chloride matrix which undergoes rapid hydrolytic decomposition during pyrolysis producing $\text{HCl}_{(g)}$. This mechanism may be applicable also to the matrices containing chlorides which undergo rapid hydrolysis producing $\text{HCl}_{(g)}$. In such cases, the optimum pyrolysis temperature would be just below the matrix decomposition temperature at which the maximum amount of matrix is removed by vaporization prior to the onset of hydrolysis. In addition, in ETAAS, for atomization from the tube wall, ascorbic acid can be used as an effective chemical modifier. In ETAAS of manganese in the MgCl_2 matrix, at pyrolysis temperatures above 700°C, ascorbic acid retards the hydrolysis reaction of the magnesium chloride matrix, and thus prevents loss of manganese during the pyrolysis cycle.

CHAPTER 2

**MECHANISM OF INTERFERENCES BY SODIUM CHLORIDE MATRIX AND
MECHANISM OF CHEMICAL MODIFICATION BY ASCORBIC ACID WITH
THE ATOMIZATION OF MANGANESE IN ELECTROTHERMAL ATOMIC
ABSORPTION SPECTROMETRY**

INTRODUCTION

Chloride matrices interfere with determination of many elements by graphite furnace atomic absorption spectrometry (GFAAS). Although the addition of nitric acid to aqueous solutions of samples to make the pH 1.5 completely removes the chloride interference with some elements (Zn, Mn, Fe)²⁴, for solid sampling it is necessary to know the cause of the chloride matrix interference in order that remedial action can be taken in direct analysis (without sample dissolution) of solid samples containing chloride matrices. However, of more fundamental importance is the fact that knowledge and understanding of reactions between chloride species, analyte species and chemical modifiers in graphite furnaces are essential for further advance in graphite furnace technique for quantitative determination.

The MgCl_2 interferences with Mn in GFAAS and ETV-ICP-MS were investigated in chapter 1 of this thesis. It was shown that these interferences occur by two distinctly different mechanisms, depending on the pyrolysis temperature used. If the pyrolysis temperature exceeds the temperature required for the hydrolytic decomposition of the magnesium chloride matrix, then manganese analyte is lost during the pyrolysis by

expulsion with the rapidly expanding HCl gas that is formed by the hydrolysis of the matrix. For pyrolysis temperatures below 700°C, where minimal matrix decomposition occurs, no manganese is lost in the pyrolysis, but the Mn atomic absorption signal is depressed by formation of gaseous molecular manganese chloride formed in the atomization cycle.

The sodium chloride interference with several elements including manganese in GFAAS has been extensively investigated, and several mechanisms have been proposed to explain these interferences^{6,25,26,27,28,29,30,31,55}. Welz *et al.*²⁶ have used dual-cavity platform atomization experiments to study the interferences by sodium chloride and nickel chloride with lead. They concluded that, despite the substantially different stabilities and volatilities of these two chlorides, the interferences appear, in general, to proceed by the same mechanism, i.e. expulsion of the analyte from the furnace along with the rapidly expanding matrix gases. Chapter 1 of this thesis confirms this mechanism in the case of hydrated magnesium chloride which hydrolyzes. Sodium chloride, however, does not hydrolyze at any temperature. Therefore, the interference by sodium chloride with Mn probably has a mechanism different from that which occurs with hydrated magnesium and nickel chlorides, which do hydrolyze during pyrolysis and atomization.

An alternative mechanism, commonly proposed to explain chloride interferences in GFAAS, is the formation of gaseous analyte chloride molecules that diffuse away from the analysis volume prior to dissociation into analyte atoms^{29,55,6}. This mechanism postulates that the following reaction occurs during the atomization, when gaseous

manganese and chlorine from the chloride matrix, are simultaneously present in the graphite furnace:

Shekiri *et al.*⁵⁶ have presented experimental evidence for the formation of gas phase manganese chloride in the graphite furnace. Using a photodiode array detection system and a deuterium continuum source, they measured the molecular absorption spectra, generated in the graphite furnace, at 0.5s intervals during the pyrolysis and atomization, over the wavelength range 200-350 nm. In the CaCl_2 or the MgCl_2 matrix, molecular absorption corresponding to gaseous manganese chloride was observed; however, in the NaCl matrix, they could not detect any manganese chloride. This was probably because the MnCl molecular absorption band which has a maximum at 242 nm was obscured by the absorption of the NaCl molecular absorption band (maximum at 247nm). An alternative explanation is that the mass ratio of the NaCl matrix to the Mn used (around 5 to 1) was not large enough to force the equilibrium reaction (Eqn. 1) sufficiently towards the MnCl side. These authors also used ascorbic acid as a chemical modifier to remove the chloride interferences by MgCl_2 and CaCl_2 matrices. They showed that as the ascorbic acid restored the Mn atomic absorption signal, there was a concurrent reduction in the intensity of the manganese chloride molecular absorption spectrum. This effect was attributed to a condensed-phase reaction in which the analyte and matrix cations were complexed by ascorbic acid so that the chloride was lost as the HCl gas prior to the vaporization of the matrix.

Gilchrist *et al.*^{42,43} have shown that the $H_{2(g)}$ and $CO_{(g)}$, generated by the pyrolysis of ascorbic acid in the graphite furnace, effectively remove the chloride interference with lead only if small amounts of residual chloride matrix are present during atomization, e.g., for a 1% HCl matrix. The hydrogen gas participates in a series of linked gas phase equilibrium reactions that reduce the partial pressure of chlorine by formation of gaseous HCl which has a relatively high bond dissociation energy.

This thesis deals with interference of the NaCl matrix with manganese. The objectives of this investigation are:

- i) to determine if the chloride interference is due to loss of analyte during the pyrolysis stage, or by a gas phase reaction during the atomization step;
- ii) to determine if a gas phase chemical modification mechanism, similar to that reported by Gilchrist *et al.*⁴², is applicable to systems that contain high concentrations of the NaCl matrix; and
- iii) to investigate the interaction between the sodium chloride matrix and the ascorbic acid chemical modifier in the condensed phase.

EXPERIMENTAL

Atomic Absorption Spectrometry

Apparatus. A Perkin-Elmer Model 5000 atomic absorption spectrometer equipped with a Zeeman Effect Background Corrector and a Heated Graphite Atomizer (HGA), Model 500, was used. Absorbance values were recorded directly from the spectrometer and were then corrected for blanks. The absorbance values versus time graphs were recorded

with an IBM-compatible computer using a software program TGP (Tech Graph Pad designed for scientists and engineers). The outputs were printed using a Hewlett-Packard Laser-Jet III printer. A Mn hollow-cathode lamp (Perkin-Elmer) and pyrolytically-coated graphite tubes (Perkin-Elmer Part No. B009-1504) were used. The temperature of the graphite tube surface just below the dosing hole was monitored with an Ircon Model 300c automatic optical pyrometer. Test solutions of 20 μL volumes were injected using a 20 μL Eppendorf pipette.

Gases. Argon gas of high-purity (99.995% pure, Matheson Gas Products, Canada) was used both as the purge gas and the sheath gas. The 5.0% v/v hydrogen gas in argon (supplied by Matheson Gas Products) was mixed with Ar gas using a flowmeter regulator to simulate the amount of H_2 gas released by the pyrolysis of ascorbic acid (when added as a chemical modifier).

Standards and Reagents. Standards and reagents were individually prepared as follows:

- (a) A stock solution of 1000 $\mu\text{g ml}^{-1}$ manganese solution was prepared by dissolving 0.5026 g of Mn metal (99.94% pure, Fisher Scientific) in 10.00 ml of 1:1 HNO_3 (Ultrex, Baker) and diluting the solution to 500.00 ml with ultrapure water.
- (b) 5 $\mu\text{g ml}^{-1}$ manganese solution was prepared by a serial dilution of the above 1000 $\mu\text{g ml}^{-1}$ Mn stock solution with ultrapure water.
- (c) 2.5% m/v NaCl solution was prepared by dissolving 2.5000 g of NaCl (99.9% pure, BDH Chemicals, AnalaR) in 100.00 ml ultrapure water.

Test solutions were prepared by serial dilution of the above solutions (b) and (c) with ultrapure water in 25.00 ml volumetric flasks immediately prior to determination.

The following solutions were also prepared in ultrapure water.

- (a) Solution A contained $0.02 \mu\text{g ml}^{-1}$ Mn and 1% v/v HNO_3 .
- (b) Solution B contained $0.02 \mu\text{g ml}^{-1}$ Mn and 1% v/v HCl solution.
- (c) Solution C contained $0.02 \mu\text{g ml}^{-1}$ Mn and 1% v/v HCl and 0.5% m/v NaCl solution.
- (d) Solution D contained $0.02 \mu\text{g ml}^{-1}$ Mn and 1% v/v HCl and 0.5% m/v NaCl and 1% m/v ascorbic acid.

The solution of ascorbic acid was prepared by dissolving 0.2500 g of L-ascorbic acid (99.5% pure, Baker Analyzed Reagent) in a minimum amount of ultrapure water. This solution was then transferred quantitatively to a 25.00 ml volumetric flask that contained appropriate amounts of solutions of the other three components of solution D. This solution was then made up to the mark with ultrapure water.

- (e) The blank for solution A was prepared to contain only 1% v/v HNO_3 (Ultrex, Baker) in ultrapure water. The blanks for solutions B to D were prepared to contain only 1% v/v HCl (Ultrex, Baker) in ultrapure water.

Ultrapure water was obtained direct from a Millipore-QTM water purification system (Millipore Corporation, Mississauga, ON., Canada) immediately prior to its use.

Experimental and Operating Conditions. The experimental and operating conditions used for the atomization of manganese are presented in Table 1. The Mn hollow cathode lamp was operated at a lamp current of 20 mA. The most sensitive line of Mn, 279.5 nm, a spectral band pass of 0.2 nm (low slit), and an integration time of 7.0 seconds were

used.

Determination of the Residual Sodium Chloride

In order to determine the cause of interference by the chloride matrix with the manganese signal, the sodium chloride matrix that remained after the pyrolysis cycle at a given pyrolysis temperature was determined as follows.

Apparatus. A Perkin-Elmer Model 603 atomic absorption spectrometer equipped with an air-acetylene flame atomizer-burner and a Deuterium Arc Background Corrector, was used to determine the sodium (as the chloride) that remained after the pyrolysis cycle. A Na hollow-cathode lamp (Perkin-Elmer) was used. The most sensitive sodium lines, 589.0-589.6 nm (the sodium doublets), and a lamp current of 15 mA were used. The absorbance signals were recorded from the digital read-out of the spectrometer and were then corrected for blanks.

The chloride that remained after the pyrolysis cycle was determined using a DIONEX series 4000i ion chromatograph, equipped with an electrical-conductivity detector. The ion chromatography column was an AS4A analytical column (Dionex), equipped with a membrane ion suppressor (MPIC, Dionex). The eluent consisted of a 1.8 mM Na_2CO_3 and 1.7 mM NaHCO_3 in ultrapure water. The membrane ion suppressor was regenerated by a 5 mM H_2SO_4 in ultrapure water. The chromatograms were recorded with a SP4290 integrator. Aqueous solutions of the sample were loaded in a 50 μL sample loop with a 1 ml plastic syringe and were injected with the automatic injection device of the ion chromatograph.

Standards and Reagents. A stock solution of 164.8 $\mu\text{g ml}^{-1}$ NaCl (which corresponded

to 64.8 μg /ml of Na and 100 μg ml⁻¹ of Cl) was prepared by dissolving 0.1648 g NaCl (99.9% pure, BDH Chemicals, AnalaR (analytical reagents)) in ultrapure water, and the volume made up to 1000.00 ml with ultrapure water.

Determination of the residual sodium and chloride in the recovery experiments required daily preparations of analytical calibration curves using standard solutions of NaCl with the chloride concentrations in the range 0.1-15 μg ml⁻¹.

Table 2 presents the experimental and operating conditions used for the determination of the residual sodium chloride.

Extraction Procedure. Recovery and clean-up experiments were performed to ensure that the extraction procedure gave ~ 100% recoveries of the residual sodium (as the chloride) and to avoid possible contamination of the next sample by carry-over of detectable amounts of the sodium or chloride because of inadequate thermal treatment for cleaning up of the graphite tube prior to its re-use.

Extractions of the sodium chloride residue, with or without the added ascorbic acid, were performed in triplicate. The sodium chloride matrix was pyrolysed at various pyrolysis temperatures using the operating procedures shown in Table 2. The residues were extracted by inserting the graphite tube (containing the residue) in 15 ml polystyrene tubes equipped with snap caps (Fisher Scientific), which contained 10.00 ml of ultrapure water. Each polystyrene tube with its contents was heated for 15 minutes at 70°C and then shaken for 5 minutes with a test tube mixer (Vortex-Genie, Fisher Scientific). Each of these extracts was analyzed for sodium and chloride using flame AAS and ion chromatography, respectively.

Electrothermal Vaporization Inductively-Coupled Plasma Mass Spectrometry

Apparatus. The inductively coupled plasma mass spectrometer (ICP-MS) used for this work was a Perkin-Elmer/Sciex Elan, Model 250. The ICP-MS was used in the positive ion detection mode. An extended quartz torch was used for all experiments. The electrothermal vaporization (ETV) device (Fig. 1) used for this investigation has been described previously in chapter 1. The ETV device consisted of a resistively-heated graphite strip measuring 11 x 4 x 1 mm connected to an IL 555 power supply (Instrumentation Laboratory Inc., Mass., USA). The sample vaporized from the graphite strip was transported to the plasma by a stream of argon gas whose flow was directed tangentially to the graphite support electrodes on which the graphite strip was mounted. A quartz cover resembling an inverted thistle tube was used to form an envelope above the vaporization surface. The tangential flow of Ar gas and the shape of the quartz cover served to minimise condensation of the sample material (the analyte and the matrix components) on the quartz surface, and thus to maximise sample transport to the plasma. The temperature of the surface of the graphite strip was monitored with an automatic optical pyrometer (Ircon Model 300c). The loss in the radiance transmission due to the quartz cover was corrected for by adjusting the emissivity setting on the optical pyrometer. The interface between the ETV unit and the ICP-MS consisted of a Tygon tubing, 1.0 m long, 6.0 mm i.d., connected direct to the plasma torch.

Pyrolytically-coated crystalline graphite (Ultra Carbon, Bay City, Michigan, USA) was used to fabricate the graphite strips. A small oval-shaped depression was machined onto the surface of each strip at its centre. The depression held the liquid sample and

prevented spreading of the sample during the drying step.

The instrumental settings for the ETV-ICP-MS are given in Table 3.

Standards and reagents. Solutions of Mn, Mn plus NaCl, and Mn plus NaCl and ascorbic acid, were identical to the solutions used for the GFAAS experiments except that in this case they were prepared in 0.04% v/v HCl for the following reasons. The samples prepared in 1% v/v HCl occasionally spread toward the graphite support electrode upon drying, which affected the reproducibility of the results. This was avoided by making all solutions in 0.04% v/v HCl. The ETV-ICP-MS signal for Cl was inordinately large for 1% v/v HCl solutions, but was much smaller for the 0.04% v/v HCl solutions. The ETV-ICP-MS signal for Mn and Na were not affected by the 1% v/v or the 0.04% v/v HCl solutions. Test solutions of 10 μ l volumes were injected onto the graphite strip using a 10 μ l Eppendorf pipette.

RESULTS AND DISCUSSION

ETAAS experiments.

The ETAAS was performed by atomization from the graphite tube wall of the HGA 500 graphite furnace in order to maximize the effects of the sodium chloride matrix interference, providing more scope for study of interference mechanisms and their removal than would have been the case if these effects were minimized by the use of atomization from a graphite platform. Moreover, the use of a graphite platform for atomization would have made recovery studies of the residual amounts of sodium chloride left in the furnace after the pyrolysis step more difficult because the matrix would have been distributed between both the platform and the cooler parts of the tube

wall after the pyrolysis cycle, making the washing out of the residue more difficult. The heating ramp time on the HGA 500 power supply was set at 1 s instead of the standard 0 s heating ramp time because the power supply of Instrumentation Laboratory (IL) 555 for the graphite strip vaporizer used in the ETV-ICP-MS experiments could provide a maximum heating ramp approximately equal to the 1 s ramp time of the HGA 500. The heating characteristics of both electrothermal atomizers used in this work were made to be similar in order that the results obtained using these two atomizers were comparable. It is emphasized here that standard experimental procedures that would have eliminated or minimized matrix interferences, e.g. atomization from a graphite platform in GFAAS, were deliberately not adopted since the objectives were to maximize matrix interferences in order to investigate their mechanisms. Hence, the effects and mechanisms that are reported in this thesis may be different from those observed under standard (optimized) experimental conditions used in GFAAS.

Figure 15 shows the pyrolysis (A) and the atomization (B) curve^{10,11} for 400 pg of manganese in 1% v/v HNO₃ and 1% v/v HCl solution. The pyrolysis curves were obtained by varying the pyrolysis temperature while holding the atomization temperature constant at 2000°C; the atomization curves were obtained by varying the atomization temperature while holding the pyrolysis temperature constant at 1100°C. The optimum pyrolysis and atomization temperatures were pre-determined to be 1100 and 2000°C, respectively. Figure 15 shows that the integrated absorbance values for the Mn in nitric acid were for the most part of the curve greater than those for the Mn in the hydrochloric acid solution. The integrated absorbance values for the atomization curve of Mn in both

Figure 15. Pyrolysis curve (A) and atomization curve (B) for 400 pg Mn in 1% v/v HNO₃ (●) and 400 pg Mn in 1% v/v HCl (■) for atomization from the graphite tube wall.

nitric acid and hydrochloric acid between 1200 and 1800°C were same. However, at pyrolysis temperatures of 400-1400°C and atomization temperatures of 1800-2400°C, the integrated absorbance values for both the pyrolysis (A) and the atomization (B) curve were always greater for the Mn in nitric acid than in hydrochloric acid solutions. Figure 15 shows results that are different from those reported by Hulanicki *et al.*³⁵. In Fig. 3 of their paper, where they have reported that the integrated absorbance values for wall atomization of 10 pg of the Mn in hydrochloric acid solution are greater than that for the Mn in nitric acid solution for the pyrolysis temperature range of 400-1600°C, which is the opposite of what was observed in this thesis research.

The experiment for obtaining the pyrolysis and the atomization curve was repeated using identical experimental conditions except that a used pyrolytically-coated graphite tube (after ~ 150 firings) was employed. The difference in the integrated absorbance values between Mn in the nitric and the hydrochloric acid solution was found to be much smaller. It seems that the physical condition of the graphite tube is important in determining Mn probably because Mn forms carbides with the graphite surface after the surface becomes exposed by the loss of pyrolytic graphite coating caused by repeated firings. McNally and Holcombe⁵⁷ have reported that destruction of the pyrolytic graphite coating results in the *total* loss of the Mn absorbance signal, and have suggested that this loss may be accounted for by formation of manganese carbide with a used graphite tube.

Figure 16 shows the pyrolysis (A) and the atomization (B) curve of 400 pg of manganese with 100 µg of sodium chloride in 1% v/v HCl, obtained by using an

Figure 16. Pyrolysis curve (A) and atomization curve (B) for 400 pg Mn + 100 μ g NaCl in 1% v/v HCl.

atomization temperature of 2000°C for the former, and a pyrolysis temperature of 1100°C for the latter. The pyrolysis curve shows a maximum integrated absorbance at 1100°C. The pyrolysis and the atomization curve of Fig. 16 indicates that Mn is lost as a molecular species (probably manganese chloride) over a narrow temperature range between 1100°C (the maximum in the pyrolysis curve) and 1200°C (the onset of atomization). In addition, some Mn is probably lost as molecular species at temperatures between 1200 and 1800°C since the sum of the integrated absorbance from the pyrolysis and the atomization curve at a given temperature within that temperature range is not equal to the integrated absorbance obtained using the optimum pyrolysis and atomization temperatures, 1100°C and 2000°C, respectively. The pyrolysis and atomization curves only indicate that the manganese is lost as molecules, not as atoms. Other experimental evidence is required for establishing the identity of the manganese molecular species that are lost.

Figure 17 shows typical atomic absorption signals of 400 pg of Mn: (A) in 1% v/v HCl, (B) in matrix A plus 100 μ g of NaCl, and (C) in matrix B plus 200 μ g of ascorbic acid, all for a pyrolysis temperature of 550°C. The addition of ascorbic acid (C) completely eliminates the NaCl matrix interference, giving complete recovery of the Mn peak-height signal, and a slight improvement in the integrated absorbance over that obtained without the ascorbic acid (A). The absorption profile is also shifted slightly to an earlier appearance time. The spike at the leading edge of peak B warrants comment. Despite the use of Zeeman effect background correction, this spike is probably due to the NaCl matrix, and suggests that the bulk of the sodium chloride matrix is vaporized

Figure 17. Typical absorbance profiles in GFAAS for Mn after pyrolysis at 550°C.
A: 400 pg Mn in 1% v/v HCl. B: A + 100 μ g NaCl. C: B + 200 μ g ascorbic acid.

simultaneously with the analyte. The spike was only observed at low pyrolysis temperatures, when larger amounts of residual matrix would be expected to remain in the furnace after the pyrolysis cycle. Welz *et al.*²⁶ observed a similar spike on the trailing edge of the Pb absorption profile obtained using 100 μg of the NaCl matrix.

Figure 18 shows the pyrolysis curves for 400 pg of Mn in 1% v/v HCl (A), 1% HCl + 100 μg NaCl (B), and 1% HCl + 100 μg NaCl + 200 μg ascorbic acid (C). An atomization temperature of 2400°C was used instead of the optimum atomization temperature of ~2000°C (Fig. 16) because for the constant heating ramp time used in this experiment the higher temperature setting corresponded to a higher heating rate, which resulted in an earlier appearance time and also, narrower absorbance profiles (the latter not shown). This also resulted in shorter (x3) peak integration times, giving longer graphite tube life, and allowing all data to be collected using the same graphite tube (< 200 firings). In Fig. 18, the pyrolysis curve of manganese plus the NaCl matrix (curve B) has a maximum at 1050°C. Therefore, the pyrolysis temperature of 1050°C represents the optimum pyrolysis temperature for removal of the maximum amount of the NaCl matrix prior to the atomization cycle. Even at the optimum pyrolysis temperature of 1050°C, the Mn AA signal is not equal to that for the Mn without NaCl (curve A), suggesting there is some interference by the residual chloride left after from the decomposition of the NaCl matrix, i.e. by the chloride that remains within the furnace during the atomization cycle. The maximum interference with the Mn signal occurs at pyrolysis temperatures between 400 and 850°C, and the interference then decreases between 850 and 1050°C. The suppression of the Mn absorbance at

Figure 18. Pyrolysis curves in GFAAS for Mn in various matrices. A: 400 pg Mn in 1% v/v HCl. B: A + 100 μ g NaCl. C: B + 200 μ g ascorbic acid.

temperatures below 1050°C could be explained by one of two mechanisms:

- a) Formation of molecular manganese chloride species by gas phase reactions between Mn and the residual NaCl matrix vaporized during the atomization or;
- b) Loss of the Mn analyte by co-volatilisation and expulsion with the vapour of the NaCl matrix during pyrolysis.

The latter mechanism (b) seems less likely since little of the NaCl matrix should be vaporized at pyrolysis temperatures below 900°C⁵⁸. The ETV-ICP-MS experiments, described in the next section, should permit a clear experimental differentiation between these two mechanisms.

The most striking feature of Fig. 18 is the effect of ascorbic acid chemical modifier (curve C). At all pyrolysis temperatures, the addition of ascorbic acid completely removes the chloride interference to give an integrated absorbance value which is approximately 20% greater than that for the Mn in 1% v/v HCl solution. These results agree with those of Hydes⁴⁰ and Tominaga *et al.*³⁹, who have reported recoveries in the peak height for Mn of up to 100% in a matrix of up to 3.5% m/v NaCl using ascorbic acid chemical modifier.

The remainder of this research addresses two questions raised in this section: "Is the suppression of the Mn atomic absorption signal due to the analyte loss during pyrolysis? What is the mechanism of chemical modification by the chemical modifier ascorbic acid?"

ETV-ICP-MS experiments.

The test solution containing the manganese solution plus the sodium chloride

matrix, with or without the ascorbic acid chemical modifier, was deposited on the electrothermal vaporizer (ETV), vaporized, and the vapour generated during the entire pyrolysis and atomization step was transported to the ICP-MS for simultaneous multi-element determination. In general, most molecular species, vaporized either during the pyrolysis and the atomization step (in addition to vaporized atoms), would be dissociated in the hot argon plasma to yield atoms, which were then ionised in the plasma and detected as atomic ions by the mass spectrometer⁵⁴. The ETV-ICP-MS technique allows detection of ionic species as a function of the temperature of the vaporizing graphite strip surface (ETV) throughout the equivalent process of pyrolysis and atomization (including the temperature range) used in the graphite furnace. For each sample tested, the ETV-ICP-MS signal for $^{55}\text{Mn}^+$, $^{37}\text{Cl}^+$, and $^{23}\text{Na}^+$ were recorded simultaneously; no memory effect was detected for any of the above ions. The ETV-ICP-MS signals were corrected for blanks.

