**ATOMIC ABSORPTION SPECTROMETRY WITH
ATOMIZATION BY CATHODIC SPUTTERING
IN A GLOW DISCHARGE**

by

Ghodratollah Absalan, B.Sc., M.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

August 9, 1996

© copyright 1996

Ghodratollah Absalan

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 0-612-19395-0

Name Ghodratollah Absalan

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.

Atomic Absorption Spectrometry with Atomization by
Cathodic Sputtering in a Glow Discharge

0486
SUBJECT CODE

U-M-I

Subject Categories

THE HUMANITIES AND SOCIAL SCIENCES

COMMUNICATIONS AND THE ARTS

Architecture 0729
Cinema 0700
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 0488
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

LANGUAGE, LITERATURE AND LINGUISTICS

Language 0679
Ancient 0289
Linguistics 0290
Modern 0291
Literature 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 0318
General 0321
Biblical Studies 0319
Clergy 0320
History of 0322
Theology 0469
SOCIAL SCIENCES
American Studies 0323
Anthropology 0324
Archaeology 0326
Cultural 0327
Physical 0310
Business Administration
General 0272
Accounting 0770
Banking 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
Albanian 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 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
Botany 0308
Cell 0309
Cell 0309
Ecology 0329
Entomology 0353
Genetics 0349
Limnology 0793
Microbiology 0410
Molecular 0307
Neuroscience 0317
Oceanography 0416
Physiology 0423
Radiation 0821
Veterinary Science 0778
Zoology 0472
Biophysics
General 0786
Medical 0760
EARTH SCIENCES
Biogeochemistry 0425
Geochemistry 0996

GEODESY, GEOLOGY AND PHYSICS

Geodesy 0370
Geology 0372
Geophysics 0373
Hydrology 0300
Mineralogy 0411
Paleobotany 0345
Paleontology 0426
Paleozoology 0418
Palynology 0985
Polymer 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 Safety 0254
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 0405
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 0732
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 0545
Hydraulic 0546
Industrial 0547
Marine 0794
Materials Science 0794
Mechanical 0548
Metallurgy 0743
Mining 0551
Nuclear 0552
Packaging 0549
Petroleum 0765
Sanitary and Municipal 0554
System Science 0790
Geotechnical 0428
Operations Research 0796
Plastics Technology 0795
Textile Technology 0994
PSYCHOLOGY
General 0421
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,

ATOMIC ABSORPTION SPECTROMETRY WITH ATOMIZATION

BY CATHODIC SPUTTERING IN A GLOW DISCHARGE

submitted by

GHODRATOLLAH ABSALAN, B.Sc., M.Sc.

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

Chair, Department of Chemistry

Thesis Supervisor

External Examiner

Carleton University

August 9, 1996

Abstract

Atomic absorption spectrometric (AAS) determination of selected metals using cathodic sputtering in a glow discharge was studied. The effect of discharge conditions on the sputtering of atoms in a demountable, radiofrequency glow discharge (RFGD) atomizer were investigated and spatial distribution and transport patterns of the sputtered atoms measured. Independent control of flow rate and pressure of the sputtering gas (Ar) was found to be critical in determining the spatial distributions and the total amount of sputtered atoms within the atomizer chamber. Results obtained for sputtering of Cu indicate that the plume of the glow discharge (GD) is constricted by an increase in the Ar gas pressure. Higher Ar gas pressures increase redeposition of the sputtered atoms on the cathode surface. In a low-pressure GD, Ar ions have a smaller energy distribution and most of the sputtered Cu atoms are localized in the front of the sampling orifice. The influence of the anode geometry on the sputtering characteristics of the GD was also studied. The results show that the RFGD source enables the sequential atomic absorption spectrometric determination of elements, and also depth profiling of solid samples. Interferences with the atomic absorption determination of aqueous solution residues of Au, Fe and Mg salts by the direct current glow discharge (DCGD) technique were also studied. A laboratory-built atomizer was used for the RFGD technique for AAS. The use of RFGD was found either to remove or to reduce greatly the interferences found with DCGD. Rate of weight loss and temporal atomic absorption profiles of RF-sputtered Si atoms from a quartz sample were also investigated. The use of the pulse mode of atomization for depth analysis of metals in glass samples by AAS

is discussed. The results of this study show that the laboratory-built atomizer is a promising apparatus for atomization of nonconductive solids and solution residues for AAS.