The ETV-ICP-MS results obtained can be interpreted only qualitatively since the effects of the various matrices (mainly Na) on the mass transport efficiency and plasma properties, which affect the ion counts are not yet fully understood⁵⁹, nor can these effects be fully quantified. In Figs. 19 to 22, the pyrolysis step, consisting of a heating ramp time of 20 s and a holding time of 20 s, is from 0 to 40 s. The high temperature vaporization step is from 40-50 s. In Figs. 19 and 20, the temperature of the graphite strip (curve B) shows an upward drift during the pyrolysis step. Therefore, the pyrolysis temperature of the graphite strip (ETV) is reported as the mean temperature of the last 20 s of the pyrolysis cycle.

2

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

Figure 19a shows the $^{55}\text{Mn}^+$ ETV-ICP-MS signal (curve A) for 200 pg of manganese in 0.04% v/v HCl at a pyrolysis temperature of 550°C. The effects of the addition of NaCl (50 μg) and ascorbic acid chemical modifier (100 μg) are shown in Figs. 19b and 19c, respectively. These ETV-ICP-MS results showed no signal for manganese analyte during the pyrolysis step (between 20 and 40 s) even when 50 μg of the NaCl matrix was present (Fig. 19b). Figure 20 shows the $^{55}\text{Mn}^+$ ETV-ICP-MS trace for 200 pg of Mn, in a matrix of 50 μg of NaCl, at a pyrolysis temperature of 900°C. Again, no signal for manganese analyte was observed during the pyrolysis period between 20 and 40 s. These results contrast sharply with those reported earlier in this thesis for Mn in the magnesium chloride matrix, where the ETV-ICP-MS results showed considerable analyte loss during the pyrolysis cycle. These results clearly indicate that the NaCl interference with manganese is not due to loss of manganese analyte during the pyrolysis, and that the mechanisms of interferences with manganese by the NaCl and by the hydrated MgCl_2 matrices are different.

Although a quantitative comparison of the Mn ion counts is not possible because of the different matrix effects on the mass transport efficiency and plasma properties, some qualitative comparisons can be made. At a pyrolysis temperature of 550°C (Fig. 19), the $^{55}\text{Mn}^+$ ion count appeared to be suppressed in the NaCl matrix, and although the ion count was improved by the addition of ascorbic acid chemical modifier, the signal was not completely recovered, as was the case in the graphite furnace experiment (Fig. 17).

The simultaneous multi-element capability of the ETV-ICP-MS technique allows

Figure 19. Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS for various matrices at pyrolysis temperature 550°C . A: 200 pg Mn. (a) 0.04% v/v HCl. (b) 50 μg NaCl. (c) 50 μg NaCl + 100 μg ascorbic acid. B: Temperature profile of the graphite strip.

Figure 20. Temporal behaviour of $^{55}\text{Mn}^+$ in ETV-ICP-MS for A: 200 pg of Mn + 50 μg NaCl in 0.04% v/v HCl; pyrolysis temperature, 900°C. B: Temperature profile of the graphite strip.

the observation of the signals by both the analyte and the matrix components (Na and Cl) separately during the pyrolysis and the vaporization cycle. Figures 21a and 21b show the ETV-ICP-MS signals for $^{23}\text{Na}^+$ and $^{37}\text{Cl}^+$, over the same time scale as that for the $^{55}\text{Mn}^+$ signal, for a pyrolysis temperature of 900°C . Because of the relatively large amount of the NaCl matrix used ($50\text{ }\mu\text{g}$), and the high analytical sensitivity of ICP-MS for sodium, the peaks were off-scale. Again, only a qualitative analysis of these results is justified. Figure 21a shows that large amounts of sodium were vaporized from the ETV from 18 s onwards throughout the pyrolysis and the vaporization cycle. The same result was observed in the presence of ascorbic acid chemical modifier (curve B). Again, the onset of the large off-scale Na peak coincided with the onset of the pyrolysis. A relatively small amount of Na also appeared during the temperature ramp between the drying and the pyrolysis cycle (10-15s), which, because of the high sensitivity of ICP-MS for $^{23}\text{Na}^+$, represents only a small amount of the NaCl matrix that was carried away by spattering during this temperature ramp. Less NaCl was released during this period when ascorbic acid chemical modifier was added (curve B).

Figure 21b shows the ETV-ICP-MS trace for $^{37}\text{Cl}^+$ corresponding to that of $^{23}\text{Na}^+$. Again, the onset of the large Cl peak coincided with the commencement of pyrolysis at 20 s; this peak also coincided with the onset of release of Na (Fig. 21a), as would be expected since NaCl was the major species vaporized. Note that the large Cl peak, though off-scale at its maximum, did come back on-scale at around 42 s, unlike the Na peak, presumably because the ICP-MS sensitivity for $^{37}\text{Cl}^+$ was less than that for $^{23}\text{Na}^+$.

Figure 21. Temporal behaviour of (a) $^{23}\text{Na}^+$ and (b) $^{37}\text{Cl}^+$ in ETV-ICP-MS at a pyrolysis temperature 900°C . A: 200 pg Mn + 50 μg NaCl in 0.04% v/v HCl. B: A + 100 μg ascorbic acid.

There are two differences between Figs. 21a and 21b. In the 0-10 s region, which corresponded to the temperature ramp period between the drying and the pyrolysis cycles, the addition of ascorbic acid produced a signal for a significant amount of Cl. However, comparatively little Na appeared in the presence of ascorbic acid in the corresponding region of Fig. 21a. Since Cl appeared unaccompanied by Na in this 0-10 s region this Cl appearance can only be due to the formation of a small amount of HCl, presumably by the reaction between ascorbic acid and NaCl in the condensed phase at relatively low temperatures before the maximum pyrolysis temperature was attained. The second difference was the appearance of a sharp, narrow, off-scale $^{37}\text{Cl}^+$ peak centred around 41s; this point of time corresponded to the rapid temperature ramp for the vaporization following the pyrolysis cycle. This narrow peak can be attributed to the NaCl matrix, which remained after a 900°C pyrolysis and was released during the rapid, high-temperature vaporization ramp. A qualitative comparison of peak areas for this sharp peak, and the broader peak, between 20 and 40 s, shows that for 900°C pyrolysis, the majority of the NaCl matrix was removed during the pyrolysis cycle, but a smaller amount remained after the pyrolysis cycle and was released simultaneously with the Mn analyte at around 41s. The addition of ascorbic acid thus appears to make little difference to the pattern of Cl release in the 20-42 s region. However, it was not possible to determine from these traces the exact chemical form of the species which released Cl; it could be NaCl, HCl, or a combination of both. Since the $^{23}\text{Na}^+$ signal was off-scale throughout this region because of the higher ICP-MS sensitivity for $^{23}\text{Na}^+$ it was not possible to determine if HCl was present. However, this point will be

discussed again in a later section.

The relative amount of the NaCl matrix removed at different pyrolysis temperatures is shown in Fig. 22. For a pyrolysis temperature of 550°C (curve A), very little $^{37}\text{Na}^+$ appeared during the pyrolysis cycle between 20 and 40 s. The onset of the release of the bulk of the NaCl matrix coincided with the start of the high-temperature vaporization ramp at around 40 s, which also coincided with the release of the Mn analyte. This result confirms the earlier observation that the NaCl matrix does not cause a loss of Mn analyte during the pyrolysis cycle. At this low pyrolysis temperature, an insufficient amount of the NaCl matrix is vaporized during the pyrolysis cycle to cause any loss of the Mn analyte by co-volatilisation, and consequently no loss of the Mn analyte was observed in the ETV-ICP-MS signal in this pyrolysis region (Fig. 19b). Figure 22 shows that for a higher pyrolysis temperature of 900°C, the onset of release of Na coincided with the start of pyrolysis at 20 s. However, no concomitant signal of the Mn analyte was observed in the ETV-ICP-MS signal (Fig. 20) in this pyrolysis region even when a large amount of the NaCl matrix was vaporized during the pyrolysis cycle, i.e. no Mn analyte was lost from the furnace during the pyrolysis cycle even though excessive gas evolution from the NaCl matrix was observed. Therefore, if the Mn analyte was not lost during the pyrolysis cycle, then the observed loss of the Mn analyte must have occurred during the vaporization cycle (or during the equivalent atomization cycle in GFAAS). Hence, a mechanism similar to the one proposed by Welz *et al.*²⁶ is not applicable to manganese in the NaCl matrix. The most probable mechanism for the observed loss of manganese analyte is a gas-phase interference as

Figure 22. Temporal behaviour of $^{23}\text{Na}^+$ in ETV-ICP-MS for 200 pg Mn + 50 μg NaCl in 0.04% v/v HCl for two different pyrolysis temperatures. A: 550°C. B: 900°C.

proposed by Dittrich *et al.*⁵⁵, and Frech *et al.*⁶, that involves a reaction between manganese atoms and chlorine to form gaseous manganese chloride in the vaporization cycle (or the atomization) cycle in GFAAS as follows:

The manganese is then lost from the furnace in GFAAS as vapour-phase, undissociated manganese chloride.

Gas-phase chemical modification.

In order to determine if the elimination of the NaCl matrix interference by ascorbic acid can be accounted for by a gas phase chemical modification model, similar to the one reported by Gilchrist *et al.*⁴², GFAAS pyrolysis curves, similar to those of Fig. 18, were constructed with hydrogen added to the argon purge gas. Gilchrist *et al.*⁴² have shown that pyrolysis of the amount of ascorbic acid taken in their work produces about 1% v/v hydrogen gas in the gas phase in the pyrolysis cycle of GFAAS. If a gas phase chemical modification process similar to that of Gilchrist *et al.*⁴² can justifiably be applied to the NaCl matrix interference, then addition of an equivalent amount of hydrogen gas to the argon purge gas should cause an increase in the integrated absorbance, and a shift to an earlier appearance temperature for manganese.

To test this hypothesis, an experiment was therefore done in which hydrogen was added to the argon purge gas throughout the duration of the heating programme. Figure 23 shows the results of the above experiments. Addition of 1% v/v hydrogen to the argon purge gas had no effect on the pyrolysis curve for manganese in the NaCl matrix.

Figure 23. Pyrolysis curves in GFAAS for 400 pg Mn + 1% v/v HCl in argon gas (A); in argon gas containing 5% v/v H₂ gas (B); for 400 pg Mn + 100 μg NaCl + 1% v/v HCl in argon gas (C); in argon gas containing 5% v/v H₂ gas (D).

To determine if higher concentrations of hydrogen would have any effect, 5% v/v hydrogen gas was added to the argon purge gas. The addition of 5% v/v hydrogen gas to manganese in 1% v/v HCl solution (curve B) increases the integrated absorbance by about 20% with respect to manganese in 1% v/v HCl in argon purge gas (curve A) over the whole range of the pyrolysis temperature. This improvement is comparable with that in the integrated absorbance of manganese in 1% v/v HNO₃ solution relative to the signal of manganese in 1% v/v HCl solution, reported in Fig. 15. This means that 1% HCl solution causes a small matrix interference, presumably because of the small amounts of residual HCl acid retained by the graphite tube after drying and pyrolysis. Addition of hydrogen gas removes such small residual matrix effects, as reported previously¹¹. However, Fig. 23 shows that when large amounts of the NaCl matrix are present with manganese, addition of 5% v/v hydrogen to argon (curve D) is totally ineffective in removing the interference when compared with argon purge gas (curve C). For pyrolysis temperatures below 900°C, curves C and D nearly merge; at temperatures above 900°C, suppression of manganese signal occurs in the presence of hydrogen gas. Since the addition of hydrogen gas at concentrations equal to or above those generated by pyrolysis of ascorbic acid did not have the same effect as that of direct addition of ascorbic acid (see pyrolysis curves of Fig. 18), the mechanism for removal of the NaCl interference by ascorbic acid is probably not a gas-phase reaction, and probably involves some condensed-phase reaction that occurs at the graphite tube surface during the pyrolysis and/or the atomization step.

The above hypothesis is tested in the following section by studying changes in the

composition of the NaCl matrix in the presence of ascorbic acid after pyrolysis at different temperatures in GFAAS.

Mechanism of removal of chloride interference by ascorbic acid.

The composition of the NaCl matrix after pyrolysis at various temperatures, both in the presence and in the absence of ascorbic acid, was determined by a method similar to that described previously in this thesis. The matrix remaining in the graphite furnace at the end of the pyrolysis cycle (but prior to atomization) was extracted with water and the amounts of sodium and chloride residue were determined by flame atomic absorption spectrometry and ion chromatography, respectively. Figure 24 shows the percentage recovery of sodium and chloride, with or without ascorbic acid, as a function of the pyrolysis temperature. The solutions used were identical to those used for the pyrolysis curves of Fig. 18, i.e. 20 μ l volumes containing 100 μ g of NaCl, with or without 200 μ g of ascorbic acid. These results shows that:

- a) significant amounts of the NaCl matrix were removed only when the pyrolysis temperature was above 850°C, and
- b) for pyrolysis temperatures above 900°C, ascorbic acid removed relatively larger amounts of chloride during the pyrolysis cycle.

The effect of the addition of ascorbic acid as a chemical modifier is better understood when these data are replotted as mole ratios of Na:Cl (Fig. 25). When no ascorbic acid chemical modifier was present, the mole ratio of Na:Cl for the residual NaCl matrix remained close to 1.0 for all pyrolysis temperatures. When the ascorbic acid chemical modifier was present, the mole ratio of Na:Cl increased to about 1.20 for

Figure 24. Percentage of residual sodium and chloride as a function of the pyrolysis temperature. ● %Na and ■ %Cl for 100 μg NaCl. ○ %Na and □ %Cl for 100 μg NaCl + 200 μg ascorbic acid.

Figure 25. Mole ratio of sodium to chloride remaining after pyrolysis as a function of the pyrolysis temperature. A: 100 μg NaCl. B: 100 μg NaCl + 200 μg ascorbic acid.

pyrolysis temperatures below 900°C, and rose sharply between 900 and 1000°C. This clearly indicates that the chloride is preferentially removed from the furnace, probably by reaction with ascorbic acid in the condensed-phase during the pyrolysis cycle. At pyrolysis temperatures $\leq 900^\circ\text{C}$ only about 15% more chloride than sodium was removed from the furnace, but as the temperature rose to 1000°C about 60% of the residual chloride was removed, resulting in a Na:Cl mole ratio of about 2.5. For a 900°C pyrolysis, when about 15% of the chloride was removed, the ETV-ICP-MS trace of Fig. 21b gave a good indication of just when, in the heating cycle was this chloride removed. The smaller Cl peak that appeared during the temperature ramp between the drying and the pyrolysis (centred at around 5s) cycles should correspond to the above-mentioned 15% loss of chloride, since it appeared only when ascorbic acid was added. Moreover, this Cl signal occurred in this 0-10 region with no significant amount of sodium signal (see curve B, Fig. 21a). This suggests that the chlorine was probably released in the form of HCl when ascorbic acid was present.

Figure 25 presents an apparent contradiction. Although ascorbic acid is inefficient in removing much chloride from the furnace for pyrolysis temperatures below 900°C, the pyrolysis curves of Fig. 18 show that the addition of ascorbic acid, in fact, completely removed the chloride interference with manganese in GFAAS at pyrolysis temperatures below 900°C. This apparent contradiction can be resolved by considering the steeply rising Na:Cl mole ratio when the pyrolysis temperature rises above 900°C (see Fig. 25), which indicates that much more of the chloride was preferentially removed by ascorbic acid at temperatures above 900°C. Hence, even if the pyrolysis temperature

was well below 900°C, the atomization temperature must rise above 900°C during the atomization cycle. As the temperature rose through 900°C, any chloride left after the pyrolysis was removed as HCl during this temperature ramp and prior to the appearance of the Mn signal at around 1200°C⁸.

In order to test the above hypothesis, a further ETV-ICP-MS experiment was conducted. The time resolution of the ETV-ICP-MS was increased by using a faster detector response, which allowed a better temporal resolution of the Mn and Cl signals. Also, the plasma torch was positioned further from the MS interface in order to prolong the duration of the Cl signal for the entire vaporization cycle. The repositioning of the torch resulted in a lower rate for the vaporized sample to reach the mass spectrometer. Data were then collected over a narrower time range (5s) in the region around 40 s, which corresponded to both the release of the manganese analyte (Fig. 19a) and the sharp Cl peak which appeared during the high temperature ramp of Fig. 21b. The ETV-ICP-MS traces for 200 pg Mn plus 50 µg NaCl in 0.04% v/v HCl without ascorbic acid, and also with 100 µg ascorbic acid are presented in Figs. 26a and 26b, which show the ⁵⁵Mn⁺ (curve A) and ³⁷Cl⁺ (curve B) signals together with the temperature (curve C) of the graphite strip (ETV) during the vaporization cycle after pyrolysis at 550°C. The ²³Na⁺ signal was not recorded because it produced an off-scale peak. The Mn signal was magnified 50 times for clearer presentation; hence, the increased noise in this signal. Results similar to those presented in Figs. 26a and 26b were obtained for pyrolysis at 750°C. However, for simplicity only those obtained for pyrolysis at 550°C (Figs. 26a and 26b) will be presented. Figure 26a shows that the Cl and Mn signals appeared

Figure 26. Temporal behaviour of $^{37}\text{Cl}^+$ and $^{55}\text{Mn}^+$ in ETV-ICP-MS for various matrices at a pyrolysis temperature 550°C . A: $^{55}\text{Mn}^+$ signal $\times 50$. B: $^{37}\text{Cl}^+$. C: Temperature profile of the graphite strip. (a) 200 pg Mn + 50 μg NaCl in 0.04% v/v HCl. (b) 200 pg Mn + 50 μg NaCl + 100 μg ascorbic acid in 0.04% v/v HCl.

simultaneously. This result is consistent with a gas-phase interference mechanism since a large amount of chlorine is released when the manganese atoms are in the gas phase, which shifts the equilibrium reaction (eq. 1) to the right. The addition of ascorbic acid to the sodium chloride matrix (Fig. 26b) caused the Cl peak to appear earlier at or about 950°C, i.e. about 250°C below the appearance temperature of Mn ($\sim 1200^\circ\text{C}$)⁸. This means that the addition of ascorbic acid to the NaCl matrix causes an early release of chlorine prior to the appearance of the Mn signal during the atomization cycle. This also accounts for the fact that in GFAAS, when a relatively low pyrolysis temperature ($< 800^\circ\text{C}$) is used, the ascorbic acid is effective in removing the chloride interference. Ascorbic acid removes much of the chloride from the graphite furnace before the appearance of the Mn atomic absorption signal. However, Fig. 26b shows that the maximum of the Mn peak appeared to overlap the decaying Cl signal, yet no interference was observed in GFAAS when ascorbic acid was present. This can be explained by the fact that enough chloride was removed by the ascorbic acid prior to the maximum of the Mn peak, so the hydrogen gas generated by the pyrolysis of the ascorbic acid was sufficient to remove the small residual chloride interference via a gas-phase reaction⁴².

The chemical reaction by which ascorbic acid releases much more chloride than sodium from the NaCl matrix during the atomization cycle is not known. However, an analogy with the process used for the commercial preparation of $\text{HCl}_{(\text{g})}$ is in order. Hydrogen chloride gas is prepared commercially⁶⁰ by the action of concentrated sulphuric acid on sodium chloride:

Additional sodium chloride is then added and the resulting mixture is heated to about

500°C. A further reaction takes place that produces additional HCl gas:

The last reaction shows that a salt of a weak acid, NaHSO₄, can react with NaCl in the condensed phase, at or about 500°C, to release gaseous HCl. A weak acid source should react in a similar way with NaCl at an appropriate temperature. The pyrolysis of ascorbic acid in an inert argon atmosphere leaves a carbon char that is probably acidic, and it is possible for this acidic char to react with NaCl to produce HCl gas. To confirm this mechanism, knowledge about the nature and the composition of the char left by the ascorbic acid, with and without the sodium chloride matrix, is required, but is not available.

SUMMARY

ETV-ICP-MS is a powerful technique for the investigation of mechanisms for matrix interferences, and of their elimination by chemical modifiers. This technique permits simultaneous observation of both analyte and matrix components during the complete heating cycle.

For interferences caused by the sodium chloride matrix in the GFAAS determination of manganese, the ETV-ICP-MS results show that no analyte is lost during the pyrolysis cycle, or prior to the onset of atomization. This is in sharp contrast with the interference caused by hydrated magnesium chloride matrix, where significant

manganese analyte loss occurs for pyrolysis temperatures above 700°C. The sodium chloride interference is not due to manganese analyte loss by covoatilisation and expulsion with expanding matrix vapour, but is due to formation of molecular manganese chloride species in the gas phase during the high temperature atomization step.

The elimination of the NaCl matrix interference by ascorbic acid does not occur solely by gas-phase chemical modification when large amounts of sodium chloride matrix are present, but occurs in the condensed phase. Ascorbic acid removes the chloride preferentially from the sodium chloride matrix at two distinct stages of the heating cycle. In the low temperature region, during the heating ramp between the drying and the pyrolysis cycle, about 18% of the chloride is removed from the sodium chloride matrix as hydrogen chloride. At temperatures above 900°C, additional chloride is released during the heating ramp between the pyrolysis and the atomization cycles, presumably by reaction between the sodium chloride matrix and the residual ascorbic acid char. The onset of this chloride release occurs at a temperature about 250°C lower than the appearance temperature of manganese, and occurs earlier than the chloride release from the sodium chloride matrix alone. This reduces the amount of chloride released simultaneously with the manganese analyte in the vapour phase, preventing formation of gaseous manganese chloride species during atomization, thereby eliminating the matrix interference.

CHAPTER 3

CHARACTERIZATION AND PERFORMANCE EVALUATION OF A MODIFIED ELECTROTHERMAL VAPORIZER FOR AN INDUCTIVELY COUPLED PLASMA MASS SPECTROMETER

INTRODUCTION

The use of electrothermal vaporizers (ETV) as a sample introduction device for plasma source spectroscopy has increased considerably since its first report by Nixon *et al.*⁶¹ who vaporized samples from a tantalum filament which was connected to an inductively coupled plasma optical emission spectrometer (ICP-AES). Electrothermal vaporization sample introduction devices have since found use in with ICP-AES^{62,63,64,65,66,67,68} and interest for its use in inductively coupled plasma mass spectrometry (ICP-MS) has grown^{49,69,70,71,72,73,74,75} since the introduction of electrothermal vaporization with ICP-MS by Gray and Date⁷⁶.

At the present time, there is no "ideal" ETV for ICP-MS. The design of electrothermal vaporizers for ICP-MS have evolved round two main directions: (1) minimization of the transfer distance, i.e. the distance from the vaporization surface to the ICP torch, and (2) minimization sample condensation and adhesion to transfer line walls.

The modifications that are required for interfacing an ETV with the ICP with a minimum transfer distance are often complex. Matusiewicz *et al.*⁷⁷ minimized the transfer distance (17 cm) by interfacing an HGA 500 graphite furnace to an ICP by

mounting the furnace in a vertical position for AES measurements. The modifications to the furnace were simple but sample introduction was difficult because the furnace was turned on its side. Evans *et al.*⁷⁸ interfaced a modified HGA 500 graphite furnace to an axially mounted microwave induced plasma (MIP) system. The graphite furnace was connected direct to the microwave cavity and this design eliminated recondensation of the sample on transfer line walls during transfer to the ICP torch. The transfer distance was minimized but the modifications were complicated and the integrated design of the system made switching to other sample introduction devices difficult.

A greater attention was paid to the development of the second design approach. In general, these devices use commercial graphite furnaces or custom design specifically made to optimize the sample transport efficiency by minimizing sample condensation on the transfer line walls. The underlying principle behind minimizing sample condensation at low analyte vapour concentrations involves the formation of clusters resulting from collisions among vapour phase species which serve as condensation nuclei (called "self-nucleation"). These clusters continue to grow until they condense into particles. The ideal behaviour for analyte vaporized from ETV devices is rapid self-nucleation to form particles large enough to be efficiently transported by a carrier gas through a transfer line but small enough to avoid coagulation and deposition on transport surfaces⁷⁹.

A relatively simple and straightforward modification of an HGA 300 graphite furnace was made and the modified furnace used with an ICP-MS by Shen *et al.*⁷² and Carey *et al.*⁸⁰. They replaced the end windows of the furnace with laboratory-built stainless-steel adapters. The rear adapter had a stainless-steel tube sealed at the base and

this allowed the carrier gas flow to be introduced tangentially. The front adapter had a fitting with an O-ring seal to which a polytetrafluoroethylene (PTFE) tube was connected and attached to the base of the ICP. The dosing hole of the graphite furnace was plugged with a graphite plug. The carrier gas entered the rear adapter and flowed through the graphite tube, sweeping out the analyte vapour, and flowed out of the front adapter into the ICP torch. An important feature was the provision for the use of an external sheath gas (argon) as a coolant gas flow immediately downstream of the graphite furnace tube with the object of promoting rapid self-nucleation before the analyte vapour was carried to cool surfaces. However, the use of this cooling system resulted in some small memory effects, which required three blank firings for its complete removal. The analyte transport efficiency was improved by the use of this coolant flow; however, there was no report on the quantitative aspects of the analyte transport efficiency. A similar design (without the coolant flow) was investigated for AES⁶³.