Acknowledgements

I should like to thank my supervisor, Distinguished Research Professor C. L. Chakrabarti for his guidance and supervision throughout the work. I gratefully acknowledge the Ministry of Culture and Higher Education of Islamic Republic of Iran and Shiraz University for granting me scholarship to pursue these studies. I should like to thank also Professor M. H. Back for reading this thesis and providing invaluable comments and to thank Dr. K. L. Headrick, Dr. J. C. Hutton and V. Pavski for their help.

Table of Contents

List of Tables	x
List of Figures	xii
List of Abbreviations	xxi
Chapter 1: Cathodic sputtering in a glow discharge as an atomization mode . . .	1
Chapter 2: Cathodic sputtering of analyte atoms in a glow discharge for atomic absorption spectrometry	21
Introduction	21
Theory	21
Chapter 3: Study of atomization of Au, Fe and Mg from a sodium chloride matrix by cathodic sputtering in a glow discharge for atomic absorption spectrometry	26
Experimental	26
Apparatus	26
Gas control system	31
Test solutions and reagents	34
Procedure	35
Results and Discussion	37
Parametric evaluation	37
Study of NaCl matrix interference using ATOMSOURCE and MDX-1K power supplies	43
Direct current sputtering of bulk solids	68

	Conclusions	73
Chapter 4:	Effect of discharge conditions on the sputtering and spatial distributions of analyte atoms in an RFGD atomizer for AAS	75
	Introduction	75
	Experimental	75
	Sputtering atomizer	75
	Radiofrequency generator and impedance matching network	82
	Discharge gas	83
	Measurement system	85
	Procedure	86
	Results and Discussion	89
	Preliminary experiments	89
	Spatial distributions of analyte atoms	93
	Conclusions	116
Chapter 5:	Effects of anode dimensions and location of the inlet port of discharge-gas on the spatial distributions of Cu atoms in an RFGD atomizer for AAS	118
	Introduction	118
	Experimental	119
	Sputtering atomizer	119
	Direct current self-bias monitor	120
	Gas control system	124

Test solutions and reagents	124
Procedure	124
Results and Discussion	125
Effect of the location of the inlet port of discharge-gas on the number density of Cu atoms	125
Effect of the anode geometry on the number density of Cu atoms	130
Spatially-resolved measurement of absorbance	139
Analysis of residues of aqueous solutions	162
Conclusions	165
Chapter 6: A laboratory-built RFGD atomizer for atomic absorption spectrometry of some nonconductive materials (silica)	167
Introduction	167
Experimental	168
Sputtering atomizer	168
Measurement system	170
Standard reference materials	172
Procedure	172
Results and Discussion	173
Conclusions	188
Chapter 7: Removal of sodium chloride matrix interferences in the determination of gold and iron in solution residues by GD-AAS	189
Objectives	189

Experimental	189
DC-sputtering apparatus	189
RF-sputtering apparatus	191
Test solutions and reagents	191
Procedure	193
Results and Discussion	195
The NaCl matrix interferences in the DC-sputtering	200
The NaCl matrix interferences in the RF-sputtering	206
Conclusions	217
Appendix: k_1 and k_2 calculation procedure	221
References:	222