Specifically designed apparatus for sample introduction into the plasma are generally based on the ETV device constructed by Park *et al.*⁴⁸, which is similar to the ETV device shown in Fig. 1. It usually consists of one of the following vaporization surfaces: a graphite strip (Fig. 1), a graphite rod⁶², or a graphite cup⁶¹; a rhenium filament^{48,49}; a tungsten strip⁷¹. The vaporization surface is connected to two electrodes and is enclosed inside a glass or quartz envelope. The vaporization surface is heated to incandescence by passing a large amount of electrical current through it. A carrier gas (usually argon) sheaths the internal surface of the glass or quartz envelope, prevents the analyte vapour from condensing on the envelope surface, and allows transportation of the

analyte particles to the ICP torch. There are two major problems with the above design: (1) the analyte loss by condensation on the wall cannot be totally eliminated^{62,81,82} and; (2) there is excessive dilution of the analyte vapour by the volume of the argon gas contained in the envelope, which causes a decrease in sensitivity⁷¹.

It is not known which design will provide the "ideal" ETV device. All the ETV devices so far have suffered from one or a combination of the following problems: (1) complex modifications to the hardware are required; (2) there is excessive dilution of the sample by the carrier and sheath gas; (3) there is analyte loss from condensation at cool surfaces.

The objectives of this research are to develop an ETV device that will fulfil the following requirements: (1) requires simple modification of the hardware; (2) minimizes the analyte dilution by the carrier gas, and also analyte loss at cool surfaces. The transport of analyte materials through the dosing hole of a conventional graphite tube furnace to the ICP torch has not been thoroughly investigated by other researchers; this subject will be explored with the new ETV design. Also, all the ETV devices mentioned above had a design that allowed only one analytical signal to be measured such as the mass spectrometric signal or the atomic emission spectrometric signal. The new ETV design should allow the atomic or molecular absorption signal and the mass spectrometric signal to be measured simultaneously. Therefore, twice as much information about a particular sample will be available for mechanistic studies. It will be shown that the combined information provided by the new ETV design can be used to investigate important problems in electrothermal atomic absorption spectrometry (ETAAS), such as

the chloride matrix interferences in determination of manganese by ETAAS, and the mechanism of aluminium spike formation in ETAAS.

EXPERIMENTAL

Apparatus.

The inductively coupled plasma mass spectrometer (ICP-MS) used for this work was a Perkin-Elmer/Sciex Elan, Model 5000. The ICP-MS was used in the positive ion detection mode. A demountable ICP torch made of one-piece quartz tubing and equipped with an alumina injector tube was used through out this work. An offset voltage applied to the ion lens of the mass spectrometer, called OmniRange, was used when necessary. The ion intensity of a selected mass-to-charge value could be reduced to a level that is within the linear dynamic range ($0-10^6$ counts s^{-1}) of the ICP-MS detector by selecting an appropriate OmniRange setting. Solution nebulization was used for the determination of ^{109}Ag isotope concentration in the enriched solution used for the isotope dilution technique. For solution nebulization, a peristaltic pump (Gilson Minipuls 3, Gilson Medical Electronics) delivered the sample to a Ryton spray chamber (Scott type) and nebulizer at a flow of 1 ml min^{-1} .

Modifications of the graphite furnace, Model HGA 76B (Perkin-Elmer), were made as shown in Fig. 27. Photographs of the modified furnace are presented in Fig. 28 with the graphite furnace opened (Fig. 28a) and closed (Fig. 28b). The new ETV device was simple in design. The furnace brass-body was redesigned such that a brass-lip extended about 4mm from the interior face of each brass-contact electrode. All surfaces of the furnace brass-body were chrome-plated. The interior of each

Figure 27. Schematic diagram of the modified Perkin-Elmer HGA 76B graphite furnace.

(a)

(b)

Figure 28. Photographs of the modified Perkin-Elmer HGA 76B graphite furnace.
(a) open position. (b) closed position.

brass-contact electrode was coated with a carbon coating using a carbon vapour coating device used for sample preparation with scanning electron microscopy (SEM). This carbon coating reduced the ICP-MS background signals of Cr, Cu, and Fe, by preventing the erosion of the chrome plating (mainly composed of Cr, Cu, and Fe) by the argon carrier gas. A high temperature silicon O-ring was fitted inside each brass-lip. From a quartz tube of 50 mm o.d., a ring of 15 mm width was cut and a hole of 8 mm was drilled at the centre. A male bald joint (size No.10) made of quartz was fused to the ring at the hole location (called a "spout" in Fig. 27) and a female bald joint (size No.10) made of quartz was clamped against the male bald joint. The quartz ring was positioned between the two brass-contact electrodes which were then clamped together. The O-rings located between the quartz ring and the brass-lips allowed for the interior of the furnace to be sealed from the outside. The interface between the ETV unit and the ICP torch consisted of a 75 x 0.5 cm (i.d.) Teflon tubing with a three-way stopcock located midway between the ETV and the torch assembly. The Ar carrier gas was taken from the nebulizer line provided on the ICP-MS equipment. The Ar gas nebulizer line was divided in two by a plastic Y-connector and each Ar gas line was connected to a gas flowmeter (Matheson, Model 602). One Ar gas line was connected to the external sheath gas entry port of the modified furnace and the other Ar gas line was connected to the internal purge gas entry port of the modified furnace. This configuration allowed for changes in internal purge gas flow rate without changing the total flow of the Ar carrier gas. A graphite furnace power supply for model HGA 500 (Perkin-Elmer), was used with the modified graphite furnace. New, pyrolytic graphite coated graphite tubes

(Perkin-Elmer, Part No. 091504) were used. Laboratory-made single-cavity platforms made of anisotropic pyrolytic graphite were used.

The simultaneous measurement of the atomic or molecular absorption signal and the mass spectrometric signal required additional equipment. Figure 29 shows a diagram of the simultaneous measurement system. The system works as a single-beam spectrometer for both atomic and molecular absorption spectrometry. The sample is vaporized in the furnace and the atomic and/or molecular vapour is carried away by the argon carrier gas from the furnace to the ICP-MS where it is measured as ionic species. The atomic or molecular absorption can be simultaneously measured provided that the concentration of atomic or molecular vapour is above the limit of detection of the species of interest and that the residence time of the atoms or molecules is not too small (i.e. greater than the detector response). Molecular absorption measurements are described in Chapter 4. The silver and the manganese hollow cathode lamps (Perkin-Elmer) were operated at 10 mA and 15 mA, respectively. A deuterium lamp (Perkin-Elmer) was operated at 20 mA and was used for background correction. Focusing lenses of 12.5 cm focal length were positioned in order to focus the light from the radiation source to the centre of the graphite furnace and to focus the transmitted light from the centre of the furnace to the entrance slit of the monochromator. The entrance slit was set at 200 μm for all experiments, which provided a spectral bandpass of 0.7 nm. The wavelengths used to make the atomic absorption measurements for Ag and Mn were their resonance lines, 328.1 nm and 279.5 nm, respectively. The resonance line of each element was isolated by a 0.5m Ebert-mount grating monochromator, 50 X 50 mm grating, ruled with

Figure 29. Block diagram of the ETAAS-ICP-MS simultaneous measurement apparatus.

638 lines mm^{-1} (Varian Techtron, Australia). The monochromator was fitted with a Hamamatsu R216 photomultiplier tube (Hamamatsu, Middlesex, USA) for the measurement of the transmitted radiation. The hollow-cathode lamp power supply and the lock-in amplifier were laboratory made and were synchronously modulated at 843 Hz. The detector response was set at 22 ms. The atomic or molecular transient signals were recorded on a digital oscilloscope (Nicolet, Model 4094).

Standards and Reagents. A $1000 \mu\text{g ml}^{-1}$ stock solution of Ag was prepared by dissolving 0.1579 g of AgNO_3 (99.99%, Anachemia) in ultrapure water; the solution was then transferred quantitatively into a 100.00 ml calibrated flask that contained 0.2% v/v HNO_3 (Ultrex, Baker). A series of standard solutions in the range 0.2-200 ng ml^{-1} were prepared by serial dilution of the above $1000 \mu\text{g ml}^{-1}$ Ag stock solution. All standard solutions and their dilutions used as test solutions contained 0.2% v/v HNO_3 (Ultrex, Baker). A solution of 0.02 $\mu\text{g ml}^{-1}$ manganese plus 1% m/v magnesium chloride in 0.04% v/v HCl was prepared in the same manner as described in Chapter 1. A $1000 \mu\text{g ml}^{-1}$ stock solution of NaCl was prepared by dissolving 0.1000 g of NaCl (99.9%, Analar, BDH Chemicals) in 25.00 ml of ultrapure water. From the $1000 \mu\text{g ml}^{-1}$ stock solution of NaCl, a 20 $\mu\text{g ml}^{-1}$ of NaCl test solution was prepared by serial dilution and 5 μl of that solution (containing 100 ng of NaCl) per sample was used for chemical modification in silver determination experiments. The isotope dilution ICP-MS experiments were accomplished by spiking the geological reference materials in solution with ^{109}Ag -enriched silver (99.4% ^{109}Ag pure, US Services Inc.). A stock solution of ^{109}Ag was prepared by dissolving a grain of ^{109}Ag -enriched salt in 5 ml of 0.2% v/v

HNO_3 . The concentration of the ^{109}Ag stock solution was determined by solution nebulization ICP-MS technique and was found to be 76 parts-per-billion (ppb). The ^{109}Ag stock solution was diluted by a factor of 1000 to give a solution with a final ^{109}Ag concentration of 0.076 ppb. The above reference materials were obtained in solution and were provided by the Geological Survey of Canada. The reference materials were prepared for the analysis using a standard sample dissolution method⁸³. The test solution for the determination of Ag by isotope dilution was prepared by mixing 500 μl of the solution containing the geological reference material with 500 μl of the 0.076 ppb ^{109}Ag solution and was allowed to equilibrate for two hours before its use with the ETV-ICP-MS. Stock solutions containing 10 $\mu\text{g ml}^{-1}$ concentration of mixed analytes; designated ICPMS-1, ICPMS-2, and ICPMS-4 (Delta Scientific) were diluted with 0.2% HNO_3 (Ultrax) to give standard solutions of 10 ng ml^{-1} concentration of mixed analytes. Stock solution of 10 $\mu\text{g ml}^{-1}$ concentration of mixed analytes; ICPMS-2 (Delta Scientific) was diluted with 0.2% v/v HCl (Ultrax). These standard solutions were used for the determination of limits of detection and sensitivity of the modified furnace. For the determination of limits of detection and sensitivity, the seawater reference solution NASS-1 (3.5% m/v of chloride salts) was diluted by a factor of 500 with ultrapure water and then used as a chemical modifier for the standard solutions of the above mixed analytes. A 5 μl volume of the test solution was deposited into the graphite furnace with an Eppendorf microlitre pipette. The pipette was inserted through the quartz spout and the graphite tube dosing hole and the test solution was deposited on the graphite tube wall directly below the dosing hole.

RESULTS AND DISCUSSION

Parametric evaluation.

The modified graphite furnace was evaluated for the following parameters: the flow of Ar gas inside the graphite tube furnace, the total flow of Ar gas delivered to the ICP torch, and the vaporization temperature of the graphite furnace. Calibration curves for Ag under various conditions were also obtained from which limits of detection and linear dynamic ranges were calculated. Silver was chosen as the test element because its mechanism of atomization is simple and well known. It is generally accepted that Ag atoms are formed by direct vaporization of condensed silver^{6,9,84}. The experimental and operating conditions used for the parametric evaluation of the modified graphite furnace are presented in Table 4.

Internal flow. A 5 μ l volume of the test solution of a 250 ng ml⁻¹ Ag standard solution was deposited onto the graphite tube surface and was vaporized. The total Ar flow delivered to the ICP torch was set at 1 l min⁻¹ on the mass flow controller of the ELAN 5000. Figure 30 shows the particular flowmeter set-up used for this experiment, and also that the flowmeter set-up can be represented as an equivalent electrical circuit with two variable resistors in parallel. The flowmeter FM1 and FM2 are equivalent to the variable resistors R1 and R2, respectively. The Ar flow was then equivalent to the current circulating in the circuit. From laws of electricity and magnetism¹⁰⁰ the total current in the circuit will be equal to the sum of the current circulating in each arm of the circuit. Therefore, the flow of Ar inside the furnace was varied without changing the total flow of Ar entering the ICP. The gas flowmeters were adjusted so each

Table 4. Experimental and operating conditions of the ETV-ICP-MS for the parametric evaluation of the modified furnace and for the determination of silver.

The experimental conditions and the heating cycle of the modified electrothermal vaporizer

	Step		
	Drying	Pyrolysis	Vaporization ^a
Temperature/°C	120	500	2200/variable/2400
Ramp time/s	10	10	1
Hold time/s	30	20	5

Sample volume 5 μ l

Mass spectrometer interface and Plasma conditions

The same as those shown in Table 3 except when stated otherwise.

Dwell time^b 30 ms

R.f. power 1.05 kW

^aThe vaporization temperature was set at 2200°C for studying the effect of the Ar flow (both internal and total flow) on the Ag⁺ signal; was variable temperature for studying the effect of the vaporization temperature on the Ag⁺ signal; was set at 2400°C for the analytical calibration curves and for quantitative determinations of Ag.

^bThe dwell time is defined as the time which the detector spends measuring a given mass.

Figure 30. Block diagram of the flowmeter set-up with its equivalent electric circuit diagram.

delivered an identical flow of 500 ml min^{-1} . Subsequently, only the first flowmeter FM1 that controlled the internal flow was varied.

Figure 31 shows the change in the integrated ion intensity of 50 ng ml^{-1} of Ag when the internal flow of Ar gas was varied. A maximum integrated ion intensity of Ag was obtained at an internal flow of 450 ml min^{-1} . At internal flows lower than 450 ml min^{-1} , Ag atoms may be lost because of diffusion of Ag atoms towards the cooler end of the tube. The strong temperature gradient that existed along the tube length^{85,86} would allow Ag atoms to diffuse towards the end of the tube and would favour recondensation of Ag at the end of the tube. However, this would be expected to be important only for low internal convective flow, such as 50 ml min^{-1} , where transport by diffusion would compete with that due to a low convective flow in the opposite direction. Another possible reason for the decreased integrated ion intensity of Ag at low internal flow was that Ag vapour might not exit the graphite furnace rapidly enough to allow an optimum self-nucleation. Dean and Snook⁸⁷ measured the atomic absorption signal of Ag at different vertical position above a graphite rod used as an ETV and showed that Ag persisted as atoms for a distance of up to 2 cm for an Ar flow of 1 l min^{-1} . Discrete atoms are more reactive than clusters and aggregates of atoms and they may react with and/or be adsorbed on to the surface with which they come into contact. The external gas was flowing along the graphite tube and would create a barrier to the exiting Ag atomic vapour provided that the external flow was much greater than the internal flow. This could possibly be the case at internal flow of $50\text{-}250 \text{ ml min}^{-1}$ where the much greater external flow would hinder the exiting Ag atomic vapour from flowing direct

Figure 31. The effect of internal Ar flow on the integrated ion intensity of 50 ng ml⁻¹ of Ag vaporized from the tube surface.

through the hole of the graphite cone. A significant amount of Ag atomic vapour would then be directed towards the surfaces of the graphite tube and the graphite cones where Ag could be lost by physical and chemical reactions with the graphite surfaces.

An optimum self-nucleation process would allow better mass transport efficiency and, therefore, an increased integrated ion intensity. It is expected that the cooler external Ar gas that flows inside the quartz ring and outside the graphite tube furnace would cool the hot Ag vapour coming out of the graphite tube. There should be an optimum ratio of internal flow to external flow of Ar gas that would provide a rapid cooling which, consequently, would promote better self-nucleation⁷⁹. The optimum ratio of internal flow (450 ml min^{-1}) to external flow (550 ml min^{-1}) for Ag with this particular modified furnace was calculated to be 0.818. An optimum self-nucleation of Ag would result in a dry aerosol⁷⁹ of Ag which would then undergo elastic collision with the transfer line without loss of silver⁸⁷.

The integrated ion intensity of Ag for internal flow greater than 450 ml min^{-1} decreased at a lower rate compared to the lower internal flow. The internal flow was greater than the external flow and the external Ar flow was not expected to hinder to any significant extent the flow of Ag vapour coming out of the graphite tube. The high internal flow would have allowed the Ag vapour to flow direct through the dosing hole of the graphite tube up to the opening of the spout. It is possible that under the high internal flow conditions, Ag persisted as atoms up to the spout opening and that upon contact with the quartz surface, Ag atoms reacted with or were adsorbed onto the surface. This is possible since the internal radius of the quartz ring was 2.4 cm and the

internal radius of the graphite tube was 0.3 cm. If one assumes that Ag vapour began to cool down only after they exited the graphite tube, the net distance that Ag vapour travelled before they reached the opening of the spout was 2.1 cm, and according to Dean and Snook⁸⁷, Ag would then exist as free atoms and they would be reactive enough to be lost on to the quartz surface. At internal flow greater than 450 ml min⁻¹, a significant amount of Ag vapour did not have enough time to self-nucleate appropriately before collision with any surface.

Total flow. A 5 µl volume of the test solution of a 50 ng ml⁻¹ Ag standard solution was deposited onto the graphite tube surface and was vaporized. The effect of the varying total Ar flow on the integrated ion intensity of Ag is presented in Fig. 32. The same flowmeter set up used for the internal flow parametric evaluation was employed in this experiment. The internal flow was set at 400 ml min⁻¹ for a total flow of 1 l min⁻¹ and the setting of the flowmeters for both the internal flow and the external flow remained the same for the duration of this experiment. The total flow was controlled by changing the setting on the mass flow controller of the ELAN 5000. This allowed the ratio of the internal flow to the external flow to remain constant at 0.818 when the total flow was changed. Fig. 32 shows a maximum integrated ion intensity of Ag at 950 ml min⁻¹. The effect of the total carrier gas flow on the ICP-MS signal is well documented^{48,72,88}. A change in the total flow of the carrier gas causes the analyte residence time in the ICP to vary inversely, i.e. a decrease in the total flow causes the residence time of Ag in the ICP to increase. This means that the analyte may not be totally dissociated and ionized if the residence time is too short or the analyte may undergo a double ionization if the

Figure 32. The effect of the total Ar flow on the integrated ion intensity of 50 ng ml⁻¹ of Ag vaporized from the tube surface.

residence time is too long⁸⁹. As well, the optimum ionization zone of the ICP relative to the load coil is dependent on the total flow of the carrier gas⁸⁸. The low integrated ion intensity of Ag obtained at low total flow may also be due to a change in the Ag nucleation process. The external Ar flow at 600 ml min⁻¹ total flow of the carrier gas is approximately 330 ml min⁻¹, which is 1.7 times smaller than the external flow of 550 ml min⁻¹ at 1 l min⁻¹ total flow of the carrier gas. Hence, the cooling effect from the external flow of the carrier gas was diminished greatly and that might have permitted an optimum self-nucleation to take place.

Vaporization temperature. A 5 μ l volume of the test solution of a 20 ng ml⁻¹ Ag standard solution was deposited onto the graphite tube surface and was vaporized. The internal Ar gas flow was set at 450 ml min⁻¹ and the total Ar gas flow was set at 1 l min⁻¹.

Figure 33 shows the variation in the integrated ion intensity of Ag when the vaporization temperature was changed. A maximum integrated ion intensity of Ag was obtained at a vaporization temperature of 2400°C. Kantor⁷⁹ reported that a minimum analyte vapour concentration is required for self-nucleation to occur. At low vaporization temperatures, the rate of vaporization of Ag may be too low to produce a Ag vapour concentration sufficient to allow an adequate self-nucleation. At the optimum temperature of 2400°C, the rate of vaporization of Ag was probably optimum and an optimum self-nucleation occurred. However, if the vaporization temperature is increased above the optimum temperature, the following two processes could happen separately or together. First, the rate of vaporization of Ag above 2400°C could be such that the Ag vapour concentration would exceed a threshold value for optimum self-nucleation,

Figure 33. The effect of the vaporization temperature on the integrated ion intensity of 20 ng ml⁻¹ of Ag vaporized from the tube surface.

resulting in the formation of particles sufficiently large to coalesce and deposit on transport surface in spite of large carrier gas flows⁷⁹. Secondly, the temperature of Ag atoms leaving the furnace would then be higher and, hence, the Ag atoms would require more time, or in this case, a greater distance to cool down before efficient nucleation could occur, and this may result in the loss of Ag on the cool surfaces located along the transit path of Ag vapour to the ICP. In both cases, a loss of Ag to the transport surfaces would occur, resulting in a decrease in the integrated ion intensity. This effect is analogous to what is observed in ETAAS when the atomization temperature is increased. In ETAAS, the atomization efficiency and the diffusion loss of analytes are increased to a different degree when the atomization temperature is increased, resulting in the existence of an optimum temperature at which the difference between the rates of atom formation and of loss (by diffusion) is a maximum. Similarly, the optimum vaporization temperature of 2400°C represents the temperature at which the difference between the rate of vaporization and loss of analyte (presumably by adsorption or by reaction with the transport surfaces⁷⁴) is a maximum.

Analytical calibration curve. Analytical calibration curves were prepared using net signals obtained by vaporization of the sample from the surface of the graphite tube or the graphite platform. A series of standard solutions of Ag in 5 μl volume, covering the range of concentrations 0.2 to 200 ng ml^{-1} , were injected into the graphite furnace with an Eppendorf pipette fitted with disposable plastic tips. When sodium chloride was used as a chemical modifier, a volume of 5 μl of a 20 $\mu\text{g ml}^{-1}$ NaCl solution, i.e. 100 ng per injection, was deposited inside the graphite tube after adding and drying the Ag standard

solution droplet. Sodium chloride was selected for evaluation as a chemical modifier because it has been shown to be beneficial for the determination of Ag by ETV-ICP-MS⁵⁹. A total flow of 1 l min⁻¹, an internal flow of 400 ml min⁻¹ of the carrier gas, and a vaporization temperature of 2400°C were used to obtain the data for the analytical calibration curve - these experimental conditions provided the optimum value or near optimum value for the modified furnace with Ag as the test analyte. Other experimental and operating conditions of the ETV-ICP-MS are given in Table 4.

The analytical calibration curves for silver are shown in Fig. 34. The analytical calibration curves obtained without addition of NaCl (Curve A and B, Fig. 34) were not linear. A curvature of the analytical calibration curve in the low mass range (0-50 pg of Ag) was observed for both vaporization of Ag alone from the graphite tube surface and for vaporization of Ag alone from the graphite platform surface. The analytical calibration curve for Ag obtained with the addition of 100 ng NaCl was linear over the entire mass range covered, and the slope was 1039 counts pg⁻¹ with the intercept equal to zero. There was only a slight improvement in the sensitivity for Ag vaporized alone from the the graphite platform surface compared to Ag vaporized alone from the graphite tube surface. Ediger and Beres⁵⁹, and Grégoire *et al.*⁹⁰ have reported a curvature of the analytical calibration curve with increasing mass of several analytes. They attributed the non-linearity of analytical calibration curves to a mass transport effect. The greater the mass of analyte, the better was the transport efficiency because large masses condensed rapidly into transportable particles which reduced the probability of condensation on the transport line surfaces. Grégoire *et al.*⁹⁰ showed a curvature of the analytical calibration

Figure 34. Analytical calibration curves for Ag. A, Ag alone vaporized from the tube surface; B, Ag alone vaporized from the platform surface; C, Ag plus 100 ng NaCl vaporized from the platform surface.

curve for Ag in the low mass range (0-4 ng of Ag) when silver was vaporized from a graphite strip ETV. A small curvature of the analytical calibration curve for Ag in the low mass range (0-50 ng of Ag) was observed in this research with the modified furnace for vaporization from both platform and tube surface.

The addition of NaCl on the platform where Ag was deposited greatly improved the sensitivity for Ag with NaCl compared to Ag alone. Figure 35 shows typical $^{107}\text{Ag}^+$ transients for 100 pg of Ag with and without 100 ng NaCl for vaporization from the platform surface, and shows clearly the enhancement in the $^{107}\text{Ag}^+$ ICP-MS signal when NaCl is added as a chemical modifier to Ag compared to Ag vaporized alone.

The enhancement of analytical sensitivity in ICP-MS due to the addition of a chemical modifier has been reported for many elements using various chemical modifiers^{59,73,74,90,91}. Ediger and Beres⁵⁹, and Grégoire *et al.*⁹⁰ suggested that chemical modifiers acted as physical carriers of the analysed elements resulting in improved transport efficiency of the analyte between the vaporization surface and the ICP. The large amount of chemical modifier that is vaporized condenses into particulate material more rapidly than the analyte. This allows the analyte vapour to condense onto these particulate material and to be transported efficiently to the ICP rather than being lost onto the cool surfaces of the ETV. This mechanism is consistent with those of Kantor⁷⁹ and Grégoire⁷⁴, who underlined the possible vapour-phase interactions that might increase the transport efficiency of the analyte to the ICP.

Ediger and Beres⁵⁹ reported a 2-fold enhancement in the Ag sensitivity upon the addition of 100 ng of sodium chloride to 100 pg of silver and vaporization from the tube

Figure 35. Ag transient in ICP-MS with the modified furnace ETV. A, 100 pg of Ag; B, 100 pg of Ag plus 100 ng NaCl.

surface. They used a Perkin-Elmer HGA 600MS graphite furnace where the sample was transported from the middle of the tube furnace through the end cone and the transfer line on to the ICP. An adapter replaced the end window and a Teflon transfer line connected the adapter to the ICP. The small difference in sensitivity between vaporization from the tube surface and the platform surface should allow a direct comparison of the results of this work with those reported by Ediger and Beres⁵⁹. The 4.6-fold enhancement in the sensitivity, for 100 pg of Ag obtained using the modified furnace described in this work with 100 ng NaCl as the chemical modifier, was more than a 2-fold improvement in the sensitivity for Ag compared to that obtained by Ediger and Beres⁵⁹ using the HGA 600MS and similar experimental conditions. The improvement in the sensitivity for Ag with the modified furnace compared to the HGA 600MS may be attributable to the differences in the design between the two furnaces; the modified furnace allowed more material to be transported to the ICP than did the HGA 600MS furnace.

The addition of sodium chloride to Ag also improved the repeatability of determination. This has been previously reported by Grégoire *et al.*⁹⁰. The mean value of the relative standard deviation (RSD) for the range 10-250 pg of silver was reduced from 19.0 to 12.8 %RSD when sodium chloride was added to silver. This was probably due to a more uniform nucleation of Ag in the presence of NaCl

Limits of detection, based on a 5 μ l sample volume, for the Ag vaporized alone from the tube surface, for Ag vaporized alone from the platform surface, and for Ag plus 100 ng NaCl vaporized from the platform surface, and the results were 340, 320, and

46 parts-per-trillion, respectively. In order to determine the limits of detection for Ag vaporized alone from both the tube surface and the platform surface, the linear portion of the analytical calibration curves (50-1000 ng) were extrapolated to zero. Comparison of limits of detection of Ag obtained with other analytical techniques are discussed later in this chapter.

Comparison of signal characteristics of ETAAS and ICP-MS.

In order to correlate the combined measurement of the ETAAS and the ETV-ICP-MS signals, various factors such as the difference in the appearance time of analytes measured in ETAAS and ETV-ICP-MS, the relative peak broadening, and the relative distortion of scale were assessed. In addition, a pre-requisite to the investigation was to verify that the carrier gas flow was not a turbulent flow, but was rather a laminar flow. *Qualitative evaluation of the carrier gas flow.* The flow of a fluid is either turbulent or laminar. An ideal laminar flow is characterized by a series of thin layers of fluid that travel in the same parallel direction without any mixing of the layers. A turbulent flow is a very complex flow of fluid whereby the layers of fluid are all mixed together. The existence of a laminar flow can be assessed by calculating the Reynolds number⁹². A flow that has a Reynolds number < 2000 is considered to be laminar. The Reynolds number for the modified ETV system was calculated at a temperature of 20°C using the following equation:

$$Re = \frac{\rho VD}{\mu} \quad (8)$$

where Re is the Reynolds number, a dimensionless quantity; ρ is the density of the fluid

(Ar); V is the average fluid velocity; D is the diameter of the transfer line; and μ is the viscosity of the fluid (Ar). For a Ar flow of 1 l min^{-1} , and a transfer line of $75 \text{ cm} \times 0.5 \text{ cm}$ i.d., the Reynolds number was found to be 341. This would indicate that the flow was laminar. Further evidence for the laminar flow is shown in Fig. 36. Fig. 36 shows a photograph of the ETV into which a piece of plastic was deposited and vaporized at 2200°C . It can be observed that a small stream of smoke is flowing out the tube furnace direct through the opening of the quartz spout and that the smoke plume is confined in the vertical direction. This observation supports the conclusion that a laminar flow existed within the ETV device with the experimental conditions and instrumental set-up used in this work. The dead volume from the dosing hole to the quartz spout for a column of gas of 2 mm diameter (diameter of the dosing hole) was estimated to be 0.07 cm^3 . Hence, little dilution of the analyte vapour occurred inside the quartz ring.

Appearance time. Figure 37 shows the simultaneous recording of the atomic absorption (Fig. 37b) and the mass spectrometric signals (Fig. 37a) for 250 pg of Ag vaporized from the graphite tube surface. The internal flow was set at 150 ml min^{-1} and the total flow at 1 l min^{-1} . All other experimental conditions are given in the experimental section and in Table 4. The appearance time, τ_1 , is defined as the time at which the atomic absorption signal becomes barely visible above the baseline noise in ETAAS, or the time at which the mass spectrometric signal becomes barely detectable above the baseline noise in ICP-MS. The appearance time of silver in ETAAS and ICP-MS was 1.25 s and 2.10 s , respectively. Both appearance times remained the same when the internal carrier gas flow was reduced to 50 ml min^{-1} , which meant, that the ICP-MS signal lagged behind

Figure 36. Photograph showing the smoke plume from a piece of plastic vaporized at 2200°C. The plume is confined in the vertical direction.

Figure 37. Temporal behaviour of 250 pg of Ag with simultaneous measurement of the ETAAS and ICP-MS signals. (a) ICP-MS signal; and (b) AAS signal. Vaporization from the tube surface at 2400°C. FWHM stands for "full width at half maximum" of each peak.

the ETAAS signal by 0.85 s. This was due to the fact that it took a finite time to transport the Ag vapour from the ETV to the ICP-MS (transit time), whereas in ETAAS, the graphite tube served both as the atomization surface and the analysis volume, thereby eliminating the transit time. The transit time for Ag vapour from the ETV to the ICP-MS was calculated by assuming that once the analyte vapour entered the mass spectrometer interface, the detection was instantaneous. It is a reasonable assumption considering the reduced pressure inside the mass spectrometer ($\approx 10^{-6}$ Torr) and the relatively high electrostatic voltage applied to accelerate the ions towards the channel electron multiplier detector⁹³. The transit time, for a total flow of 1 l min⁻¹ and a transfer line of dimension 75 X 0.5 cm i.d. was calculated to be 0.88 s, and correlated well with the difference of 0.85 s between the appearance time of silver measured by ETAAS and ICP-MS.

Peak broadening. The broadening of one peak relative to another can be evaluated by measuring and comparing the full width at half maximum (FWHM) of each peak. Figure 37 shows that the FWHM of the ICP-MS signal (Fig. 37a) is greater than that of the ETAAS signal (Fig. 37b). The Ag peak in ICP-MS was 45% broader than the corresponding Ag peak in ETAAS. The FWHM of the silver peak in ICP-MS and in ETAAS was 0.46 s and 0.34 s, respectively. At lower internal carrier gas flows, the silver peak in ICP-MS broadened even more. The FWHM of the silver peak in ICP-MS was 56% greater than that obtained in ETAAS for an internal carrier gas flow of 50 ml min⁻¹. The broadening was probably due to diffusion broadening of the Ag vapour during its transport in the transfer line and in the plasma. The broadening of the peak

in ICP-MS might be important when investigating phenomena closely related in time, such as the appearance of lead double peaks⁹⁴ or the formation of aluminium spikes²² in ETAAS, the details of which may not be observable in ICP-MS.

Difference in the time scale. The previous section pointed out that broadening of the ICP-MS peak might be important for fundamental studies of events that are closely related in time. Also, disparity between the time scale of the ICP-MS and the ETAAS signals can present additional problems when carrying out mechanistic studies in ETAAS. For example, if an ETAAS signal, composed of two or more distinct events, cannot be correlated with the corresponding ICP-MS signal by a common time scale, then a distortion of the time scale would exist between the ETAAS and the ICP-MS measurements. Hence, conclusions based on the simultaneous measurement of the ETAAS and ICP-MS signals could be erroneous. This difference in the time scale was assessed by vaporizing 2 μg of Al as the nitrate at a low heating rate in order to form atomic absorption spikes of aluminium²². It was reported that the atomization of relatively large amount ($\approx$ microgram amount) of aluminium at low heating rate ($\approx 5\text{--}20^\circ\text{C s}^{-1}$) caused Al atomic absorption spikes to appear on top of a smoothly rising Al atomic absorption signal. A more detailed discussion of aluminium spikes formation is provided in Chapter 4, and no further details are necessary at this point to assess this difference of time scale between the ICP-MS and the ETAAS signals. The experimental conditions for the assessment of this difference in the time scale are shown in Table 5. Figure 38 shows the simultaneous recording of the ETAAS (Fig. 38b) and the ICP-MS (Fig. 38a) signals for aluminium spikes. The appearance time,

Table 5. Experimental and operating conditions of the ETV-ICP-MS for the evaluation of the difference in the time scale.

	Step		
	Drying	Pyrolysis	Vaporization
Temperature/°C	120	1200	2250
Ramp time/s	10	10	105
Hold time/s	40	10	2

Sample volume 5 μ l

Mass of Al deposited 2 μ g taken as the nitrate

Carrier gas flow-rate

Total 1.0 l min⁻¹

Internal 0.05 l min⁻¹

Mass spectrometer interface and plasma conditions

Same as those shown in Table 3 except when stated otherwise.

Dwell time 30 ms

OmniRange* 5.0 for ²⁷Al⁺

R.F. power 0.8 kW

*The OmniRange provided an offset voltage on the ion lens of the mass spectrometer at a selected mass-to-charge ratio (m/z) value in order to reduce the ion intensity of that selected m/z value.

Figure 38. Temporal behaviour of 2 μg of Al with simultaneous measurement of the ETAAS and ICP-MS signals. (a) ICP-MS signal; (b) ETAAS signal. Vaporization (atomization) from the tube surface at a heating rate of 10°C s^{-1} with an initial temperature of 1650°C .

T_1 , T_2 , and T_3 , of the first three peaks in Fig. 38a, was to 27.0, 40.1, and 51.3 s, respectively. Similarly, the appearance time, T_1 , T_2 , and T_3 , of the first three peaks in Fig. 38b, was 26.5, 39.5, and 50.5 s, respectively. The appearance time of the aluminium spikes in the ICP-MS correlated well with its ETAAS analogue and the difference between the appearance time was not greater than the transit time of 0.88 s required for the Al vapour to travel from the ETV to the plasma of the ICP. Also, the time separating a peak maximum from the next peak maximum, $\Delta t_{\max}$, was calculated for both AAS (Fig. 38b) and ICP-MS (Fig. 38a) signals. For the first peak maximum to the second peak maximum, $\Delta t_{\max}$ for both ETAAS and ICP-MS signals was 13.40 and 12.95 s, respectively; for the second peak maximum to the third peak maximum, $\Delta t_{\max}$ for both ETAAS and ICP-MS was 11.10 and 10.90 s, respectively; and for the third peak maximum to the fourth peak maximum, $\Delta t_{\max}$ for both ETAAS and ICP-MS was 8.05 and 8.30 s, respectively. The above results showed clearly that there is no difference in the time scale since T and $\Delta t_{\max}$ values correlated well (within experimental uncertainties) between ETAAS and ICP-MS peak analogues. This implied that investigations of fundamental processes occurring in ETAAS can be studied by measuring simultaneously the AAS and ICP-MS signals, provided that the broadening of the ICP-MS peaks has no significant impact on the interpretation of the experimental results.

Interferences with Mn determination by the $MgCl_2$ matrix (revisited).

It was pointed out in Chapter 1 of this thesis that the graphite strip ETV used with

the ICP-MS to investigate the interferences by the MgCl_2 matrix with the ETAAS determination of Mn may behave differently from a conventional tube type graphite furnace used in graphite furnace atomic absorption spectrometry (GFAAS). The formation and dissipation of atoms from a graphite strip may be different from those occurring in a graphite tube furnace in GFAAS even if the heating characteristics of the atomization surface are identical. The gas-phase temperature and the probability of atoms colliding against the graphite surface leading to secondary reactions in a tube furnace are expected to be different from those in a graphite strip. Therefore, in Chapter 1, the pre-atomization loss observed in the ETV-ICP-MS experiments may not be comparable to the actual pre-atomization loss that occurred in the ETAAS experiments. In order to verify that the pre-atomization loss observed in the ETV-ICP-MS was not specific to the ETV unit used, but was rather a genuine effect caused by the hydrolytic decomposition of the MgCl_2 matrix, the interferences by the MgCl_2 matrix in the determination of Mn was again investigated using the modified furnace. The modified Perkin-Elmer HGA 76B furnace presented the same heating and geometric characteristics of the Perkin-Elmer HGA 500 graphite furnace used to perform the ETAAS experiments in Chapter 1. The experimental and operating conditions for the ETAAS measurements were the same as those given in Table 1 and the experimental and operating conditions for the ICP-MS were the same as those given in Table 3. The test solutions were the same as those used in the ETV-ICP-MS experiments of Chapter 1.

Figure 39 shows the simultaneous measurements of the ETAAS (Fig. 39b) and ICP-MS (Fig. 39a) signals for 200 pg of Mn in 1% v/v HCl plus 100 μg of MgCl_2 with

Figure 39. Temporal behaviour of 100 pg of Mn in 1% HCl plus 200 pg of MgCl_2 with simultaneous measurement of the ETAAS and ICP-MS signals. (a) ICP-MS signal; (b) ETAAS signal. Vaporization (or atomization) from the tube surface at 2500°C with a pyrolysis temperature of 1000°C .

a pyrolysis temperature of 1000°C. The ICP-MS signal (Fig. 39a) shows clearly that a large amount Mn is lost during the pyrolysis step. The ETAAS signal (Fig. 39b) shows no Mn atomic absorption signal during the pyrolysis step other than a small signal (20-26 s) due to background interferences not fully corrected by the deuterium arc background correction system. This indicates that the Mn must have been lost as molecular manganese species since no atomic absorption signal was detectable during the pyrolysis step. The pre-atomization loss of Mn in ETV-ICP-MS for a pyrolysis temperature of 1000°C was calculated to be 90.6%, with the remaining 9.4% Mn vaporized during the atomization step. The corresponding pre-atomization loss in ETAAS for the same pyrolysis temperature was calculated by taking the ratio of the integrated absorbance for the Mn in the 1% v/v HCl plus MgCl₂ solution (Fig. 4, curve B) and the integrated absorbance for the Mn in the 1% v/v HNO₃ solution (Fig. 4, curve E). In ETV-ICP-MS, the integrated ion intensity for Mn in the 1% v/v HCl was the same as for Mn in the 1% v/v HNO₃ which indicated that there was no interference by HCl with the Mn signal. However, there was an interference by the 1% v/v HCl matrix with the Mn integrated absorbance (Fig. 4, curve E) compared to the 1% v/v HNO₃ matrix solution (Fig. 4, curve A). Therefore, it was necessary to calculate the ratio of the integrated absorbance using the Mn in the 1% v/v HNO₃ (the chloride interference free solution) since it represented the total amount of Mn measured from a solution free from chloride interferences. The pre-atomization loss of Mn in ETAAS was equal to 89.7% with the remaining 10.3% Mn vaporized during the atomization step. The Mn pre-atomization loss of 89.7% in ETAAS correlated well with the Mn pre-atomization loss of 90.6% in

ETV-ICP-MS. Therefore, the pre-atomization loss of Mn observed in both graphite strip ETV-ICP-MS and graphite tube furnace ETV-ICP-MS corresponded to pre-atomization loss of Mn observed in ETAAS and the conclusions that were drawn using the graphite strip ETV in Chapter 1 were valid.

Quantitative determination.

The HGA 76B graphite furnace was modified not only to allow the investigation of fundamental processes occurring in electrothermal atomizers by measuring ETAAS and ICP-MS signals simultaneously, but also to provide an efficient sample introduction device for ICP-MS.

Limits of detection and sensitivity. The limits of detection (LOD) and the sensitivity for 65 elements were determined using the modified furnace with ICP-MS. However, only the limits of detection and sensitivity of 57 elements are presented in Table 7. The results for the following elements: Ca, K, Mg, Na, P, S, Se, and Si were suspect because of strong isobaric interferences by the blank or large blank values of NASS-1 used as a matrix modifier. The experimental and operating conditions are shown in Table 6. The preparation of the NASS-1 chemical modifier solution and the standard solutions of analytes are described in the experimental section. The LOD and the sensitivity were obtained using standard solutions with and without NASS-1 chemical modifier and with vaporization from the tube surface or from the platform surface.

Recently, Grégoire^{99,95} introduced the use of NASS-1 (seawater reference material) as a chemical modifier for ETV-ICP-MS and obtained very good limits of detection and sensitivity for about 10 elements. NASS-1 is seawater reference material

Table 6. Experimental and operating conditions of the ETV-ICP-MS for determination of the limits of detection of the modified electrothermal vaporizer.

Experimental conditions and heating cycle of the modified electrothermal vaporizer

	Step	
	Drying	Vaporization
Temperature/°C	120	2500/2650 ^a
Ramp time/s	10	0
Hold time/s	30	10

Sample volume 5 μ l

Carrier gas flow-rate

Total 1.0 l min⁻¹

Internal 0.3 l min⁻¹

Mass spectrometer interface and plasma conditions

Same as those shown in Table 3 except when stated otherwise.

Dwell time 1 ms

R.F. power 1.1 kW

OmiRange applied on NASS-1 components:

Na 35

K, Mg, Cl 20

Ca 5

^aThe appropriate vaporization temperature of a particular experiment is given in the text.

(deep ocean water) which is very well characterized and of high purity (sub-ng g⁻¹ levels of trace elements)⁹⁵. NAAS-1 is an aqueous solution of mainly of chloride salts of Na, K, Mg, and Ca with a nominal 3.5% dissolved salts content. Hence, NAAS-1 was used as a chemical modifier for the determination of the limits of detection and the sensitivity of 57 elements.

Table 7 shows the limits of detection of 57 elements that were obtained using the modified HGA 76B graphite furnace with the ICP-MS and a comparison with LODs of other commonly used analytical techniques. The LOD obtained with the modified furnace and shown in Table 7 represented the mean of seven replicates, giving a signal equal to $3\sigma/\text{slope}$ of the analytical calibration curve (σ = standard deviation of the blank). In general, the LODs found with the modified furnace were lower than or similar to those obtained by ETAAS with an autosampling device⁹⁸, and were higher than or similar to those obtained by solution nebulization (SN) ICP-MS⁹⁸, and much higher than those obtained by Grégoire⁹⁹ with an HGA 600MS ETV-ICP-MS and an autosampling device. The LODs obtained with the modified furnace were not much lower than those obtained with ETAAS and SN-ICP-MS, or were similar to those obtained with HGA 600MS. The reason for this was that they were obtained from samples deposited manually with an Eppendorf pipette instead of being deposited with an autosampling device. The ICP-MS signal, like ETAAS⁹⁶, is sensitive to the vaporization processes of the sample which is dependant on repeatability of sample insertion⁹⁷. A poor repeatability of the vaporization processes would be reflected by a poor repeatability of the integrated ion intensity in ICP-MS. The relative standard

Table 7. Limits of detection in parts-per-trillion (ppt) for the modified electrothermal vaporizer and other literature values.

Elements	This work ^a , (%RSD) ^b	ETAAS ^{98,c}	SN-ICP-MS ⁹⁸	ETV-ICP-MS ^{99,d}
¹⁰⁷ Ag	76 ^c , (14%)	5	40	
²⁷ Al	460 ^f , (6.0%)	40	100	
⁷⁵ As	760 ⁱ , (16%)	200	50	
¹⁹⁷ Au	420 ⁱ , (5.5%)	100	100	
¹¹ B	1080 ^g , (1.3%)	20000	100	
¹³⁸ Ba	640 ^f , (7.0%)	100	20	
⁹ Be	2400 ^f , (10%)	10	100	
²⁰⁹ Bi	34 ⁱ , (7.4%)	100	40	
¹¹⁴ Cd	940 ^f , (19%)	3	20	17.4
¹⁴⁰ Ce	1540 ⁱ , (16%)		10	2.3
⁵⁹ Co	178 ^f , (2.8%)	10	20	2.8
¹³⁹ Cs	42 ⁱ , (7.4%)	50	20	1.1
⁶³ Cu	82 ^f , (1.8%)	20	30	8.5
¹⁶⁴ Dy	114 ⁱ , (8.2%)		40	

Table 7 (continued).

Elements	This work ^a , (%RSD) ^b	ETAAS ^{98,c}	SN-ICP-MS ⁹⁸	ETV-ICP-MS ^{99,d}
¹⁶⁶ Er	360 ⁱ , (11%)		20	
¹⁵³ Eu	134 ^e , (7.4%)		20	
⁵⁶ Fe	330 ^f , (7.1%)	20	1000	
⁶⁹ Ga	72 ^f , (1.2%)	100	80	
¹⁵⁸ Gd	900 ⁱ , (12%)		40	
⁷⁴ Ge	144 ^g , (2.9%)	200	80	
¹⁸⁰ Hf	640 ^e , (21%)		30	
²⁰² Hg	1660 ^e , (4.2%)	1000	30	
¹⁶⁵ Ho	100 ⁱ , (7.2%)		10	
¹¹⁵ In	36 ^h , (11%)	50	20	
¹⁹³ Ir	84 ^e , (15%)	2000	60	
¹³⁹ La	460 ⁱ , (5.3%)		10	1.8
¹⁷⁵ Lu	74 ⁱ , (6.2%)		10	
⁵⁵ Mn	400 ^f , (3.7%)	10	40	2.3

Table 7 (continued).

Elements	This work ^a , (%RSD) ^b	ETAAS ^{98,c}	SN-ICP-MS ⁹⁸	ETV-ICP-MS ^{99,d}
⁹⁹ Mo	820 ^e , (20%)	40	80	
⁹³ Nb	4020 ^g , (17%)		20	
¹⁴² Nd	38 ^e , (26%)		20	1.3
⁵⁸ Ni	194 ⁱ , (2.5%)	100	30	9.4
²⁰⁸ Pb	74 ^f , (18%)	50	20	1.7
¹⁰⁶ Pd	760 ^g , (13%)	250	60	
¹⁴¹ Pr	320 ⁱ , (16%)		10	
¹⁹⁵ Pt	52 ^e , (6.1%)	500	80	
⁸⁵ Rb	108 ^f , (4.1%)	50	20	
¹⁸⁷ Re	200 ⁱ , (7.0%)		60	
¹⁰³ Rh	148 ^g , (11%)		20	
¹⁰² Ru	280 ^g , (6.1%)		50	

Table 7 (continued).

Elements	This work ^a , (%RSD) ^b	ETAAS ^{98,c}	SN-ICP-MS ⁹⁸	ETV-ICP-MS ^{99,d}
¹²¹ Sb	360 ^g , (8.5%)	200	20	
⁴⁵ Sc	44 ⁱ , (17%)		80	4.4
¹⁵² Sm	600 ⁱ , (8.5%)		40	3.6
¹²⁰ Sn	900 ^g , (5.0%)	200	30	
⁸⁸ Sr	780 ^f , (6.4%)	20	20	
¹⁸¹ Ta	5800 ^g , (10%)		20	
¹⁵⁹ Tb	280 ⁱ , (12%)		10	
¹³⁰ Te	780 ^g , (24%)	100	40	
²³² Th	1420 ^c , (23%)		20	3.8
²⁰⁵ Tl	8 ⁱ , (12%)	100	20	0.57
¹⁶⁹ Tm	74 ⁱ , (5.8%)		10	
²³⁸ U	1320 ^c , (9.4%)		10	1.6
⁵¹ V	3280 ^f , (18%)	200	30	7.2

Table 7 (continued).

Elements	This work ^a , (%RSD) ^b	ETAAS ^{98,c}	SN-ICP-MS ⁹⁸	ETV-ICP-MS ^{99,d}
¹⁸⁴ W	3200 ⁱ , (6.9%)		60	
⁸⁹ Y	1240 ⁱ , (4.3%)		20	3.0
¹⁷⁴ Yb	72 ^e , (3.1%)		30	0.44
⁶⁴ Zn	440 ^f , (3.1%)	10	80	10.3

^aLimits of detection = mass[†] / volume[‡]. [†]Mass of analyte giving a signal = 3 σ /slope of the analytical calibration curve. [‡]Volume based on 5 μ l sample.

^bPercent relative standard deviation.

^cLimits of detection of ETAAS are based on 100 μ l sample volumes.

^dLimits of detection of ETV-ICP-MS are based on 10 μ l sample volumes.

^eStandard solutions vaporized from the surface of a graphite platform at 2650°C.

^fStandard solutions plus 350 ng of NASS-1 vaporized from the surface of a graphite platform at 2500°C.

^gStandard solutions plus 350 ng of NASS-1 vaporized from the surface of a graphite platform at 2650°C.

^hStandard solutions plus 350 ng of NASS-1 vaporized from the surface of a graphite tube at 2500°C.

ⁱStandard solutions plus 350 ng of NASS-1 vaporized from the surface of a graphite tube at 2650°C.

deviations (RSD) shown in Table 7 are much higher than the 2-3 %RSD that would be obtained if an autosampler were used⁹⁶. Consequently, the LODs were occasionally poorer than those obtained by other analytical techniques that used an autosampler for sample insertion. Because of the design of the modified furnace, an autosampler could not be used without some permanent modifications to the sampling arm of the autosampler which would render the autosampler unusable with its current apparatus.