List of Tables

Table 3.1	Experimental conditions for DC-sputtering with the ATOMSOURCE power supply	29
Table 3.2	Discharge parameters for DC-sputtering of solution residues with the ATOMSOURCE power supply	30
Table 3.3	Experimental conditions for DC-sputtering with the MDX-1K power supply	32
Table 3.4	Rate constants for transient atomization of Au solution residue, deposited on Cu cathode surface, sputtered in the presence of various masses of NaCl using the ATOMSOURCE power supply	57
Table 4.1	Sample weight loss rates and mean free-paths of Cu atoms at different Ar gas pressures using the ATOMSOURCE gas-control box	111
Table 4.2	Sample weight loss rate in RF-sputtering of Al	112
Table 5.1	Distance of the absorbance maximum from the cathode surface at various discharge conditions	163
Table 5.2	Experimental conditions for sputtering of Au atoms from solution residues deposited on a Cu cathode	164
Table 6.1	Effect of the backing material on AAS signal of RF-sputtered Si atoms from the unknown sample (quartz)	174
Table 6.2	Kinetic analysis for RF-sputtered Si atoms from a quartz sample	186
Table 7.1	Experimental conditions for RF-sputtering of Au and Fe atoms from solution residues on a Cu cathode	192

Table 7.2	Experimental conditions for RF-sputtering of Fe atoms from solution residues deposited on a graphite cathode surface	197
Table 7.3	Minimum mass of NaCl matrix which gives less than 100% recoveries of Fe and Au	210
Table 7.4	Experimental conditions used for determination of Fe spiked in NASS-3 matrix	219

List of Figures

Figure 3.1a	Schematic diagram of the laboratory-built atomizer	27
Figure 3.1b	Schematic diagram of the gas control apparatus	33
Figure 3.2	Variation of peak-height and peak-area absorbances with Ar gas pressure for DC-sputtered solution residues of Au using the MDX-1K power supply	38
Figure 3.3	Cathode potential as a function of Ar gas pressure in DC-sputtering of solution residues of Au using the MDX-1K power supply	39
Figure 3.4	Variation of peak-height and peak-area absorbances with Ar gas pressure for DC-sputtered solution residues of Au in a NaCl matrix using the MDX-1K power supply	41
Figure 3.5	Variation of peak-height and peak-area absorbances with Ar gas flow rate for DC-sputtered solution residues of Au using the MDX-1K power supply	42
Figure 3.6	Variation of peak-height and peak-area absorbances with Ar gas flow rate for DC-sputtered solution residues of Au in a NaCl matrix using the MDX-1K power supply	44
Figure 3.7	Variation of peak-height and peak-area absorbances with discharge power for DC-sputtered solution residues of Au using the MDX-1K power supply	45
Figure 3.8	Variation of peak-height and peak-area absorbances with discharge power for DC-sputtered solution residues of Au in a NaCl matrix using the	

	MDX-1K power supply	46
Figure 3.9	Percent peak-height and peak-area recoveries of Fe from solution residues with NaCl matrix, DC-sputtered from a Cu cathode using the ATOMSOURCE and the MDX-1K power supplies	48
Figure 3.10	Variation of the cathode sheath voltage with increasing mass of NaCl matrix in DC-sputtering of Fe solution residues using the ATOMSOURCE power supply	50
Figure 3.11	Percent peak-height and peak-area recoveries of Fe from solution residues with NaCl matrix, DC-sputtered from a Cu cathode for different applied powers using the MDX-1K power supply	52
Figure 3.12	Percent peak-height and peak-area recoveries of Au from solution residues, with NaCl matrix, DC-sputtered from a Cu cathode using the ATOMSOURCE and the MDX-1K power supplies	54
Figure 3.13	Comparison of the theoretical and the experimental absorbance profiles of Au sputtered from solution residues	56
Figure 3.14	Percent peak-height and peak-area recoveries of Au, Fe and Mg solution residues sputtered from NaCl matrix	58
Figure 3.15a	Variation of peak-height recovery with Ar gas pressure for DC-sputtered solution residues of Au in a NaCl matrix from a Cu cathode using the MDX-1K power supply	60
Figure 3.15b	Cathode potential as a function of Ar gas pressure in DC-sputtering of solution residues of Au using the MDX-1K power supply	61