Table 8 summarizes the effect of NASS-1 on the sensitivity for each element in Table 7, and shows data obtained using vaporization from the tube surface or the platform surface and at two different vaporization temperatures. In general, the addition of NASS-1 improved the sensitivity of the modified furnace ICP-MS for almost every element. Very little or no improvement in sensitivity was noted for As, Eu, Hf, Hg, La, Mo, Re, Sm, Ta, Te, Tm, and W. Some of these elements such as Hf, Mo, Re, Ta, and W have a high boiling point¹⁰³ ($> 4500^{\circ}\text{C}$) and would not be expected to vaporize well in electrothermal atomizers. A few elements such as Hf, La, Mo, Ta, and W may form refractory carbides that would not vaporize well. In fact, refractory carbide coating of the graphite tube has been used in the past to improve the analytical condition of many analyte elements⁹⁶. In addition, it has been reported⁹⁶ that Ta, Mo, and W formed chloride salts that can be strongly intercalated within the basal layers of graphite and the intercalated compound would remain entrapped within the graphite layers⁹⁶. Therefore, the addition of NASS-1 was not expected to improve the vaporization efficiency of Ta, Mo, and W. Figure 40 shows the temporal distribution of Hg, Tm, and Re (Fig. 40a) and the temporal distribution of Na, Ca, and Cl from NASS-1 (Fig. 40b) in

Table 8. Effect of NASS-1, vaporization temperature, and vaporization surface on the sensitivity (counts pg^{-1}) of the elements determined using the modified electrothermal vaporizer.

Elements	STD, platform, 2500°C ^a	STD+ NASS-1, platform, 2500°C ^b	STD+ NASS-1, platform, 2650°C ^c	STD+ NASS-1, tube surf. 2500°C ^d	STD+ NASS-1, tube surf., 2650°C ^e
¹⁰⁷ Ag	161	667		601	1076
²⁷ Al		3176		292	910
⁷⁵ As	20	68		81	110
¹⁹⁷ Au	186	550	1039		1281
¹¹ B		39431			1714
¹³⁸ Ba	42	425			
⁹ Be	21	74			
²⁰⁹ Bi	675	2563		3476	3813
¹¹⁴ Cd	2	234		184	209
¹⁴⁰ Ce	9		10		67
⁵⁹ Co	59	488			
¹³⁹ Cs	549	2584		2968	3498
⁶³ Cu	67	1073		378	909

Table 8 (continued).

Elements	STD, platform, 2500°C ^a	STD+ NASS-1, platform, 2500°C ^b	STD+ NASS-1, platform, 2650°C ^c	STD+ NASS-1, tube surf., 2500°C ^d	STD+ NASS-1, tube surf., 2650°C ^e
¹⁶⁴ Dy	40		106		337
¹⁶⁶ Er	30		89		328
¹⁵³ Eu	306		419		695
⁵⁶ Fe		7977			
⁶⁹ Ga	59	375			
¹⁵⁸ Gd	6		18		52
⁷⁴ Ge	29		232		156
¹⁸⁰ Hf	6		10		
²⁰² Hg	86	175			
¹⁶⁵ Ho	155		335		1061
¹¹⁵ In	454	2486		2973	2988
¹⁹³ Ir	35	369	1139		1217
¹³⁹ La	5		18		66
¹⁷⁵ Lu	25		155		570
⁵⁵ Mn	113	544			

Table 8 (continued).

Elements	STD, platform, 2500°C ^a	STD+ NASS-1, platform, 2500°C ^b	STD+ NASS-1, platform, 2650°C ^c	STD+ NASS-1, tube surf., 2500°C ^d	STD+ NASS-1, tube surf., 2650°C ^e
⁹⁹ Mo	65		169		162
⁹³ Nb			22		42
¹⁴² Nd	14		52		171
⁵⁸ Ni	19	504		222	577
²⁰⁸ Pb	757	2004			
¹⁰⁶ Pd	19	92	231		174
¹⁴¹ Pr	12		59		347
¹⁹⁵ Pt	59	207	305		338
⁸⁵ Rb	238	1152			
¹⁸⁷ Re	504		923		2284
¹⁰³ Rh	41	256	643		599
¹⁰² Ru	11	58	234		228

Table 8 (continued).

Elements	STD, platform, 2500°C ^a	STD+ NASS-1, platform, 2500°C ^b	STD+ NASS-1, platform, 2650°C ^c	STD+ NASS-1, tube surf., 2500°C ^d	STD+ NASS-1, tube surf., 2650°C ^e
¹²¹ Sb	49	246	432		386
⁴⁵ Sc	3		46		88
¹⁵² Sm	87		160		322
¹²⁰ Sn	123	477	630		558
⁸⁸ Sr	178	1330			
¹⁸¹ Ta			22		13
¹⁵⁹ Tb	20		124		341
¹³⁰ Te	161	348	482		401
²³² Th	21				4
²⁰⁵ Tl	387	1833		2991	3752
¹⁶⁹ Tm	614		930		1453
²³⁸ U	17				
⁵¹ V		96			

Table 8 (continued).

Elements	STD, platform, 2500°C ^a	STD+ NASS-1, platform, 2500°C ^b	STD+ NASS-1, platform, 2650°C ^c	STD+ NASS-1, tube surf., 2500°C ^d	STD+ NASS-1, tube surf., 2650°C ^e
¹⁸⁴ W	12		55		81
⁸⁹ Y	4		39		50
¹⁷⁴ Yb	453		520		655
⁶⁴ Zn	30	247			

^aStandard solutions (STD) vaporized from the surface of a graphite platform at 2500°C.

^bStandard solutions (STD) plus 350 ng of NASS-1 vaporized from the surface of a graphite platform at 2500°C.

^cStandard solutions (STD) plus 350 ng of NASS-1 vaporized from the surface of a graphite platform at 2650°C.

^dStandard solutions (STD) plus 350 ng of NASS-1 vaporized from the surface of a graphite tube at 2500°C.

^eStandard solutions (STD) plus 350 ng of NASS-1 vaporized from the surface of a graphite tube at 2650°C.

Figure 40. Temporal behaviour of some analytes in ICP-MS with vaporization from the platform surface at 2500°C. (a) 50 pg of Hg, Tm, and Re, plus 350 ng of NASS-1; (b) Na, Ca, and Cl from the salts of 350 ng of NASS-1.

ETV-ICP-MS. The temporal distribution of Hg, Tm, and Re demonstrated one of the shortcomings of using NASS-1 to improve the sensitivity of some elements. The temporal distribution of K and Mg in NASS-1 was the same as those of Na and Ca, respectively. The signal profiles of Na, Ca, and Cl overlapped only with Hg and hence, Hg may form a volatile chloride in the gas-phase and/or in the condensed phase. Thulium forms a chloride having a relatively low boiling point¹⁰⁰ (b.p. 1440°C); and hence, thulium chloride may form in the condensed phase, but not in the gas-phase since the bulk of NASS-1 has been already vaporized out from the furnace (Fig 40b, 0.6-2.6 s) at the time the Tm appeared in the gas-phase (Fig. 40a, 2.8-7 s). In addition to the above mentioned problems associated with the some elements, it is probable that some volatile chlorides, such as mercury chloride, do not nucleate efficiently on NASS-1 particles, and thulium chloride, do not self-nucleate. Consequently, they would be readily lost somewhere in the transfer line. The above explanation may also apply to Eu. The other refractory elements of high boiling points, such as Re, could not benefit from the addition of NASS-1 since NASS-1 was already vaporized and lost from the furnace at the time these elements appeared in the gas-phase.

Except for a few refractory elements, the addition of NASS-1 improved the sensitivity of the other elements investigated. Table 8 shows that an improvement of one to two orders of magnitude was obtained for Ag, Au, Ba, Cd, Co, Er, Ho, Lu, Ni, Pd, Pr, Tl, and Y (see Table 8). Figure 41 shows the effect of the addition of NASS-1 on the ion intensity and the temporal distribution of Ni, Ga, and Co. Fig. 41b shows that the signal profiles for Co, Ga, and Ni is very low, flat, and with tailing effects.

Figure 41. Temporal behaviour of some analytes in ICP-MS with vaporization from the platform surface at 2500°C. (a) 50 pg of analyte plus 350 ng of NASS-1: Ni (solid line), Ga (broken line), and Co (solid line); (b) 50 pg of analyte without NASS-1: Ni (solid line), Ga (broken line), and Co (solid line).

The addition of NASS-1 (Fig. 41a) improved greatly the signal profiles of Co, Ga, and Ni, producing much sharper peaks but the tailing effects remained. In addition, the Ni signal was shifted to a lower appearance time, whereas no significant shift in the appearance time was observed for Ga and Co. The shift towards a lower temperature in the appearance time of Ni could not be explained on the basis that nickel formed a low boiling point chloride that would vaporize at a lower temperature than the nickel oxide formed without the NASS-1. Sturgeon *et al.*⁸ have shown that nickel had the same appearance time whether it was vaporized as the chloride or as the nitrate and proposed that nickel atoms were formed from the dissociation of nickel dimer in the gas-phase and from direct vaporization of the condensed-phase metal. However, Weiz *et al.*²⁶ suggested that large amount of chloride salts could stabilize the nickel as chloride and allow co-volatilization of the nickel chloride with other chlorides.

Figure 42 shows the ETV-ICP-MS temporal distribution of Co, Ga, and Ni (Fig. 42a) in the presence of NASS-1 and the ETV-ICP-MS temporal distribution of Na, Ca, and Cl from the salts of NASS-1 (Fig. 42b). Figure 42 shows that Ni signal overlapped with the signal profile of Ca (and also Mg, but not shown) and to lesser extent with Na (and K) and Cl. This strongly suggests a co-volatilization processes²⁶, and perhaps an expulsion mechanism as proposed in Chapter 1 since the presence of hydrolyzable salts such as CaCl_2 and MgCl_2 can result in the expulsion of Ni along with HCl gas. Therefore, the shift in the appearance time would be associated with the co-volatilization of Ni with the chloride salts of NASS-1. In the same manner, the increased sensitivity would be associated with the condensation of Ni on NASS-1 particles allowing better

Figure 42. Temporal behaviour of some analytes in ICP-MS with vaporization from the platform surface at 2500°C. (a) 50 pg of Ni, Ga, and Co, plus 350 ng of NASS-1; (b) Na, Ca, and Cl, from the salts of 350 ng of NASS-1.

transport efficiency of Ni from the ETV to the ICP. The above phenomenon may be typical of other stable chloride forming salts such as Cd, Cu, Mn, Pb, Sn, and Tl.

It is not clear why the addition of NASS-1 improved the sensitivity of Ga and Co. There was no overlap of their temporal distribution with the temporal distribution of the components of NASS-1. Gallium chloride¹⁰⁰ is not stable at the temperature at which Ga appeared in the ETV-ICP-MS spectra. Cobalt forms a stable chloride with a boiling point of 1049°C¹⁰⁰, but cobalt is thought to be atomized through a mechanism identical to Ni⁸. A possible explanation is that the vaporization surfaces were altered by NASS-1 such that the analytes were not directly in contact with the graphite surface but rather with a thin layer of the metal salts. Figure 42b shows that some Na and Ca (the latter to a lesser extent) remained in the furnace at the appearance time of Ga and Co. The amount of remaining Na and Ca were greater than they appeared in Fig. 42b. Because of the large quantities of salts in NASS-1, an offset voltage (OmiRange setting) was applied on the ion lens in the determination of Na, K, Ca, Mg, and Cl to allow their detection without producing an off-scale signal. The Omirange setting reduced the signal intensity by approximately 25-70%⁹⁸, depending on the analyte. Hence, a small signal corresponded to a relatively large amount of the analyte being detected. It is possible that Na and Ca underwent a smooth "distillation process" from the graphite furnace from 3 s and beyond. Therefore, it is reasonable to propose that Ga and Co were vaporized from a modified surface which would be composed of graphite and metal salts such oxychlorides and oxides, but not chlorides since no Cl was detected after 3.5 s. The vaporization of Ga and Co would then be more efficient than it would be from an unaltered graphite surface.

Other elements that showed the same characteristics as Ga and Co were Al, Ba, and Sr.

Increasing the vaporization temperature either produced a large enhancement in the integrated ion intensity or had very little effect. Figure 43 shows the temporal behaviour in ICP-MS of Ag, Cu, and Ni vaporized from the graphite tube surface at either 2500°C (Fig. 43a) or 2650°C (Fig. 43b). Figure 43b shows that the peaks of Ag, Cu, and Ni are sharper and are approximately 65% greater in peak height intensity and peak area. This was probably because their rate of vaporization increased as the temperature was increased from 2500°C to 2650°C and therefore more analytes could condense on NASS-1 particles. Increasing the ambient tube temperature with vaporization from the platform surface produced similar results as above, i.e. the ICP-MS signal of some elements either improved or remained essentially the same. Besides Ag, Cu, and Ni, other elements which benefited the most from an increase in the vaporization temperature were Au, Al, Ir, Pd, Rh, and Ru. These elements have high boiling point¹⁰³ ($> 2200^{\circ}\text{C}$) and were therefore expected to show an improvement in the integrated ion intensity in ICP-MS with an increase in the vaporization temperature.

Figure 44 shows the temporal distribution of Te and Pt vaporized from the platform surface at either 2500°C (Fig. 44a) or 2650°C (Fig. 44b) in ICP-MS. The integrated ion intensity remained virtually the same for both Te and Pt with increasing temperature. The only benefit that was observed with the increased vaporization temperature was the formation of sharper peaks but at the expense of shorter tube life time. There were two trends that were observed for the elements that did not benefit greatly from an increase in the vaporization temperature. First, the elements with low

Figure 43. Temporal behaviour in ICP-MS of Ag, Cu, and Ni in the presence of 350 ng of NASS-1 with vaporization from the graphite tube surface. (a) 2500°C; (b) 2650°C.

Figure 44. Temporal behaviour in ICP-MS of Pt (solid line) and Te (broken line) in the presence of 350 ng of NASS-1 with vaporization from the platform surface. (a) 2500°C; (b) 2650°C.

boiling points¹⁰³ ($< 1600^{\circ}\text{C}$), such as As, Bi, Cd, Cs and Tl, did not benefit from an increase in the vaporization temperature since it was likely that at either 2500°C or 2650°C , the maximum rate of vaporization of these elements has already been attained. Second, the refractory elements that were discussed previously, such as Hf, La, Ta, Te, Tm, and W, did not benefit from the increase in the vaporization temperature since their boiling points were at least 1500°C greater than the maximum temperature of 2650°C . Also, there is a possibility that a smaller amount of the sample would vaporize at higher temperatures due to the formation of refractory carbides. For some metals such as Hf, La, Ta, and W, this would likely increase with increased temperature.

It should be pointed out that suppression of the integrated ion intensity such as was observed for silver (Fig. 33) when the vaporization temperature was increased from 2400 to 2600°C was not observed with any of the elements when NASS-1 was present. For the temperatures studied, NASS-1 would presumably allow the analytes to condense on the NASS-1 components with equal efficiency at 2500°C and 2650°C and would alleviate the problem of inadequate nucleation due to a change in the vaporization temperature.

In general, changing the vaporization surface from a platform surface to a tube surface improved the integrated ion intensity of the analytes. Figure 45 shows the temporal distribution in ICP-MS of Eu and Yb vaporized from the platform surface (Fig. 45a), and from the tube surface (Fig. 45b) at 2650°C . The ICP-MS signals of Eu and Yb are typical of the rare earth elements where an improvement in the sensitivity was observed when the rare earth elements were the analytes. The above observation was to be expected on the following grounds. Chakrabarti *et al.*¹⁰¹ have demonstrated that at

Figure 45. Temporal behaviour in ICP-MS of Eu (solid line) and Yb (dotted line) in the presence of 350 ng of NASS-1 with vaporization temperature of 2650°C. (a) vaporization from the platform surface; (b) vaporization from the tube surface.

a given heating rate of the graphite tube surface, the temperature of the graphite tube surface increased more rapidly than the temperature of the platform surface since the graphite tube was heated by Joule heating effect¹⁰² (motion of electrons in a resistor), whereas the platform is heated by radiational energy transfer from the heated tube surface. Therefore, the analytes gained heat more rapidly from the graphite tube surface than from the platform surface and, consequently, their rate of vaporization increased. Figure 45 clearly shows that the signals for Eu and Yb were much sharper with vaporization from the graphite tube surface (Fig. 45b) than with vaporization from the platform surface (Fig. 45a). This is indicative of a faster rate of vaporization of Eu and Yb due to their vaporization from the graphite tube surface than their vaporization from the platform surface.

There is no clear pattern that would indicate optimum experimental conditions that should be used with the modified furnace ICP-MS for determination of any elements investigated in this work. However, it seems that rare earth elements and some of the refractory elements, such as Hf, Re, Ta, and W, will benefit from vaporization from the graphite tube surface at the highest vaporization temperature available.

Determination of silver in Geostandards. Silver was determined in two geological reference materials, BHVO-1 and AGV-1, with the modified furnace in order to test its performance in the analysis of real samples. The determination of silver was carried out using the isotope dilution technique because it is one of the most accurate analytical techniques, is fairly rapid compared to the standard addition technique, and it has been shown that ETV-ICP-MS coupled with the isotope dilution technique could give a

precision of approximately 2-5% for Mo, W, Tl, Fe, Pd, Pt, Ru, and Ir^{49,74,103}. The preparation of samples is described in the experimental section and the experimental and operating conditions of the ETV-ICP-MS were the same as those given in Table 6, with the sample being vaporized from the platform surface at 2500°C.

The concentration of Ag using the isotope dilution technique was determined using the following equation:

$$C = \frac{M_s K(A_s - B_s R)}{W(BR - A)} \quad (9)$$

where C is the concentration of analyte in $\mu\text{g g}^{-1}$, M_s is the mass of the stable isotope spike in μg , K is the ratio of the natural to the spike isotope relative atomic masses, A_s is the abundance of the reference isotope in the spike, B_s is the abundance of the spike isotope in the spike, R is the experimentally measured ratio of the reference to the spike isotope corrected for mass discrimination, W is the mass of the sample in g, B is the natural abundance of the spike isotope, and A is the natural abundance of the reference isotope. A mass discrimination effect was observed on the experimentally measured ratio of ^{107}Ag to ^{109}Ag for a range of 10-100 ng ml^{-1} standard solution of silver and a correction factor, by which R had to be multiplied, was calculated to be 1.0408.

Table 9 shows the results obtained for the determination of Ag in geostandards BHVO-1 and AGV-1, using the isotope dilution technique with the modified graphite furnace ICP-MS. Figure 46 shows a typical temporal distribution of ^{109}Ag (solid line) and of ^{107}Ag (broken line) for BHVO-1 (Fig. 46a) and AGV-1 (Fig. 46b). The results obtained correlated well with the recommended values (see Table 9). The observed large

Table 9. Determination of Ag in geological reference material using the isotope dilution technique.

Concentration [†] of Ag in geostandards (parts-per-billion)		
	This work	Recommended values ^{104, ‡}
BHVO-1 [*]	82 ± 38	55
AGV-1 ^b	78 ± 25	78

[†]The concentration represents the mean of 5 replicates.

[‡]The standard deviation were not available in reference 104.

^{*}Andesite from east wall of Guano Valley, Lake County, Oregon, USA¹⁰⁴.

^bBasaltic lava from Kilauea caldera, Kilauea volcano, Hawaii, USA¹⁰⁴.

Figure 46. Temporal distribution in ICP-MS of ^{109}Ag (solid line) and ^{107}Ag (broken line) from enriched ^{109}Ag added to geostandard materials. (a) BHVO-1; (b) AGV-1.

standard deviation might be attributable to the irregular sample insertion due to manual sampling with an Eppendorf pipette.

The ^{109}Ag and ^{107}Ag signal profiles for both BHVO-1 and AGV-1 were characterized with a rather long tail (Fig. 46a and Fig. 46b). The composition of the geostandards is complex and the concentration of dissolved solids is high¹⁰⁴. The concentration of SiO_2 and Al_2O_3 in BHVO-1 was 49.94% m/v and 13.80% m/v, respectively, and the concentration of SiO_2 and Al_2O_3 in AGV-1 was 58.79% m/v and 17.14% m/v, respectively. The SiO_2 is vaporized from the sample using HF, but relatively large amount of lithium metaborate is added as a flux to fuse the residue obtained from the acid decomposition of the sample. Also, numerous metal oxides were present at low percentage and sub-percentage levels. The tailing effect could be due to an entrapment effect of silver in the matrix. The silver would be trapped in the predominant metal oxide matrix and would diffuse out slowly producing a long tail in ICP-MS signal. Unfortunately, a pyrolysis temperature greater than 600°C would cause a pre-atomization loss of silver. Therefore, large amounts of matrix remained in the ETV during the vaporization step and the remaining amount of matrix would envelope silver and prevent it from being vaporized at once.

SUMMARY

Modifications to a commercial graphite furnace were made in order to allow its use as a sample introduction device with ICP-MS and to allow simultaneous measurement of the atomic absorption and mass spectrometric signal. The modified furnace has been characterized with respect to the effect of the internal carrier gas (Ar) flow, the total Ar

carrier gas (Ar) flow, and the vaporization temperature on the integrated intensity of Ag signal in ICP-MS. For the internal carrier gas (Ar) flow, the total carrier gas (Ar) flow, and the vaporization temperature, the optimum values were 450 ml min⁻¹, 950 ml min⁻¹, and 2400°C, respectively. Linear analytical calibration curves were obtained for Ag for vaporization from the graphite tube surface and for the platform, with and without the sodium chloride chemical modifier. The best limits of detection and sensitivity for Ag were obtained from the vaporization from the platform with the addition of sodium chloride chemical modifier.

For simultaneous measurement of the ETAAS and ICP-MS signals, it was observed that the carrier flow was laminar and that the Ag transient in ICP-MS appeared 0.85 s after the transient in ETAAS. A relative broadening of the Ag peak was observed in ICP-MS compared to the Ag peak in ETAAS and that broadening was dependant on the internal carrier gas flow. It was possible to use simultaneous measurement of both ETAAS and ICP-MS signals for investigating fundamental processes occurring in electrothermal atomizers. The interferences from MgCl₂ matrix with the determination of Mn in ETAAS was re-investigated with the modified furnace using the simultaneous detection mode. Direct evidence of Mn pre-atomization loss were obtained from the ICP-MS signal, whereas no atomic absorption of Mn was measured during the pyrolysis step, indicating that Mn was lost as a manganese molecule.

The modified furnace was used to carry out quantitative determinations of 57 elements of the Periodic Table. Limits of detection and sensitivities were determined for 57 elements using NASS-1 as a chemical modifier with vaporization from the tube

surface or from the platform at two different vaporization temperatures. In general, limits of detection are better than those of ETAAS, or similar to solution nebulization-ICP-MS, but worse than those of the commercial Perkin-Elmer HGA 600MS electrothermal vaporizer. Problem with imprecise sample delivery by manual syringing was found to be a possible reason for poorer limits of detection compared to those obtained with the HGA 600MS electrothermal vaporizer. Improvement in the sensitivity for most of the elements studied were observed upon the addition of NASS-1 as a chemical modifier. No (or very little) sensitivity improvement was observed for some refractory elements when NASS-1 was added as a chemical modifier. Most of these refractory elements have high boiling points and form refractory carbides. Increasing the vaporization temperature had a significant effect only on refractory, carbide-forming elements and rare earth elements. Vaporization from the graphite tube surface instead of the platform surface, with the addition of NASS-1 as a chemical modifier, improved the sensitivity of most elements. Silver was determined in geological reference materials using the isotope dilution technique with the modified furnace ICP-MS. Good agreement with the recommended values was obtained.

CHAPTER 4

MECHANISM OF ALUMINIUM SPIKE FORMATION AND DISSIPATION IN ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

INTRODUCTION

Aluminium in various samples at trace levels (ng ml^{-1}), such as in blood¹⁰⁵ or metallurgical samples^{106,107}, is regularly determined by electrothermal atomic absorption spectrometry (ETAAS). Although the determination of aluminium by ETAAS is carried out routinely in analytical laboratories, there are still many unanswered questions regarding the mechanism of aluminium atomization and other anomalous observations related to the atomization of aluminium.

Among the anomalies that were reported on atomization of aluminium were the appearance of a second aluminium atomic absorption peak after the main Al peak⁵⁷, the high residence time of Al atoms within the electrothermal atomizer¹⁰⁸, and under special conditions, the appearance of Al atomic absorption spikes against the background of a smooth increase in the Al atomic absorption signal^{20,21}.

A few mechanisms for the atomization of aluminium have been proposed. Smets⁹ reported that the activation energy for aluminium atomization correlated well with the dissociation energy of $\text{AlO}_{(g)}$. Sturgeon and Chakrabarti⁸ proposed that one or more of the gaseous oxide species, AlO , Al_2O , Al_2O_2 , O_2 , and O , may be involved in the atomization of aluminium and that $\text{Al}_{(g)}$ may be formed by direct decomposition of $\text{Al}_2\text{O}_{3(g)}$. Using high-temperature chemical equilibrium calculations for aluminium, Frech

*et al.*⁶ reported that $Al_{(g)}$ was a product of dissociation of $Al_2O_{3(g)}$. However, their calculations did not take into account the presence of carbides and cyanides which are known to be present during the atomization of aluminium. Therefore, the theoretical modelling of aluminium atomization made by Frech *et al.*⁶ may not agree with the reality. Another mechanism proposed by L'vov^{20,21,109} suggests that for many elements which form oxides, free atoms are formed by reduction of the metal oxide by gaseous carbides (the ROC model). The ROC model involves the autocatalytic reduction of oxides by gaseous carbides to form atoms:

occurring as two concurrently developing reactions:

The reaction described by equation (11) occurs on the surface of the graphite and reaction (12) occurs on the surface of the oxide.

L'vov and Savin¹¹⁰ observed a very interesting effect with the atomization of some refractory oxides such as Al_2O_3 and Yb_2O_3 . When the graphite furnace was slowly heated ($5-20^\circ C \text{ min}^{-1}$) and large amounts of sample (μg quantity) were used, a series of relatively fast bursts (called spikes) of atomic absorption signals were observed on top of a smoothly increasing signal, presumably produced by the thermal dissociation of the oxide. L'vov *et al.*²² applied the ROC model to explain the occurrence of spikes during the atomization of aluminium, ytterbium, thulium, and manganese. They indicated that

the rapid formation of aluminium atoms would be interrupted by "encapsulation" of the aluminium oxides with a carbon film. This carbon film would be formed by the decomposition of excess of gaseous carbides and the resulting solid carbon would coat the oxide particles. This carbon film is thought to be somewhat disordered structure of solid carbon nuclei rather than a dense coating. The coverage of the oxide by the carbon film would inhibit the autocatalytic process of aluminium atom formation until the temperature is high enough to allow the oxidation of the carbon film on the oxide particles. However, it would not affect the thermal dissociation of the aluminium oxide and vaporization of aluminium metal to continue since the area covered by the carbon film on the oxide particle can be a small fraction of the total area of the sample surface.

The validity of the ROC model relies mainly on the existence of the gaseous metal carbides concurrently with Al. As well, the ROC model implies the existence of an over-equilibrium excess of carbides, carbon vapours, and metal vapours over the oxide surface^{7,109}. L'vov and Savin¹¹⁰ recorded a molecular absorption band at 205 and 255 nm which was coincident with the appearance of Al absorption spikes, and they assigned these bands as being absorption bands of Al_2C_2 . The assignment of these molecular absorption bands to Al_2C_2 was questionable because it was not confirmed experimentally by an independent technique¹². Doidge¹¹¹ argued that the identification of the absorption spectra at 205 nm with those of Al_2C_2 was questionable since this molecule was not found in secondary sources. Recently, mass spectrometric investigation has provided new evidence on carbothermal reduction of metal oxides by gaseous carbides, i.e. the ROC model. Holcombe *et al.*¹² and Styris and Redfield¹³ showed that aluminium

suboxides were among the most abundant species and that they appeared concurrently with aluminium atoms. On the other hand, Al_2C was observed in the absence of Al_6 ,¹² and was more abundant than Al_2C_2 ¹² which was supposed to be the reacting carbide in the ROC model^{20,21}. Al spikes were also observed from atomization of Al pure metal¹². In addition, the presence of over-equilibrium excess of carbides and carbon vapours was ruled out by two independent groups, Katskov *et al.*⁷ and Iwamoto *et al.*¹¹².

Gilmutdinov *et al.*^{16,17} used a cine-camera equipped with a film that was sensitive in the UV range to image the interior of the graphite furnace during atomization of elements. This imaging system allowed them to investigate the dynamics of formation and the structure of the absorption layer of several elements including aluminium. They proposed, on the basis of the results obtained with the imaging system and the mass spectrometric investigation carried out by Holcombe *et al.*¹², that aluminium atoms were generated from the reduction of Al_2O at the graphite surface. They observed that in the graphite tube furnace, the concentration of aluminium atoms was greater near the graphite tube surface than at the centre of the graphite tube, and that the concentration of aluminium containing species (shown as Al_2O) was at a maximum in the centre of the tube. These features were complimentary to one another. Hutton²³ refined the imaging system used by Gilmutdinov *et al.*^{16,17} by replacing the cine-camera with a charge-coupled device (CCD) camera which greatly improved the optical set-up, and allowed Hutton to acquire images with greater sensitivity and to extract quantitative results from the images. Hutton²³ investigated the atomization of aluminium with the CCD camera and his findings were consistent with those reported by Gilmutdinov *et al.*¹⁷, i.e. thermal dissociation of

$Al_2O_{3(s)}$ to form gaseous Al atoms and gaseous aluminium sub-oxides,

and oxidation of the gaseous Al atoms to form gaseous Al sub-oxides,

and finally, heterogeneous reduction of the gaseous sub-oxides of aluminium at the hot graphite tube surface.

However, the experimental conditions used by Hutton²³ were not the conditions prevailing during aluminium spikes formation, i.e. he used a high heating rate and a small mass of aluminium. Also, the results from the SSF imaging by Gilmutdinov *et al.*^{16,17} were not complete, i.e. results with internal argon flow conditions were not obtained and their SSF imaging system lacked adequate sensitivity, preventing observation of small absorbance (absorbance < 0.2).

In order to better understand the behaviour of aluminium atoms and aluminium species during the atomization step, the mechanism of aluminium spike formation and dissipation was investigated using two relatively new approaches: simultaneous measurement of the Al atomic absorption signal, or the Al oxide(s) molecular absorption signal, and the ETV-ICP-mass spectrometric signal, which provided temporal behaviour of the various species. In addition, the fundamental processes occurring inside the

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

graphite furnace when aluminium spikes appeared were imaged using the imaging system of Hutton²³. The spatial and temporal behaviour of Al atoms and aluminium sub-oxides were obtained which together with the ETV-ICP-MS results provided new experimental evidence on the mechanism of Al spikes formation.

EXPERIMENTAL

Apparatus.

Simultaneous measurement of ETAAS and ETV-ICP-MS signals. The modified Perkin-Elmer HGA 76B graphite furnace (Perkin-Elmer, Norwalk, Connecticut) described previously in chapter 3 was used for the simultaneous measurement of the ETAAS signal, or the electrothermal molecular absorption spectrometric (ETMAS) signal, and the ETV-ICP-MS signal. Modifications of the graphite furnace are shown in Figure 27, and photographs of the modified furnace are presented in Figure 28 with the furnace open (Fig. 28a) and closed (Fig. 28b). The modified graphite furnace was coupled to a Perkin-Elmer/Sciex Elan, Model 5000 inductively coupled plasma mass spectrometer (ICP-MS). The ICP-MS was used in the positive ion detection mode. A demountable torch made of one-piece quartz tubing and equipped with an alumina injector tube was used throughout this work. Solution nebulization for ICP-MS was used for the determination of ⁵¹V, ⁴⁴Ca, ⁷²Ge, and ⁶⁶Zn concentrations as impurities in the aluminium test solution used for this work. For solution nebulization, a peristaltic pump (Gilson Minipuls 3, Gilson Medical Electronics) delivered the sample to a Ryton spray chamber (Scott type) with a delivery rate of 1 ml min⁻¹. The R.F. power and the dwell time used for solution nebulization ICP-MS was 1.05 kW and 200 ms, respectively. A graphite

furnace power supply, Model HGA 500 (Perkin-Elmer), was used with the modified graphite furnace.

The combined measurements of the atomic or molecular absorption signal and the ICP-MS signal required additional equipment which have been described in the experimental section in Chapter 3. Figure 29 shows a diagram of the simultaneous measurement system. The system works as a single beam spectrometer for both atomic and molecular absorption spectrometry. The sample is vaporized in the graphite furnace and the atomic and/or molecular vapour are carried by the argon carrier gas from the graphite furnace to the ICP-MS where it is detected as ionic species. The atomic and molecular absorption can be detected provided that the concentration of atomic or molecular vapour is above the limits of detection of the species of interest and that the residence time of the atoms or molecules is greater than the detector response time. Focusing lenses of 12.5 cm focal length were positioned in order to focus the light from the hollow-cathode (or electrodeless-discharge) lamp to the centre of the graphite furnace and to focus the transmitted light from the centre of the graphite furnace to the entrance slit of the grating monochromator. The entrance slit was set at 200 μm for all elements, which provided a spectral bandpass of 0.7 nm. The resonance line of each element was isolated by a 0.5m Ebert-mount monochromator, 50 X 50 mm grating ruled with 638 lines mm^{-1} (Varian Techtron, Australia). The monochromator was fitted with a Hamamatsu R216 photomultiplier tube (Hamamatsu, Middlesex, USA) for the measurement of the transmitted radiation. The hollow-cathode lamp power supply and the lock-in amplifier were laboratory-made and were synchronously modulated at 843

Hz. The electrodeless-discharge lamp power supply was manufactured by Perkin-Elmer and synchronously modulated with the lock-in amplifier at 843 Hz. The detector response was set at 22 ms. The atomic or molecular transients were recorded on a digital oscilloscope (Nicolet, Model 4094). A deuterium lamp (Perkin-Elmer) was operated at 20 mA and was used for background correction. An aluminium hollow-cathode lamp (Perkin-Elmer) was operated at 10 mA and the aluminium 396.1 nm resonance line was used for the AAS measurements. A vanadium hollow-cathode lamp (Perkin-Elmer) was operated at 15 mA and the vanadium 318.4 nm resonance line was used for the atomic absorption spectrometric (AAS) measurements. A mercury electrodeless-discharge lamp was operated at 4 W and the mercury resonance line at 253.7 nm was used for the molecular absorption spectrometric (MAS) measurements. The molecular absorption band measured at 255 nm by several workers overlaps the mercury resonance line. The temperature of the modified graphite furnace was determined with an Ircon automatic optical pyrometer, Model 300c (Ircon, Niles, Illinois), which was focused on the bottom of the graphite tube directly under the sample injection hole. The output voltage of the pyrometer was converted into temperature using the conversion tables provided by the manufacturer. Table 10 shows the experimental and operating conditions used for the investigation of Al spikes with simultaneous measurement of the ETV-ICP-MS and ETAAS signals.

Graphite and tungsten strip ETV-ICP-MS. The graphite strip ETV described in Chapter 1 (Fig. 1) and used in both Chapters 1 and 2 was again used for this work. For the tungsten strip ETV, the graphite strip and contact electrodes were removed and replaced

Table 10. Experimental and operating conditions of the ETV-ICP-MS and the ETAAS for the investigation of Al spikes formation.

Temperature programme of the modified furnace ETV-ICP-MS and the ETAAS.

	Step		
	Drying	Pyrolysis	Vaporization
Temperature/°C	120	1200	2250
Ramp time/s	10	10	105
Hold time/s	40	10	2

Sample volume 5 μ l

Mass spectrometer interface and Plasma conditions

Same as those shown in Table 3 unless stated otherwise.

OmniRange 5.0

Dwell time* 20 ms

R.F. power 0.75 kW

*The dwell time is the time spent by the detector for measuring a given mass.

with a tungsten strip of dimension 0.2 x 7 x 22 mm and stainless steel contact electrodes. A small cavity of approximately 2 mm diameter was made at the centre of the tungsten strip in order to contain the test solutions. A Perkin-Elmer HGA 76B power supply was used with the graphite strip ETV, and a power supply with a variable voltage output (Variac) was used with the tungsten strip ETV. The ICP-MS used with the graphite and tungsten strip ETV was the same as that described in the previous section. The temperature measurement of both graphite and tungsten strip ETV was performed as described in the previous section. Table 11 shows the experimental and operating conditions used with the graphite strip and the tungsten strip ETV-ICP-MS.

The imaging system. The digital imaging system used for acquiring spatially and temporally resolved spectra of the graphite furnace interior was described and characterized by Hutton²³. Therefore, only a general description of the imaging system will be given. The main component of the imaging system was the charge-coupled device (CCD) camera which was a Photometrics Series 200 CCD Camera System (Photometrics Ltd., Tucson, Arizona). This camera consisted of a CH250/A passive air-cooled camera that housed a Thompson Th7883 CCD chip. Imaging in the UV region was made possible by applying a coating, Metachrome™ II, on the working surface of the CCD. Narrow-bandpass interference filters (Andover Corp., Lawrence, Massachusetts) were used to isolate the wavelengths of interest and to reduce the amount of background emission from the graphite furnace. The filter used for imaging the atomic absorption spectra had a central maximum at 395 nm which allowed the two aluminium resonance lines at 394.4 and 396.1 nm to be isolated. For imaging the

Table 11. Experimental and operating conditions of the graphite strip and the tungsten strip ETV-ICP-MS.

Temperature programme for the graphite strip ETV-ICP-MS.

	Step		
	Drying	Pyrolysis	Vaporization
Temperature/°C	120	700/1000	2300
Ramp time/s	15	15	55
Hold time/s	30	10	5

Temperature programme for the tungsten strip ETV-ICP-MS.

	Step		
	Drying	Pyrolysis	Vaporization
Temperature/°C	~ 110	900	2300
Voltage/V	1.5	4.5	10.4
Hold time/s	30	10	5

Sample volume 5 μ l

Mass spectrometer interface and Plasma conditions

Same as those shown in Tables 3 and 10 unless stated otherwise.

molecular absorption spectra, the filter had a central maximum at 254 nm which allowed the mercury resonance line at 253.7 nm to be isolated. The filters had a full width at half maximum (FWHM) of 10 nm. The hollow-cathode lamp power supply was taken from a Varian Techtron AA5 atomic absorption spectrometer (Techtron Pty. Ltd., Melbourne, Australia) and the electrodeless-discharge lamp power supply was manufactured by Perkin-Elmer. The aluminium hollow-cathode lamp and the mercury electrodeless-discharge lamp were the same as those described previously and were operated at 25 mA and 7 W, respectively. The camera was operated in the frame transfer mode. This mode of operation allows only one half of the CCD chip to be illuminated. The image formed on this half portion of the chip was then transferred rapidly to the dark half of the CCD chip. This electronic transfer allowed for a quick read-out and digitizing of the image which was necessary in order to obtain time-resolved spectra. The light from the hollow-cathode lamp or the electrodeless-discharge lamp was chopped to avoid any blurring of the image during the transfer of the image. A variable-frequency chopper (Model SR540, Stanford Research Systems Inc., Sunnyvale, California) was used for this purpose. The frequency output of the chopper was connected to the Photometrics AT200 controller so that the image was transferred when the CCD working surface was darkened by one of the chopper's blades. The Photometrics AT200 controller was a 16-bit computer interface board which controlled the operation of the camera and received the digitized information from the CCD. This computer board was installed in a Raven 386/16 AT-computer (16 MHz 80386SX main processor with 80387 math co-processor). The images were collected at a rate of 20 Hz

with a spatial resolution of $\sim 1 \times 10^{-2} \text{ mm}^2$, unless stated otherwise. A Perkin-Elmer HGA 500 graphite furnace with a Perkin-Elmer HGA 500 power supply was used for the imaging experiment. The experimental and operating conditions of the electrothermal atomizer HGA 500 were the same as those given in Table 10. The test solutions were inserted into the furnace using a Perkin-Elmer AS-40 Autosampler.

Standards and Reagents.

New, pyrolytic graphite coated graphite tubes (Perkin-Elmer, Part No. 091504) were used for all experiments employing a graphite tube furnace. Laboratory-made single cavity platforms made from anisotropic pyrolytic graphite were also used. Argon gas (99.99% pure, Matheson Gas Products) with less than 5 ppm of oxygen and water obtained from a steel cylinder and equipped with a particulate filter was used for all experiments.

A standard stock solution of $400 \mu\text{g ml}^{-1}$ of aluminium was prepared by dissolving 0.4000 g aluminium powder (SPEX) in a minimum volume of 1:1 v/v HCl:H₂O with heating and the solution was diluted to 1000.00 ml with 0.2% v/v HNO₃. Both HCl and HNO₃ were ULTREX brand (Baker Chemical Co.). Ultrapure water was obtained direct from a Milli-Q2 water purification system (Millipore Corp.). A $100 \mu\text{g ml}^{-1}$ aluminium standard solution in 0.2% v/v HNO₃ was prepared by appropriate dilution of the above aluminium standard stock solution. For the determination of the impurities in the aluminium test solutions by solution nebulization (SN) ICP-MS, standard solutions of Ca, Ge, V, and Zn in 0.2% v/v HNO₃ in the range of 0.2-50 ng ml⁻¹ were prepared by serial dilution of the 1000 $\mu\text{g ml}^{-1}$ stock solution of the appropriate analytes (SPEX). For the

experiments with vaporization of solid powders of AlCl_3 and Al_2O_3 , these standards were certified reagent grade quality with purity better than 99% (Fisher Scientific Co., Fair Lawn, New Jersey). All test solutions were prepared daily.

RESULTS AND DISCUSSION

All ICP-MS signals reported in this thesis arose from positive ions; however for simplicity, the positive superscript sign with the chemical symbols has been omitted.

Determination of impurities in the aluminium test solution.

The species of interest determined by ICP-MS can suffer from isobaric overlaps (i.e., interference), i.e. some other species of same mass-to-charge (m/z) ratio may be present in the matrix and thus be detected as if it were the species of interest. However, there were no isobaric interferences with Al, but for AlO an isobaric overlap (at $m/z = 43$) with ^{43}Ca , natural abundance (N.A.) 0.13%¹⁰⁰, was possible. As well, Al_2O ($m/z = 70$) may suffer from an isobaric overlap with ^{70}Ge , N.A. 20.52%¹⁰⁰, and ^{70}Zn , N.A. 0.62%¹⁰⁰, and AlC_2 can suffer from an isobaric overlap (at $m/z = 51$) with ^{51}V , N.A. 99.76%¹⁰⁰. All of the above overlapping species are minor isotopes of the respective elements, except for ^{51}V which is the major isotope of vanadium, N.A. 99.76%¹⁰⁰.

In order to quantify the level of isobaric interferences so that they can be corrected for, the concentration of calcium, germanium, vanadium, and zinc were determined by SN-ICP-MS. Limits of detection for calcium (isotope ^{42}Ca), germanium (isotope ^{72}Ge), vanadium (isotope ^{51}V), and zinc (isotope ^{66}Zn) were 6.0, 0.10, 0.05, and 0.12 ng ml⁻¹, respectively. Germanium and vanadium were found to be below their

limits of detection in the aluminium test solution. Calcium and zinc were found to be present in the aluminium test solution at concentrations of 12 and 2 ng ml⁻¹, respectively. Therefore, the concentration of calcium and zinc in the sample was 6 and 1 µg g⁻¹, respectively.

The isobaric interference by ⁴³Ca and ⁷⁰Ge at m/z 43 and 70, respectively, were corrected using the software provided with the ICP-MS. The correction for a particular isobaric interference was made as follows. In addition to all other signals measured, the ICP-MS also measured the signal of the interfering element at a m/z free of interference. For calcium and zinc, the isotope of m/z 42, N.A. 0.64%, and m/z 67, N.A. 4.11%, were selected. The measured signal is then converted to a signal equivalent to the analyte m/z using known natural abundance ratio. This converted signal was then subtracted from the signal measured at the m/z where the interference occurred. Hence, a net signal free of isobaric interferences for both calcium and zinc were obtained.

ETV-ICP-MS signals for vaporization from the graphite or the tungsten strip.

The experimental and operating conditions of the graphite or the tungsten strip ETV-ICP-MS are shown in Table 11. For both the graphite and the tungsten strip ETV-ICP-MS, 5 µl of a 400 µg ml⁻¹ aluminium solution was deposited onto the surface of the strip with an Eppendorf pipette; this amounted to 2 µg of aluminium.

Although ICPs are designed to achieve nearly 100% atomization efficiency (i.e. no Al-molecules left unatomized), it was possible to have Al-molecules in the plasma by vaporizing large amounts of aluminium salts (µg quantities), by cooling the plasma sufficiently by lowering the R.F. power and by increasing the total Ar carrier gas flow

rate. Huang *et al.*¹¹³ reported that lowering the R.F. power from 1 kW to 0.75 kW caused the gas kinetic temperature of a dry plasma to decrease from 4500 K to 4000 K. Also, the plasma was reduced in size, i.e. in height and in radius. Increasing the flow rate of the carrier gas is equivalent to reducing the mean residence time of the species in the plasma. Because of spending less time in the plasma, a fraction of the molecules of interest may survive through the plasma without being atomized. In addition, when large amounts of aluminium salts are vaporized large amounts of Al and Al-containing species are transported to the ICP. It is reasonable to expect that a measurable fraction of these aluminium species which are entering a cooler and smaller plasma for a shorter time, will be ionized and transported through the mass spectrometer. The number of collisions that species undergo with Ar^+ in the ICP ($> 10^6$ collisions), the gas kinetic temperature and the electron number density in the ICP are still high enough to allow ionization of the species^{93,113}. The following experiments were carried out with a R.F. power of 0.75 kW and a flow rate of carrier gas (Ar) of 1.1 l min⁻¹.

Figure 47 shows the ICP-MS signals of Al and Al-containing species vaporized from the graphite strip ETV. The characteristic aluminium spikes were accompanied by the spectra of AlO , Al_2O , and AlC_2 . All of these Al-containing species have been observed previously in the spectra obtained by mass spectrometry with vaporization under vacuum¹² or under nitrogen atmosphere¹³ and were predicted by thermodynamic calculations^{6,7}. However, these atoms and molecules from samples vaporized in an Ar atmosphere at nearly atmospheric pressure have not been reported in the literature. The vaporization of aluminium species from the graphite strip represents closely a supply

Figure 47. Temporal behaviour in the graphite strip ETV-ICP-M/S of Al (broken line), AlO (◇), Al₂O (Δ), and AlC₂ (□).

function where most of the aluminium species are transported to the ICP, with some loss due to condensation on the transport surfaces. Secondary reactions with the graphite surface such as second-wall reactions have low probability of occurring since the aluminium vapour is immediately swept away from the graphite strip to the ICP transfer line by a high flow of Ar carrier gas flowing tangentially to the graphite strip. Although vaporization from a graphite strip may not exactly represent chemical and physical processes occurring in a graphite tube furnace, it provided a device for generating species that are likely to appear in a conventional tube-type graphite furnace. Figure 47 shows clearly that aluminium suboxides (AlO and Al_2O) have features similar to the Al spikes. The AlO spikes are coincident in time with the Al spikes, and the AlO peak intensity from peak-to-peak matches approximately those of the Al spikes. The Al signal is the sum of Al atoms, or clusters of atoms, formed in the ETV and Al atoms generated from further dissociation in the ICP of Al-containing molecules. The AlO signal is most likely the sum of the AlO formed in the graphite strip ETV and the AlO that originated from the dissociation of higher aluminium oxides in the ICP. The signal of the Al_2O is much weaker than that of AlO presumably because much less Al_2O can survive the ICP. A signal of AlC_2 was measured, and unlike the aluminium suboxides, AlC_2 showed no spikes and produced a peak maximum several seconds after the aluminium atoms appeared from the ETV. Again, this signal was most likely the sum of AlC_2 formed in the ETV and of AlC_2 formed by dissociation of higher carbides in the ICP. A signal of AlC was measured at m/z 39 and it appeared as a smooth increasing signal with a peak maximum at 110 s. Because of a high background signal due to ^{39}K impurity and overlap

from a strong Ar^+ ($m/z = 40$) signal, this signal was judged to be spurious, and only the signal for AlC_2 was measured hereafter. A quantitative determination of these signals was not possible since no reference standard materials were available for these species, but they were qualitatively interpreted. The most significant fact about the result illustrated in Fig. 47 is that aluminium suboxides behave similarly to aluminium spikes, whereas aluminium carbides do not, which means that correlation between the formation of aluminium spikes and the presence of aluminium suboxides is more probable than with the presence of aluminium carbides.

The measured ICP-MS signals of AlO , Al_2O , and AlC_2 could also be the result of ion-neutral recombination at the mass spectrometer interface (see Fig. 2) or in the plasma of the ICP torch. As well, these processes may take place during the supersonic jet expansion of the plume in the mass spectrometer⁹³. Hence, it was necessary to demonstrate that the signal measured for the Al-containing molecules was due to processes occurring in the ETV and not in the ICP-MS.

To study the formation of aluminium carbides, two ETVs were required: one graphite strip and one tungsten strip ETV. The Ar carrier gas line of each ETV were joined together by a Y-junction at the back of the ICP torch. A sample of 2 μg of aluminium was vaporized from the tungsten strip ETV with the graphite strip ETV being simultaneously heated. Then, a sample of 2 μg of aluminium was vaporized from the graphite strip ETV to compare with the vaporization from the tungsten strip ETV. This approach was adopted because aluminium carbides cannot be formed in a tungsten strip ETV; hence, any aluminium carbides found must be formed by reactions between the

aluminium sample vaporized from the tungsten strip ETV and carbon vaporized from the graphite strip ETV. Figures 48a and 48b show the results obtained for the vaporization of aluminium from the tungsten strip ETV, and the graphite strip ETV, respectively. The signals of Fig. 48b have been off-set for better presentation, and therefore, overlap between signals of Figs. 48a and 48b have no meaning. By comparing the Al signal (dotted line) from both ETVs, it can be seen that the vaporization efficiency from the tungsten strip ETV was lower than the graphite strip ETV. However, by normalizing the Al signal obtained from the tungsten strip ETV to the Al signal from graphite strip, Fig. 48 shows that AlC_2 (solid line) from the graphite strip ETV is at least 6 times greater than AlC_2 from the tungsten strip, i.e. $\sim 15\%$ of the AlC_2 measured from the graphite strip ETV can be accounted for as being formed by recombination and the remainder, $\sim 85\%$, was formed in the graphite strip ETV. Therefore, one can be confident that the measured signal at m/z 51 is in general due to AlC_2 formed in the graphite strip ETV when aluminium is vaporized under the experimental conditions described previously.