Figure 3.16	Variation of discharge current with Ar gas pressure for DC-sputtered solution residues of Au from a Cu cathode using the MDX-1K power supply	62
Figure 3.17	Variation in the peak-height and peak-area recoveries with Ar gas pressure for DC-sputtered solution residues of Fe in a NaCl matrix from a Cu cathode using the MDX-1K power supply	64
Figure 3.18	Variation in the peak-height recovery with Ar gas flow rate for DC-sputtered solution residues of Au in a NaCl matrix from a Cu cathode using the MDX-1K power supply	65
Figure 3.19	Cathode potential as a function of Ar gas flow rate in DC-sputtering of solution residues of Au using the MDX-1K power supply	66
Figure 3.20	Variation in the normalized absorbance and cathode potential with applied DC current for DC-sputtered Fe from brass using the MDX-1K power supply at various Ar flow rates	69
Figure 3.21	Variation in the normalized absorbance and cathode potential with applied DC current for DC-sputtered Fe from brass using the MDX-1K power supply at various Ar gas pressures	71
Figure 4.1	A schematic diagram of the RFGD atomizer	76
Figure 4.2	Front view of the sampling orifice disk	78
Figure 4.3	Side view of the sampling orifice disk	79
Figure 4.4	Modified impedance matching network	84
Figure 4.5	Absorbance versus time in the steady-state mode of RF atomization of	

	cleaned pre-sputtered Cu cathode surface	87
Figure 4.6	Variation in the absorbance of Cu atoms as a function of time	91
Figure 4.7a	Spatial distribution of Cu atoms inside the atomizer: Ar gas pressure, 8 Torr; Ar gas flow rate, 0.4 SLPM; applied RF power, 40 W	95
Figure 4.7b	Spatial distribution of Cr atoms inside the atomizer: Ar gas pressure, 8 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 40 W	96
Figure 4.7c	Spatial distribution of Cu atoms inside the atomizer: Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 40 W	97
Figure 4.7d	Spatial distribution of Cu atoms inside the atomizer: Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 55 W	98
Figure 4.8	Absorbance of sputtered Cu atoms as a function of applied RF power at Ar gas flow rate of 0.1 SLPM and Ar gas pressure of 3.7 Torr . .	104
Figure 4.9	Spatial distributions of Cu atoms when the atomizer was set at the vertical position of -2 mm	106
Figure 4.10	Absorbance of Cu atoms as a function of Ar gas pressure and flow rate at a constant applied RF power	109
Figure 4.11a	Absorbance of Cu atoms as a function of RF power, using the ATOMSOURCE gas-control box	114
Figure 4.11b	Absorbances of Cu atoms as a function of applied RF power at Ar gas flow rate of 0.2 SLPM and Ar gas pressure of 5 Torr	115
Figure 5.1a	Front view of the sampling orifice disk with gas inlet port	121
Figure 5.1b	Side view of the sampling orifice disk with gas inlet port	122

Figure 5.2	A schematic diagram of the laboratory-built DC self-bias monitor .	123
Figure 5.3a	Absorbance of Cu atoms measured along the horizontal axis for Ar gas flow rate of 0.1 SLPM, Ar gas pressure of 3.7 Torr. and applied RF power of 40 W	128
Figure 5.3b	Absorbance of Cu atoms measured along the horizontal axis for various Ar gas flow rates, Ar gas pressure of 8 Torr, and applied RF power of 40 W	129
Figure 5.4	Effect of sampling orifice disk diameter on the absorbance of Cu atoms. RF-sputtered from a Cu cathode	131
Figure 5.5	Effect of the sampling orifice diameter on sample weight loss rate of Cu atoms when the unmodified atomizer was used	132
Figure 5.6	AA signals of Cu atoms RF-sputtered from a Cu cathode for various sampling orifice disk thicknesses	134
Figure 5.7a	Effect of the sampling orifice disk thickness on the absorbance of Cu atoms, RF-sputtered from a Cu cathode	135
Figure 5.7b	Effect of the thickness of the sampling orifice disk on sample weight loss rate of Cu atoms when the unmodified atomizer was used	138
Figure 5.8	Spatial distribution of Cu atoms inside the atomizer chamber of the modified RF atomizer	141
Figure 5.9	Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas pressure of 5.4 Torr and an applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for various Ar	