An approach similar to the one described above cannot be used for determining the origin of aluminium suboxides. In the above experiment, it was possible to separate physically the source of carbon from aluminium, but separating oxygen from aluminium when aqueous solutions of aluminium are used is obviously impossible. Attempts to measure signals from an aluminium stock solution dissolved in ^{18}O -labelled water ($m/z = 43$, $^{27}\text{Al}^{16}\text{O}$, and $m/z = 45$, $^{27}\text{Al}^{18}\text{O}$) repeatedly failed presumably because of the buffering effect on ^{18}O from the large ingress of oxygen from the ambient air into the

Figure 48. Temporal behaviour of Al in ICP-MS (dotted line), C (dash-dotted line), and $m/z = 51$ (solid line). (a) Combined graphite strip ETV and tungsten strip ETV. (b) Graphite strip ETV.

plasma. However, vaporization of anhydrous aluminium chloride powder from the graphite ETV should not yield a signal for AlO unless it is formed by recombination reactions in ICP-MS. On the other hand, vaporization of anhydrous aluminium oxide powder should produce a signal for AlO since $\text{Al}_2\text{O}_3(\text{s})$ can undergo thermal dissociation to yield aluminium suboxides according to Eqn. 13. Figures 49a and 49b shows the Al (broken line) and AlO (solid line) signals obtained from the vaporization of $\sim 30 \mu\text{g}$ of Al_2O_3 and AlCl_3 , respectively. No pyrolysis step was used and the measurement of the signals were carried out immediately after the drying step. The signals were relatively small for such sample mass because of the poor physical contact between the powders and the graphite surface which caused only a fraction of the sample to be vaporized. It can be seen that the AlO signal from the Al_2O_3 sample increased smoothly as the Al signal appeared, whereas the AlO signal from the AlCl_3 remained at the background level even when the large Al signal appeared. These observations suggest that AlO observed previously when aluminium test solution was vaporized from the graphite strip ETV (Fig. 47) was due to aluminium suboxides formed in the graphite strip ETV and not by recombination. In fact, recombination processes involving oxygen are more likely to occur when a "wet" plasma is used, as is the case of solution nebulization (SN) ICP-MS. Vaughan and Horlic⁸⁹ have tabulated the most probable oxide, hydroxide, doubly charged analyte species that can occur in SN-ICP-MS. Formation of AlO was not reported by these authors, suggesting that Al is not a strong oxide-forming element in SN-ICP-MS. However, they reported that at concentrations $> 1000 \mu\text{g ml}^{-1}$, almost any element formed oxide species in ICP-MS. The experimental conditions used in this work, i.e.

Figure 49. Temporal behaviour of Al (broken line); AlO (solid line) in the graphite strip ETV-ICP-MS. (a) Al_2O_3 powder. (b) AlCl_3 powder.

dry plasma and concentrations of $400 \mu\text{g ml}^{-1}$, should not allow any appreciable formation of oxides.

The general conclusion that can be drawn from the previous observations and arguments is that the measured AlC_2 and AlO signals hereafter are attributable to their formation in the furnace and not to other processes occurring in the ICP-MS.

Simultaneous measurement of atomic or molecular absorption and ICP-MS signals.

The modified graphite furnace described in Chapter 3 was used to vaporize aluminium (taken as the nitrate) at a slow heating rate and at nearly atmospheric pressure. The ICP-MS signal together with the atomic absorption spectrometric (AAS) or the molecular absorption spectrometric (MAS) signal were measured during the atomization step. When a deuterium lamp was used for background correction, the absorption signal at 396.1 and 253.7 nm of an aluminium sample repeatedly yielded a flat baseline. The simultaneous measurement of the AAS-ICP-MS and MAS-ICP-MS signals are shown in Figs. 50 and 51, respectively. Figure 50a shows the ICP-MS signals for Al , AlO , Al_2O , and AlC_2 , and Fig. 50b shows the Al atomic absorption signal (measured at 396.1 nm) obtained simultaneously with the ICP-MS signals. The sample was vaporized from the tube surface using the temperature programme given in Table 10. The internal Ar gas flow was set at 50 ml min^{-1} for both the AAS and the ICP-MS measurements. This flow rate was a compromise between the optimum AAS and the optimum ICP-MS operating conditions; an increase in the flow causes a decrease in the AAS signal, because of a decrease in the residence time within the graphite furnace, but yields an increased ICP-MS signal because of better nucleation.

Figure 50. Simultaneous measurement of AAS and ICP-MS signals. (a) Temporal behaviour in ETV-ICP-MS of Al (broken line), AlO (Δ), Al_2O ($\diamond$), and AlC_2 ($\square$). (b) Temporal behaviour in ETAAS of Al (solid line) together with the temperature profile of the electrothermal atomizer surface (broken line).

Figure 50a shows Al spikes in ICP-MS that are coincident with the Al spikes in AAS (Fig. 50b). In addition, Fig. 50a shows that AlO and Al₂O signals appeared together as spikes with the ICP-MS Al spikes. On the other hand, the ICP-MS signal for AlC₂ showed a behaviour that was different from that of the Al spikes and Al-suboxides. After the main AlC₂ peak centred at 28 s, the AlC₂ signal did not return to the baseline like the signals of the other Al species, but increased smoothly up to 39 s and then returned smoothly to the baseline at 50 s. This behaviour of the AlC₂ signal was not observed when the aluminium was vaporized from the graphite strip ETV.

Figure 51a shows again the Al and the AlO spikes in ICP-MS occurring simultaneously with the Al₂O MAS spikes (measured at 253.7 nm) in Fig. 51b. The absence of mercury in the sample was verified by ICP-MS and by the deuterium background corrector. The molecular absorption band at 255 nm was assigned in the past to the absorption of Al₂C₂^{20,21}. However, this assignment was not confirmed by another independent source. Over the last 10 years, several research groups reported that the molecular absorption measured at 255 nm might have been wrongly assigned to Al₂C₂ by L'vov and Savin^{20,21}, and that the absorption was probably due to Al₂O^{7,12,111,17,23}. Because the ICP-MS signal for AlO and Al₂O behaved similarly as the ICP-MS signal for Al spikes, and because the AlC₂ signal showed a different behaviour with respect to the Al spikes, the molecular absorption signal measured at 253.7 nm is assigned to the absorption of Al₂O in this thesis. The ICP-MS signal for AlC₂ showed the same features as observed in Fig. 50a, i.e. a smoothly increased signal which peaked at 36 s before returning smoothly to the baseline. Again, spikes were observed on top of the AlC₂ main

Figure 51. Simultaneous measurement of MAS and ICP-MS signals. (a) Temporal behaviour in ETV-ICP-MS of Al (broken line), AlO (Δ), Al_2O ($\diamond$), and AlC_2 ($\square$). (b) Temporal behaviour in ETMAS of Al (solid line) together with the temperature profile of the electrothermal atomizer surface (broken line).

signal. Bendicho and De Loos-Vollebregt¹¹⁴ investigated the formation of spikes for several elements induced by the presence of Al. They¹¹⁴ observed vanadium spikes when aluminium was added to the vanadium sample. Although no vanadium was measured in the aluminium test solution by SN-ICP-MS, it was necessary to verify that the spikes observed on top of the main AlC_2 signal were not due to vanadium that might have been inadvertently introduced in the graphite furnace along with the aluminium sample. Figure 52 shows the simultaneously measured ICP-MS (Fig. 52a) and vanadium AAS (Fig. 52b) signals when 2 μg of aluminium (as the nitrate) was vaporized under the same conditions as used previously. Although Fig. 52a shows a signal (solid line) similar to what was observed previously in Figs. 50b and 51b at m/z 51, no vanadium signal was measured in AAS. Therefore, the spikes observed at m/z 51 were not due to vanadium; even if vanadium was present in the sample, it was below its limit of detection.

The occurrence of spikes on top of the AlC_2 signal could be due to the rapid expansion of CO gas generated during the formation of the Al spike. It can be seen from Fig. 53 that rapid formation of CO gas accompanies the Al spikes, and may cause rapid expansion of Al and Al-containing species, i.e., their formation as spikes. At the termination of the spike, the AlC_2 signal continued to increase (or decrease) with the same behaviour as before the spikes.

Figure 53 shows the ICP-MS signal of Al together with the signal measured at m/z 28. The signal at m/z 28 was blank corrected and the absence of ^{28}Si was verified. Among possible species that may occur at m/z 28 are $^{14}\text{N}^{14}\text{N}$, $^{27}\text{Al}^1\text{H}$, and $^{12}\text{C}^{16}\text{O}$. Diatomic nitrogen measured by ETV-ICP-MS is likely to be the same from the blank and

Figure 52. Simultaneous measurement of AAS and ICP-MS signals. (a) Temporal behaviour in ETV-ICP-MS of Al (broken line) and AlC₂ (solid line). (b) Temporal behaviour in ETAAS of V (solid line) together with the temperature profile of the electrothermal atomizer surface (broken line).

Figure 53. Temporal behaviour in ETV-ICP-MS of Al (broken line) and m/z 28 (solid line).

from the aluminium test solution, as it was in SN-ICP-MS. Ohlsson *et al.*¹¹⁵ reported the appearance of an AlH spike together with an Al spike. They proposed that the AlH was formed in the gas-phase and that only 1% of the gaseous aluminium at 2000-2300 K would be in the monohydride form. The bond dissociation energy of AlH and CO is 68 kcal mole⁻¹ (at 25°C) and 256.7 kcal mole⁻¹ (at 25°C), respectively. The bond dissociation energy of AlH being approximately 4 times smaller than the bond dissociation energy of CO, it is more likely that CO will survive the plasma compared to AlH. Hence, the signal measured at m/z 28 was most probably due to CO formed in the in graphite furnace ETV when the aluminium solution was vaporized. Figure 53 shows clearly that CO signal appeared as spikes together with Al spikes, and the CO signal returned to the baseline at the completion of the spike. Equation 15 shows that CO was probably a reaction product when aluminium suboxides were reduced by graphite.

All of the above observations, i.e Al, Al₂O, CO spikes in AAS, MAS, and ICP-MS, and the presence of AlC₂ made in the sample vaporization from the graphite tube wall surface were also made in an identical manner when the sample vaporization was done from a graphite platform surface.

The important results to note from Figs. 50 to 53 are the following: (1) Al spikes in ICP-MS coincided with the appearance time of Al spikes in AAS; (2) Al spikes in ICP-MS coincided with the Al₂O spikes measured in MAS; (3) Al suboxides spikes appeared concurrently with the Al and Al₂O spikes in absorption spectrometry; (4) the CO spikes appeared with the Al spikes. Another important observation is the relative

size of the spikes, both in AAS and MAS, each spike relative to the other spikes. The first spike, for both AAS and MAS, was always greater in peak area than any of the other subsequent spikes and the lowest temperature that the first spike was observed was at $\sim 1840^{\circ}\text{C}$ (not shown).

CCD imaging.

In addition to the increased sensitivity, the net advantage of the CCD camera over the SSF system used by Gilmutdinov *et al.*^{16,17} was the ability to get absorbance values without additional separate measurements. Hutton²³ has previously described the procedure for acquiring absorbance values, and only general guidelines will be given in this thesis. The absorbance values were obtained by processing four images which were: the **Signal**, the **Background Emission**, the **Reference**, and the **Dark Current**. These images are those of the interior of the graphite furnace obtained under the following conditions:

- The **Signal** was obtained when the furnace was being operated with a sample and the radiation source was on.
- The **Background Emission** was obtained when the furnace was being operated and the radiation source was off.
- The **Reference** was obtained when the furnace was not being operated and the radiation source was on.
- The **Dark Current** was obtained when both the furnace and the radiation source were not operated.

The absorbance A is calculated as follows:

$$A = -\log \left(\frac{\text{Signal} - \text{Background Emission}}{\text{Reference} - \text{Dark Current}} \right) \quad (16)$$

The CCD imaging system has been calibrated with neutral density filters at two different temperatures, 20°C and 2250°C. Both calibration curves are linear with slope 1.00 and intercept 0.00.

The experimental and operating conditions for the imaging experiments are given in Table 10. An aqueous solution of Al (taken as the nitrate) containing 2 μg of Al was injected with an autosampler for all imaging experiments. All the following images are grey-scale representations of the atom densities with the darkest region representing the regions of highest concentration of atoms and the lightest regions representing the lowest concentration of atoms. The images were recorded at a rate of 20 Hz unless stated otherwise.

Vaporization from the tube surface. Figure 54 shows the atomic absorption images obtained for an aluminium spike with no internal Ar gas flow. The number within brackets stands for the frame number in the sequence of images. Figure 55 shows the absorbance contour plot for some selected frames of Fig. 54. The temperature at the onset of the spike was 2060°C. At the onset of the spike formation, Fig. 54, Frame 59, shows that Al atoms are rapidly filling the cross section of the furnace interior. Then, Frames 62, 64, and 66 of Fig. 54 show clearly that the aluminium atoms are more concentrated near the tube surface than at the tube centre. Figure 55 shows a strong non-uniformity in the distribution of Al atoms within the tube. Also, Fig. 55, Frame 62 shows that at the onset of the Al spike formation, the aluminium atoms were formed at

Figure 54. Sequence of atomic absorption images for the atomization of aluminium from the tube surface under Ar gas stop- flow conditions.

(62)

(66)

198

(72)

Figure 55. Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the tube surface under Ar gas stop-flow conditions.

the bottom of the tube where the sample was deposited. The Al concentration near the wall almost doubled the Al concentration at the centre of the tube (Frame 66, Fig. 55). A very interesting feature occurred at the end of the Al spike which resembled a "doughnut" in shape. This feature was reported previously by Gilmutdinov *et al.*^{16,17} but for molecular absorbance measurements. The doughnut structure seemed to be directly related to the presence of dosing hole which was located approximately at the upper left-hand corner of each image.

Figure 56 shows the molecular absorption images of an Al-suboxide spike obtained under the same conditions as for the atomic absorption images. Figure 57 shows the corresponding absorbance contour plot for some selected frames. The temperature at the onset of the spike was 2090°C. Similar to what had been observed in atomic absorption (Fig. 54), there was a rapid filling of space of the furnace interior by Al_2O . The greatest concentration of Al-containing molecules was always at the centre of the tube, away from the graphite surface. This observation contradicts the ROC model of L'vov and Savin²². The ROC model proposes that the Al-containing species, i.e. the Al carbide, which are precursors of Al atoms, and which are measured at 255 nm, are formed near the graphite surface. Figure 56 shows clearly that the absorbing species are concentrated at the centre of the tube, away from the graphite surface. Therefore, it can be stated unambiguously that the molecular absorption was not due to Al-carbides but rather to Al_2O . The absorption contour plot shows that there were two separate events that were taking place during the formation and dissipation of the Al_2O spikes. First, the Al_2O were formed and concentrated at the centre of the tube

Figure 56. Sequence of molecular absorption images for the vaporization of Al_2O_3 from the tube surface under Ar gas stop-flow conditions.

(90)

(92)

201

(93)

(95)

Figure 57. Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O from the tube surface under Ar gas stop-flow conditions.

(Frame 90, Fig. 57). Then, the doughnut structure was formed, and dissipated through the dosing hole or at the cooler ends of the graphite tube. Gilmutdinov *et al.*¹⁷ hypothesized that the doughnut structure was due to formation of condensed-phase fine particles of Al_2O_3 dispersed in the gas phase. This hypothesis seemed reasonable since the doughnut structure was observed at two different wavelengths, suggesting that it was due to non-specific absorption of light (light scattering) by solid particles. Unfortunately, the deuterium lamp used for background correction was not bright enough to allow observation of the doughnut structure. A Xe discharge lamp would have been sufficiently bright to allow this observation but was not available. L'vov¹⁶ has recently proposed another explanation for the formation of the doughnut structure based on the condensation of the vapour-phase species, and suggested that the spatial distribution of the doughnut structure is due to the formation of condensed-phase particles not at the tube centre, but rather at the cooler ends of the tube. L'vov has also suggested that either Al or Al_2O_3 were the species that are condensing. However, the fact that the doughnut structure appeared near the dosing hole might suggest a direct relationship between the dosing hole and the formation of condensed-phase Al_2O_3 particles. Hutton²³ reported that the ingress of oxygen through the dosing hole might be quite large, and could lead to reaction with Al_2O to form, as proposed by Gilmutdinov and co-workers¹⁷ finely dispersed Al_2O_3 particles in the gas phase. Since the temperature of the tube ends is much lower than that of the tube centre, the explanation given by L'vov¹⁶ for the formation of the doughnut structure seems reasonable. It is not clear whether the doughnut is due to formation of finely dispersed Al_2O_3 particles in the gas phase¹⁷ or due

to the condensation of matrix vapour in the gas phase¹¹⁶.

The most important point related to the above observation is the complementary features presented by both atomic and molecular absorbance contour plots. The region where Al atoms were at the greatest concentrations corresponded to the region where Al_2O molecules were at the lowest concentrations, and the region where the Al atoms were at the lowest concentrations corresponded to the region where Al_2O were at highest concentrations.

The above experiments were repeated with an internal purge gas (Ar) of 50 ml min^{-1} . The rationale for this experiment was to isolate the supply function of both Al atoms and Al-containing molecules. As well, the internal convective flow of Ar should minimize the effect of the dosing hole by inhibiting the ingress of oxygen through the dosing hole.

Figures 58 and 59 shows the atomic absorption images obtained with an internal Ar flow of 50 ml min^{-1} and the corresponding absorbance contour plots of some selected frames. The temperature at the onset of the spike formation was 2020°C . Again, there was a rapid filling of space of the furnace interior by Al atoms (Frame 12, Fig. 58), the greatest concentration of Al atoms was near the graphite surface (Frame 21, Fig. 59), but no doughnut was formed under a convective flow of Ar gas. Also, the duration of the spike was much shorter under the Ar purge gas flow conditions. It is interesting to note that under a convective flow of Ar gas, Al atoms seemed to fill the space of the interior of the furnace and to dissipate more rapidly than without the convective flow. The rapid dissipation of the spike was due to faster removal of Al atoms through the

Figure 58. Sequence of atomic absorption images for the atomization of aluminium from the tube surface under a convective flow of Ar purge gas.

(12)

(21)

205

Figure 59. Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the tube surface under a convective flow of Ar purge gas.

dosing hole by the internal purge gas (Ar). However, the reason for a more rapid generation of Al atoms under a convective flow of Ar gas is not obvious and will be discussed at the conclusion of the molecular absorption experiments under a convective flow of Ar purge gas described below.

The molecular absorption images obtained with an internal Ar flow of 50 ml min^{-1} and the corresponding absorbance contour plots of some selected frames are presented in Figs. 60 and 61, respectively. The temperature at the onset of the spike formation was 2060°C . Figure 60, Frame 30, shows that Al_2O was formed initially near the region where the sample was originally deposited, i.e. at the bottom of the tube. The Al_2O molecules rapidly filled the space of the interior of the atomizer and finally redistributed themselves at the centre of the tube (Frame 34, Fig. 61). The duration of the Al_2O spike with the convective flow of Ar purge gas was about half the duration when there was no convective flow of Ar purge gas. Here again, no doughnut was formed under the convective flow of Ar gas. Gilmudinov *et al.*¹⁷ reported that closing the dosing hole with a graphite plug completely eliminated the doughnut structure and only the initial atomization of the sample was observed. All the above observations and reasonings suggest that the doughnut structure was probably the result of two reactions occurring simultaneously: one reaction between the Al_2O and the ingressing oxygen (or perhaps nitrogen to form AlCN) to form condensed-phase Al_2O_3 particles¹⁷, and the other reaction is the condensation of the vapour-phase species at the cooler ends of the tube¹¹⁶. Beside the formation of condensed-phase Al_2O_3 dispersed in the gas phase, it was also possible that AlCN was formed. Sturgeon and Chakrabarti⁸ reported that the AAS signal of Al

Figure 60. Sequence of molecular absorption images for the vaporization of Al_2O_3 from the tube surface under a convective flow of Ar purge gas.

(30)

(34)

208

Figure 61. Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O_3 from the tube surface under a convective flow of Ar purge gas.

atomized in a nitrogen atmosphere was almost 3 times smaller than Al atomized in an Ar atmosphere and attributed this to the formation of AlCN in the nitrogen atmosphere. More recently, Iwamoto and co-workers¹¹² measured the CN absorption in a Massmann-type atomizer and calculated p_{CN} in the Ar atmosphere for various matrices from these measurements. They showed that p_{CN} was greater at the top than at the bottom of the furnace, and concluded that p_{AlCN} equalled to $\sim 5 \times 10^{-4}$ Pa (which was small). A clear understanding of the composition of the doughnut structure is still eluding us.

It seemed from Fig. 60 that the generation of Al_2O was more rapid with the convective flow of Ar gas than without it. Probably, in the absence of the convective flow, the formation of Al_2O by thermal dissociation of Al_2O_3 , as described by Eqn. 13, is governed by the vapour pressure of Al_2O immediately above the surface of Al_2O_3 . The limiting step in the formation of more Al_2O is the removal of Al_2O above the condensed-phase Al_2O_3 , and that, in the absence of the convective flow, the removal of Al_2O_3 was likely to be diffusion-controlled. However, the convective flow would allow Al_2O to be removed more rapidly from the Al_2O_3 surface, which would in turn allow formation of more Al_2O ; hence, the observed rapid filling of the space of the furnace interior. The convective flow also allowed a more rapid transport of Al_2O to the surrounding graphite surface compared to transport by diffusion only. Hence, by Eqn. 15, Al atoms were formed at a much higher rate than without the convective flow, which would explain the observation made previously about the rapid filling of space by Al atoms under the convective flow.

Vaporization from a graphite platform surface. The graphite platforms used were the

type that only touched the graphite tube surface at four corners. Figures 62 and 63 show the atomic absorption images under stop-flow condition, and the corresponding absorbance contour plots of some selected frames, respectively. At the onset of the spike formation, the temperature was 2050°C. Figure 62 shows some unique features which have not been reported yet for spike formation. First, Al atoms appeared simultaneously from the platform and from the bottom left-hand side of the tube, below the dosing hole. Secondly, a plume-like feature (Frames 39, 41, 45, 50, Fig. 62) pointing towards the dosing hole appeared and remained for almost 0.8 s until the end of the spike. The Al atoms formed at the platform were a much smaller part of the total Al atoms than those formed at the tube surface. Al atoms were formed at the platform where the sample was injected may suggest that Al atoms were formed by thermal dissociation of the aluminium oxides according to Eqn. 13. However, this should not occur only when a spike was formed, but should occur rather continuously as a smooth reaction under slow heating rates at temperature 1800-2000°C. In fact, a small Al absorbance (< 0.1) was measured prior to the appearance of the spike - this small absorbance was probably due to thermal dissociation of Al_2O_3 . The appearance of Al atoms at the tube surface can only be explained by the fact that aluminium-containing molecules migrated to the tube surface by diffusion in the gas-phase. These Al-containing molecules did not yield any atomic absorption signal. Based on previous observations and reasoning, these Al-containing molecules would be Al_2O . On contact with the hot graphite surface, Al_2O would be reduced by graphite to Al atoms. Hence, it can be stated that the major precursor of Al atoms is Al_2O . Figure 63, Frame 63 shows that absorbance is highest near the left-hand

Figure 62. Sequence of atomic absorption images for the atomization of aluminium from the platform surface under stop-flow conditions.

(33)

(37)

212

(41)

(50)

Figure 63. Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the platform surface under stop-flow conditions.

edge of the platform. The fact that the spike always appears from the side of the dosing hole still remains a mystery since it is reasonable to expect that Al_2O_3 would be reduced at the most reducing zone, i.e. under the heated graphite platform, near the right-hand edge of the platform where the most reducing conditions exist at the instant of spike formation. However, the above expectation is fulfilled later in time (i.e. after the occurrence of spikes) when the highest absorbance values are located in the most reducing zone which is now sandwiched between the heated platform and the heated tube wall, as can be seen from Frame 37, 41, and 50 of Fig. 63, where the highest absorbance values were found under the platform. Aluminium atoms persisted for quite a long time under the platform even though little absorbance could be found above the platform. Also, similar to the case of atomic absorption imaging, the absorbance was always higher near the graphite surface than at the centre of the tube.

The appearance of the strange plume-like feature of relatively high brightness with respect to the surrounding region is somewhat puzzling. This feature was never observed nor reported before. The absorbance contour map of Fig. 63 shows that at the centre of the plume, absorbance is the lowest, even reaching an absorbance value of 0.0 near the end of the spike (Frame 50, Fig. 63). The experiment was repeated with the mercury lamp turned off in order to measure the emitted radiation from any vaporized species which could account for the brightness of the plume. No measurable emission was recorded. The fact that this feature was observed with the atomization from the platform surface, but not with the atomization from the tube surface suggested that the platform played a special role in the formation of the plume. The platform acted as a physical

barrier that divided the furnace in two unequal parts, where each part possessed different chemical properties. The area under the platform was the most reducing region, whereas the region above the platform near the dosing hole was more oxidizing. In addition, the platform physically brought the source of aluminium atoms closer to the dosing hole compared to a sample deposited at the bottom of the tube furnace. The appearance of the plume close to an oxidizing region when the Al source is located closer to the oxygen-ingressing dosing hole in atomization from the platform may be due to a greater formation of finely dispersed Al_2O_3 particles in the gas phase.

The molecular absorption images under the stop-flow condition and the corresponding absorbance contour plots are shown in Figs. 64 and 65, respectively. The temperature at the onset of the spike formation was 2110°C . The results obtained were similar to those already mentioned with vaporization from the tube surface. However, it is important to note that molecular absorption did not exceed the length of the platform. This is a clear indication of strong heterogeneous interaction between Al_2O and the graphite tube surface. Little molecular absorbance was measurable under the platform because Al_2O was rapidly reduced by heated graphite under these strong reducing conditions. Again, the observations made from the atomic absorption imaging (Fig. 62-63) and the molecular absorption imaging (Fig. 64-65) are complementary.

The above experiments were repeated under gas-flow conditions and the results are shown in Fig. 66 to 69. Figure 66 shows the atomic absorption images under the gas flow of 50 ml min^{-1} and Figure 67 shows the corresponding absorbance contour plots of some selected frames. The temperature at the onset of the spike formation was 2000°C .

Figure 64. Sequence of molecular absorption images for the vaporization of Al_2O_3 from the tube surface under the gas stop-flow conditions.

(53)

(55)

216

(58)

(60)

Figure 65. Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O from the tube surface under the gas stop-flow conditions.

Figure 66. Sequence of atomic absorption images for the atomization of aluminium from the platform surface under the convective flow of Ar purge gas.

Figure 67. Absorbance contour plots of some selected atomic absorption images for the atomization of aluminium from the platform surface under the convective flow of Ar gas.

Under the gas-flow condition, no plume such as the one described in Fig. 62 was observed, and only the initial atomization and subsequent dissipation were observed. The distribution of Al atoms was much more non-uniform compared to the tube surface vaporization under the gas-flow condition (see Figs. 58 and 59). This seemed to be due to the relatively long residence time of Al atoms under the platform and to the platform itself, which together perturbed the distribution of Al atoms. Finally, the rate at which the space of the interior of the furnace was filled with Al atoms under the gas-flow condition was greater than for the gas-stop condition for the same reason as explained previously.

The molecular absorption images under the gas flow condition and their corresponding absorbance contour plots are shown in Figs. 68 and 69, respectively. The temperature at the onset of the spike formation was 2140°C. The results shown in Figs. 68 and 69 are in line with what has been discussed previously and are complementary to those described in Figs. 66 and 68.

Based on the results obtained so far, it was thought that after the first spike, the Al_2O molecules would redistribute themselves throughout the furnace and that the subsequent Al and the Al_2O spikes would be initiated from anywhere at the tube surface. To verify this possibility, the images of the furnace interior were collected at a slower rate such that the images of more than one spike could be observed during one collection sequence. Figure 70 shows the molecular absorption images under stop-flow condition for two Al_2O spikes. The images were collected at a rate of 10 Hz. Figure 70 shows clearly that the first Al_2O spike was initiated from the platform surface (Frame 39) with

Figure 68. Sequence of molecular absorption images for the vaporization of Al_2O_3 from the tube surface under the convective flow of Ar gas.

(95)

(97)

221

(98)

(100)

Figure 69. Absorbance contour plots of some selected molecular absorption images for the vaporization of Al_2O_3 from the tube surface under the convective flow of Ar gas.

Figure 70. Sequence of molecular absorption images for the vaporization of Al_2O_3 from the tube surface under the gas stop-flow conditions.

the same characteristic as described previously. However, the second spike was again initiated from the platform (Frame 95 and 96). Therefore, a redistribution of Al_2O molecules within the tube furnace after the appearance of the first spike is ruled out. According to Fig. 60, Frame 30, and Fig. 70, Frames 39 and 96, it seemed that the initiation of Al_2O spikes was localized at the region where the sample was deposited. This finding is in conflict with the observation reported by Ohlsson *et al.*¹¹⁷, who reported that a redistribution of the Al sample within the furnace occurred after the first spike. Perhaps, Al atoms can redistribute themselves within the furnace after a spike, but the evidence presented earlier does not support a major redistribution of Al_2O molecules.

Mechanism of Al spikes formation. A mechanism for formation and dissipation of aluminium spikes based on the results presented in this work and the experimental evidence presented by other researchers is proposed below. The aluminium test solution was taken as the aluminium nitrate and this aluminium nitrate was converted into Al_2O_3 at about $750\text{--}1000^\circ\text{C}^8$. The reaction described by Eqn. 13 occurs slowly at temperatures under 2050°C^{100} (the melting point of Al_2O_3). However, reactions between Al_2O_3 and carbon in the solid phase can occur at temperatures above 1450°C . Stroup¹¹⁸, in an excellent review about carbothermic smelting of aluminium, has shown that aluminium carbides and oxycarbides play an important role in aluminium metal production. Aluminium carbide (Al_4C_3) is formed via the following concurrent reactions:

which gives the overall reaction:

The formation of the oxycarbide (Eqn. 17) proceeded rapidly¹¹⁸ and the temperature at which the overall reaction (Eqn. 19) occurred was 1810°C⁵². The reaction described by Eqn. 19 occurred between unevenly mixed reactants of high concentrations and was highly exothermic. However, the Al_4C_3 was formed only if Al_2O_3 was in intimate contact with graphite and preferably at active sites of graphite such as cracks and other defects. Hence, only a little Al_4C_3 is expected to be formed compared to the total mass of Al_2O_3 under the conditions of Al spike formation. The Al_4C_3 has a melting point of 1400°C¹⁰⁰ and it appears as a melt with some Al_2O_3 dissolved in it¹¹⁸. Because of the exothermicity of the carbide formation reaction (Eqn. 19) and the temperature at which it is formed, i.e. 1810°C, it is reasonable to expect that some Al_4C_3 is vaporized and the vapour is dissociated to form aluminium atoms:

The aluminium atoms formed by the dissociation of Al_4C_3 act as seeds to trigger a self-sustaining reaction which generates aluminium atoms at a very high rate¹¹⁹. Motzfeldt and Steinmo¹¹⁹ proposed a mechanism which explained the rapid weight loss of Al_2O_3 when it was heated in a graphite crucible under a reduced pressure of argon atmosphere. According to this mechanism, aluminium atoms react with Al_2O_3 to form $Al_2O_{(g)}$:

A certain threshold value of $p\text{Al}$ over Al_4C_3 must be attained before the reaction (21) can actually take place. Then, the $\text{Al}_2\text{O}_{(g)}$ undergoes reduction at the hot graphite surface to form aluminium atoms:

Therefore, each time 4 Al atoms enter reaction (21), 6 Al atoms are produced by reaction (22), which is a multiplication factor of 1.5. This autocatalytic mechanism is consistent with the results obtained from the simultaneous measurement of AAS, or MAS, and ICP-MS signals and the CCD imaging. Reactions (21) and (22) require that Al and Al_2O be present together, and that Al_2O is the precursor of Al atoms, and that their spatial distributions should be complementary. The Al spike is terminated by one of the two limiting factors: (1) the equilibrium partial pressure of aluminium, $p\text{Al}$, over Al_4C_3 and (2) the equilibrium $p\text{CO}$ governed by reaction (22). The $p\text{Al}$ over $\text{Al}_4\text{C}_{3(s)}$ is about 10^5 higher than over $\text{Al}_2\text{O}_{3(s)}$ and this avalanche process is stopped by the attainment of the equilibrium $p\text{Al}$ and $p\text{CO}$. Then, several back reactions can occur which will quickly terminate the Al spike: (1) the reaction between Al_2O and CO to form condensed-phase Al_2O_3 particles dispersed in the gas phase, (2) the reaction between Al_2O and O_2 to form condensed-phase Al_2O_3 particles dispersed in the gas phase, and (3) the reaction between Al and CO to form both condensed-phase Al_2O_3 and Al_4C_3 particles dispersed in the gas phase. As well, it is possible that some vapour-phase species condensed at the cooler ends of the tube. This is consistent with the observation in the CCD imaging of a plume-

like structure that extended towards the dosing hole and is attributed to either the formation of finely dispersed Al_2O_3 particles in the gas phase and/or condensation of the vapour-phase species at the cooler ends of the tube. The overall process leading to the formation of another Al spike is repeated at a higher temperature when the $p\text{Al}$ over Al_4C_3 again reaches again the threshold values. The generation of $\text{Al}_{(g)}$ atoms (reaction 20) coupled with their multiplication by reactions (21) and (22) results in the observed sudden burst of $\text{Al}_{(g)}$ atom formation (called Al-spikes).

SUMMARY

The formation and dissipation of aluminium spikes were investigated by two novel approaches, i.e. the simultaneous measurement of both AAS, or MAS, and ICP-MS signals, and the CCD imaging of the reactions in the graphite furnace interior.

The simultaneous measurements of the AAS, or MAS, and ICP-MS showed the presence of aluminium carbides and suboxides when Al spikes occurred, but only the aluminium suboxides showed correlations with the occurrence of aluminium spikes.

The CCD imaging of the graphite furnace interior showed that there was a greater density of Al atoms near the graphite tube surface than at the centre of the graphite furnace. The spatial distribution of Al-containing species is consistent with the expected distribution of Al_2O . Also, the spatial distribution of Al_2O showed a greater number density at the centre of the graphite furnace than near the graphite surface, which was complementary to the spatial distribution of $\text{Al}_{(g)}$ inside the graphite furnace.

A mechanism has been proposed to explain the formation and dissipation of Al spikes based on the formation of Al_4C_3 in the condensed phase which acts as Al seeds for

an autocatalytic reaction that involves Al_2O_3 .

REFERENCES

1. Welz, B., *Atomic Absorption Spectrometry*, 1986, 2nd ed., Ed. VCH, Weinheim, Germany, 506 p.
2. Sturgeon, R., *Fresenius Z. Anal. Chem.*, 1986, **324**, 807.
3. Styris, D.L., and Redfield, D.A., *Spectrochim. Acta Rev.*, 1993, **15**, 71.
4. Slavin, W., *At. Spectrosc.*, 1983, **4**, 69.
5. Slavin, W., *Spectrochim. Acta, Part B*, 1987, **42**, 933.
6. Frech, W., Lundberg, F., and Cedergreen, A., *Prog. Anal. At. Spectrosc.*, 1985, **8**, 257.
7. Katskov, D.A., Shtepan, A.M., Grinshtein, I.L., and Pupyshev, A.A., *Spectrochim. Acta, Part B*, 1992, **47**, 1023.
8. Sturgeon, R.E., and Chakrabarti, C.L., *Prog. Anal. At. Spectrosc.*, 1978, **1**, 5.
9. Smets, B., *Spectrochim. Acta, Part B*, 1980, **35**, 33.
10. Welz, B., in *Proceedings of the 20th Colloquium Spectroscopicum Internationale and 6th International Conference on Atomic Spectroscopy, Prague, Czechoslovakia, 1977, Symposium III*, eds. Rubeška, I., Mostecký, J., and Ksandr, Z., Sborník VŠCHT v Praze, ČSSR, pp. 126-145.
11. Chakrabarti, C. L., Wan, C. C., and Li, W. C., *Spectrochim. Acta, Part B*, 1980, **35**, 93.
12. Holcombe, J.A., Styris, D.L., and Harris, J.D., *Spectrochim. Acta, Part B*, 1991, **46**, 629.
13. Styris, D.L., and Redfield, D.A., *Anal. Chem.*, 1987, **59**, 2691.
14. Majidi, V., and Robertson, J.D., *Spectrochim. Acta, Part B*, 1991, **46**, 1723.
15. Welz, B., Schlemmer, G., and Ortner, H.M., *Prog. Anal. Spectrosc.*, 1989, **12**, 11.
16. Gilmutdinov, A.Kh., Zakharov, Yu. A., Ivanov, V.P., and Voloshin, A.V., *J. Anal. At. Spectrom.*, 1991, **6**, 505.
17. Gilmutdinov, A.Kh., Zakharov, Yu. A., Ivanov, V.P., Voloshin, A.V., and Dittrich, K., *J. Anal. At. Spectrom.*, 1992, **7**, 675.

18. Smeyers-Verbeke, J., Michotte, Y., and Massart, D.L., *Anal. Chem.*, 1978, **50**, 10.
19. Segar, D.A., and Gonzalez, J.G., *Anal. Chim. Acta*, 1972, **58**, 7.
20. L'vov, B.V., and Savin, A.S., *Zh. Anal. Khim.*, 1983, **38**, 1924.
21. L'vov, B.V., and Savin, A.S., *Zh. Anal. Khim.*, 1983, **38**, 1933.
22. L'vov, B.V., Polzik, L.K., Romanova, N.P., and Yuzefovskii, A.I., *J. Anal. At. Spectrom.*, 1990, **5**, 163.
23. Hutton, J.C., *Some Theoretical and Experimental Studies in Atomic Absorption Spectrometry*, Ph. D. Thesis, 1992, Carleton University, Ottawa.
24. Sturgeon, R.E., Berman, S.S., Desaulniers, A., and Russell, D.S., *Anal. Chem.*, 1979, **51**, 2364.
25. Slavin, W., Carnrick, G.R., and Manning, D.C., *Anal. Chem.*, 1984, **56**, 163.
26. Welz, B., Akman, S., and Schlemmer, G., *J. Anal. At. Spectrom.*, 1987, **2**, 793.
27. Churella, D.J. and Copeland, T.R., *Anal. Chem.*, 1978, **50**, 309.
28. Holcombe, J.A., Rayson, G.D., and Akerlind, N., *Spectrochim. Acta, Part B*, 1982, **37**, 319.
29. L'vov, B.V., *Spectrochim. Acta, Part B*, 1978, **33**, 153.
30. Frech, W., Persson, J.A., and Cedergren, A., *Prog. Anal. At. Spectrosc.*, 1980, **3**, 279.
31. Frech, W., Cedergren, A., *Anal. Chim. Acta*, 1976, **82**, 83.
32. Cabon, J.Y., and Le Bihan, A., *Anal. Chim. Acta*, 1987, **198**, 87.
33. Hageman, L., Mubarak, A., and Woodriff, R., *Appl. Spectrosc.*, 1979, **33**, 226.
34. Ni Zhe-Ming, Han Heng-Bin, and Li Xiao-Chun, *J. Anal. At. Spectrom.*, 1986, **1**, 131.
35. Hulanicki, A., Bulska, E., and Dittrich, K., *J. Anal. At. Spectrom.*, 1990, **5**, 209.35.
36. McArthur, J.M., *Anal. Chim. Acta*, 1977, **93**, 77.
37. Carnrick, G.R., Slavin, W., and Manning, D.C., *Anal. Chem.*, 1981, **53**, 1866.
38. Pruszkowska, E., Carnrick, G.R., and Slavin, W., *Anal. Chem.*, 1983, **55**, 182.
39. Tominaga, M., and Umezaki, T., *Anal. Chim. Acta*, 1982, **139**, 279.

40. Hydes, D.J., *Anal. Chem.*, 1980, **52**, 959.
41. Regan, J.G.T., and Warren, J., *Analyst*, 1978, **103**, 447.
42. Gilchrist, G.F.R., Chakrabarti, C.L., and Byrne, J.P., *J. Anal. At. Spectrom.*, 1989, **4**, 533.
43. Gilchrist, G.F.R., Chakrabarti, C.L., Byrne, J.P., and Lamoureux, M., *J. Anal. At. Spectrom.*, 1990, **5**, 175.
44. Pingxin, W., and Tiezheng, L., *Spectrochim. Acta, Part B*, 1986, **41**, 1225.
45. Sturgeon, R.E., and Falk, H., *J. Anal. At. Spectrom.*, 1988, **3**, 27.
46. Frech, W., and Jonsson, S., *Spectrochim. Acta, Part B*, 1982, **37**, 1021.
47. Chakrabarti, C.L., in *Analytical Chemistry in the Exploration, Mining and Processing of Materials*, IUPAC, Ed. Butler, L.R.P., Blackwell, Oxford, 1986, pp. 57-62.
48. Park, C.J., Van Loon, J.C., Arrowsmith, J., and French, J.B., *Can. J. Spectrosc.* **32**, 29 (1987).
49. Park, C.J., and Hall, G.E.M., *J. Anal. At. Spectrom.* **2**, 473 (1987).
50. Erspamer, J.P., and Niemczyk, T.M., *Anal. Chem.*, 1982, **54**, 2150.
51. Welz, B., Akman, S., and Schlemmer, G., *Analyst*, 1985, **110**, 459.
52. Kántor, T., Bezúr, L., Pungor, E., and Winefordner, J.D., *Spectrochim. Acta, Part B*, 1983, **38**, 581.
53. Kántor, T., and Bezúr, L., *J. Anal. At. Spectrom.*, 1986, **1**, 9.
54. Fassel, V.A., *Pure Appl. Chem.*, 1977, **49**, 1533.
55. Dittrich, K., Mothes, W., and Weber, P., *Spectrochim. Acta, Part B*, 1978, **33**, 325.
56. Shekiro, J. M., Jr., Skogerboe, R. K., and Taylor, H. E., *Anal. Chem.*, 1988, **60**, 2578.
57. McNally, J., and Holcombe, J. A., *Anal. Chem.*, 1991, **63**, 1918.
58. Nakahara, T., and Chakrabarti, C. L., *Anal. Chim. Acta*, 1979, **104**, 99.
59. Ediger, R.D., and Beres, S.A., *Spectrochim. Acta, Part B*, 1992, **47**, 907.
60. Quagliano, J. V., "*Chemistry*", 2nd ed., Prentice-Hall, Englewood Cliffs, 1963, pp. 578-579.

61. Nixon, D.E., Fassel, V.A., Kniseley, R.N., *Anal. Chem.*, 1974, **46**, 210.
62. Schmertmann, S.M., Long, E.S., and Browner, R.F., *J. Anal. At. Spectrom.*, 1987, **2**, 687.
63. Kumamaru, T., Okomoto, Y., and Matsuo, H., *Appl. Spectrosc.*, 1987, **41**, 918.
64. Dittrich, K., Berndt, H., Broekaert, J.A.C., Schaldach, G., and Tölg, G., *J. Anal. At. Spectrom.*, 1988, **3**, 1105.
65. Barnes, R.M., and Fodor, P., *Spectrochim. Acta, Part B*, 1983, **38**, 1191.
66. Aziz, A., Broekaert, J.A.C., and Leis, F., *Spectrochim. Acta, Part B*, 1982, **37**, 369.
67. Gunn, A.M., Millard, D.L., and Kirkbright, G.F., *Analyst*, **103**, 1066.
68. Millard, D.L., Shan, H.C., and Kirkbright, G.F., *Analyst*, 1980, **105**, 502.
69. Shibata, N., Fudagawa, N., and Kubota, M., *Anal. Chem.*, 1991, **63**, 636.
70. Hulmston, P., and Hutton, R.C., *Spectroscopy*, 1991, **6**, 35.
71. Tsukahara, R., and Kubota, M., *Spectrochim. Acta, Part B*, 1990, **45**, 779.
72. Shen, W.L., Caruso, J.A., Fricke, F.L., and Satzger, R.D., *J. Anal. At. Spectrom.*, 1990, **5**, 451.
73. Grégoire, D.C., *Anal. Chem.*, 1990, **62**, 141.
74. Grégoire, D.C., *J. Anal. At. Spectrom.*, 1988, **3**, 309.
75. Park, C.J., and Hall, G.E.M., *J. Anal. At. Spectrom.*, 1988, **3**, 355.
76. Gray, A.L., and Date, A.R., *Analyst*, 1983, **108**, 1033.
77. Matusiewicz, H., Fricke, F.L., and Barnes, R.M., *J. Anal. At. Spectrom.*, 1986, **1**, 203.
78. Evans, E.H., Caruso, J.A., and Satzger, R.D., *Appl. Spectrosc.*, 1991, **45**, 1478.
79. Kantor, T., *Spectrochim. Acta, Part B*, 1988, **43**, 1299.
80. Carey, J.M., Evans, E.H., Caruso, J.A., and Shen, W.L., *Spectrochim. Acta, Part B*, 1991, **46**, 1711.
81. Ng, K.C., and Caruso, J.A., *Appl. Spectrosc.*, 1985, **39**, 719.

82. Park, C.J., *Feasibility Study of an Electrothermal Vaporizer/Inductively Coupled Plasma/Mass Spectrometry System*, Ph. D. Thesis, 1985, University of Toronto, pp. 35-38 and 125.
83. *Total dissolution method for rock samples, Method A-F-HCl-10*, Geological Survey of Canada, Mineral Resources Division, Analytical Chemistry Section, Analytical Chemistry Laboratory, 1992, p. 1-10.
84. Rowston, W.B., and Ottaway, J.M., *Analyst*, 1979, **104**, 645.
85. Findlay, W.J., Zdrojewski, A., and Quickert, N., *Spectrosc. Lett.*, 1974, **7**, 63.
86. Slavin, W., Myers, S.A., and Manning, D.C., *Anal. Chim. Acta*, 1980, **117**, 267.
87. Dean, J.R., and Snook, R.D., *J. Anal. At. Spectrom.*, 1986, **1**, 461.
88. Vaughan, M.-A., Horlic, G., and Tan, S.H., *J. Anal. At. Spectrom.*, 1987, **2**, 765.
89. Vaughan, M.-A., and Horlick, G., *Appl. Spectrosc.*, 1986, **40**, 434.
90. Grégoire, D.C., Al-Maawali, S., and Chakrabarti, C.L., *Spectrochim. Acta, Part B*, 1992, **47**, 1123.
91. Hall, G.E.M., Pelchat, J.C., Boomer, D.W., and Powell, M., *J. Anal. At. Spectrom.*, 1988, **3**, 791.
92. Rohsenow, W.M., and Choi, H.Y., *Heat, Mass, and Momentum Transfer*, Prentice-Hall Inc., Englewood Cliffs, NJ, 1961, pp 22-24.
93. Houk, R.S., Fassel, V.A., Flesch, G.D., Svec, H.J., Gray, A.L., and Taylor, C.E., *Anal. Chem.*, 1980, **52**, 2283.
94. McLaren, J.W., and Wheeler, R.C., *Analyst*, 1977, **102**, 542.
95. Sturgeon, R.E., Willie, S.N., and Grégoire, D.C., *J. Anal. At. Spectrom.*, 1993, in press.
96. Slavin, W., and Manning, D.C., *Prog. Anal. At. Spectrosc.*, 1982, **5**, 243.
97. Carey, J. M., and Caruso, J.A., *Crit. Rev. Anal. Chem.*, 1992, **23**, 397.
98. Perkin-Elmer Sciex, *A guide to the Perkin-Elmer Sciex Elan 5000 inductively coupled plasma-mass spectrometer*, 1992, 7.
99. Grégoire, D.C., private communication, 1993.
100. *Handbook of Chemistry and Physics*, 53rd ed., Weast, R.C., Ed. CRC Press, 1973.

101. Chakrabarti, C.L., Wu, S., Karwowska, R., Rogers, J.T., Haley, L., Bertels, P.C., and Dick, R., *Spectrochim. Acta, Part B*, 1984, **39**, 415.
102. Halliday, D., and Resnick, R., *Physics for Students of Science and Engineering*, John Wiley & Sons Inc., New York, USA, 1962, pp 692-693.
103. Park, C.J., and Hall, G.E.M., *Curr. Res., Geol. Surv. Can.*, 1986, **86-1B**, 767.
104. Govindaraju, K., *Geostandards Newsletter*, 1989, **13**, 1.
105. Langmyhr, F.J., and Tsalev, D.L., *Anal. Chim. Acta*, 1977, **92**, 79.
106. Shaw, F., and Ottaway, J.M., *Analyst*, 1975, **100**, 217.
107. Persson, J., Frech, W., and Cedergren, A., *Anal. Chim. Acta*, 1977, **92**, 85.
108. Zheng, Y., Woodruff, R., and Nichols, J.A., *Anal. Chem.*, 1984, **56**, 1388.
109. L'vov, B.V., *Spectrochim. Acta, Part B*, 1989, **44**, 1257.
110. L'vov, B.V., and Savin, A.S., *Zh. Anal. Khim.*, 1982, **37**, 2116.
111. Doidge, P., *Spectrochim. Acta, Part B*, 1992, **47**, 569.
112. Iwamoto, E., Ohlsson, K.E.A., Baxter, D.C., and Frech, W., *J. Anal. At. Spectrom.*, 1992, **7**, 1063.
113. Huang, M., Hanselman, D.S., Yang, P., and Hieftje, G.M., *Spectrochim. Acta, Part B*, 1992, **47**, 765.
114. Bendicho, C., and De Loos-Vollebregt, M.T.C., *Spectrochim. Acta, Part B*, 1990, **45**, 547.
115. Ohlsson, K.E.A., Cedergren, A., and Frech, W., *Spectrochim. Acta, Part B*, 1992, **47**, 1525.
116. L'vov, B.V., *Spectrochim. Acta, Part B*, 1993, in press.
117. Ohlsson, K.E.A., Iwamoto, E., Frech, W., and Cedergren, A., *Spectrochim. Acta, Part B*, 1992, **47**, 1341.
118. Stroup, P.T., *Trans. Metall. Soc. AIME*, 1964, **230**, 356.
119. Motzfeldt, K., and Steinmo, M., *3rd Nordic High Temperature Symposium*, 1973, Ed. Rasmussen, J.G., Polyteknisk Forlag, **2**, 91.

END

1 9-0 7-9 4

FIN