	gas flow rates	143
Figure 5.10	Effect of Ar gas flow rate on rate of weight loss of the sample . .	145
Figure 5.11	Horizontal distribution of Cu atoms inside the atomizer chamber at an applied RF power of 40 W and Ar gas flow rate of 0.2 SLPM when the modified atomizer was set at the vertical position of 0 mm for various Ar gas pressures	146
Figure 5.12	Effect of Ar gas pressure on sample (Cu) weight loss rates at various Ar gas flow rates when the modified RF atomizer was used	148
Figure 5.13	Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas flow rate of 0.4 SLPM and an applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for various Ar gas pressures	149
Figure 5.14	Horizontal distribution of Cu atoms inside the atomizer chamber at Ar gas flow rate of 0.6 SLPM and applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for various Ar gas pressures	150
Figure 5.15	Horizontal distribution of Cu atoms inside the atomizer chamber at Ar gas pressure of 8 Torr and an applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for various Ar gas flow rates	152
Figure 5.16	DC self-bias potential developed at the cathode surface of the modified RF atomizer as a function of Ar gas flow rate	155

Figure 5.17	Experimental and theoretical DC self-bias potentials	157
Figure 5.18	Effect of location of the Ar gas inlet port on DC self-bias	158
Figure 5.19	Horizontal distribution of Cu atoms inside the atomizer chamber at gas pressure of 8 Torr and RF power of 40 W when the atomizer was set at the vertical position of -4 mm for various Ar gas flow rates . . .	159
Figure 5.20	Horizontal distribution of Cu atoms inside the atomizer chamber for various RF powers	161
Figure 6.1	A schematic diagram of the RFGD atomizer	169
Figure 6.2	A schematic diagram of the instrumental system	171
Figure 6.3	Absorbance of RF-sputtered Si atoms sputtered from a quartz sample surface as a function of RF power	175
Figure 6.4	Absorbance of RF-sputtered Si atoms as a function of Ar gas flow rate	177
Figure 6.5	Absorbance of Si atoms, RF-sputtered from a quartz surface as a function of Ar gas pressure (Ar gas flow rate = 0.2 SLPM)	179
Figure 6.6	Absorbance of Si atoms, RF-sputtered from a quartz surface as a function of Ar gas pressure (Ar gas flow rate = 0.3 SLPM)	181
Figure 6.7	Absorption profiles for Si atomization of a quartz sample	182
Figure 6.8	AA signal of RF-sputtered Si atoms under the pulsed mode of atomization	184
Figure 6.9	Absorbance as a function of applied RF power for RF-sputtered Si atoms from the surface of a Multi-Component Glass sample	187

Figure 7.1	Depression profiles produced by six gas-jets	194
Figure 7.2	Atomic absorption signals of Fe given by RF-sputtered solution residues deposited in various locations of the cavity	196
Figure 7.3a	Absorbance profile and the related discharge voltage for sputtering of Fe solution residues using the ATOMSOURCE power supply	201
Figure 7.3b	Absorbance profile and the related discharge voltage for sputtering of Fe solution residues using the ATOMSOURCE power supply in a 500 ng NaCl matrix	202
Figure 7.3c	Absorbance profile and the related discharge voltage for sputtering of Fe solution residues using the ATOMSOURCE power supply in a 1000 ng NaCl matrix	203
Figure 7.3d	Absorbance profile and the related discharge voltage for sputtering of Fe solution residues using the ATOMSOURCE power supply in a 5000 ng NaCl matrix	204
Figure 7.4	Percent peak-height and peak-area recoveries of Fe from solution residues with NaCl matrix using DC- and RF-sputtering modes	207
Figure 7.5	Percent peak-height and peak-area recoveries of Au from solution residues with NaCl matrix using DC- and RF-sputtering modes	208
Figure 7.6	Absorbance signals and their related DC self-bias voltage profiles for Fe, RF-sputtered from solution residues containing various masses of NaCl matrix	209
Figure 7.7	Typical AA profiles and the related discharge voltages for RF-sputtering	

	of Au solution residues with and without a NaCl matrix	212
Figure 7.8a	Variations in the peak-height absorbance and its related DC self-bias voltage as a function of Ar gas pressure for Au, RF-sputtered from solution residues	213
Figure 7.8b	Variations in the peak-height absorbance and its related DC self-bias voltage as a function of Ar gas flow rate for Au, RF-sputtered from solution residues	215
Figure 7.8c	Variations in the peak-height absorbance and its related DC self-bias voltage as a function of power for Au, RF-sputtered from solution residues	216
Figure 7.9	Analytical calibration curves for determination of Fe	218

Glossary of Abbreviations

AAS:	atomic absorption spectroscopy
AES:	atomic emission spectroscopy
AFS:	atomic fluorescence spectroscopy
CSGD:	cathodic sputtering glow discharge
DCGD:	direct current glow discharge
GD:	glow discharge
GDMS:	glow discharge mass spectrometry
HA-FANES:	hollow anode-furnace atomization non-thermal excitation spectrometry
NG:	negative glow
NG/DS	negative glow/dark space
OFHC:	oxygen free hard copper
RFGD:	radiofrequency glow discharge
RSD:	relative standard deviation
SEM:	scanning electron microscopy
SIMS:	secondary ion mass spectrometry
SLPM:	standard litre per minute

CHAPTER 1

Cathodic sputtering in a glow discharge as an atomization mode

Cathodic sputtering in a glow discharge (CSGD) is a non-thermal mode of atomization [1]. In atomic absorption spectrometry (AAS), CSGD was first used for the study of the atomization mechanisms by Russell and Walsh [2]. By applying a discharge potential between two electrodes in a noble gas under a low pressure, the gas atoms are ionized by accelerated electrons and a plasma is produced. Positive ions created in the discharge are accelerated by a high potential gradient near the cathode surface, and these accelerated ions strike the cathode surface producing cathodic sputtering. Ar is almost always used in CSGD because it is easily available in a pure state and it is inexpensive. The degree of ionization of Ar gas is typically 10^{-4} [3].

The cathode plays an important role in sputtering systems because the sputtering target actually becomes the cathode of the discharge. The cathode is nearly always solid, although powders and even solution residues are sometimes used. There are some materials which are incompatible with good vacuum technology, either because of their inherent properties or because of their products under the various types of bombardment involved in the process. Organic solids are frequently unable to withstand this bombardment, and completely degrade; the temperature rise alone is often adequate to produce this effect. On the other hand, it is remarkable that polytetrafluoroethylene can nevertheless be sputtered [3].

Atoms at or near the surface that acquire sufficient energy to overcome the

binding energy of the atom with its neighbours in the crystal lattice, as well as a favourable velocity vector, can escape from the cathode and enter the vapour phase [4]. This is the process of physical cathodic sputtering in which the atoms in the gas phase are largely single, ground state neutral atoms [5-8], and with the conditions in a typical GD will have large initial energies of the order of 10 eV [9].

Chemical or reactive sputtering occurs when the incident ion and the target ion form a volatile compound, which is then volatilized into the GD [10]. For example, silicon nitride can be produced by sputtering silicon in a DC (or RF) discharge containing N_2 [3]. The system utilizes a flowing stream of discharge gas to help remove gaseous impurities, particularly water vapour, from within the atomizer. Except at the lowest operating pressure, almost all of the ejection energy of the sputtered atoms will be quickly dissipated by collisions. The incident ion will either become implanted or be reflected, probably as a neutral atom with a large loss of energy.

Cathodic sputtering occurs by a mechanism of momentum transfer [11]. The sputtering yield (defined as the number of atoms sputtered per primary ion colliding with the solid cathode surface [12]) is proportional to $m \cdot M / (m + M)^2$, where m and M are the respective atomic weights of the bombarding ion and the target cathode element [13]. Sputtering yields for H^+ and He^+ are very low, and sputtering with electrons is negligible unless they have energies in the MeV range. For moderate ion energy (e.g. 1 KeV) and atomic weight of the target (such as Cu), Ar usually provides the largest sputtering yield, whereas sputtering yields of Kr and Xe become more favourable with increasing ion energy and atomic weight of the target. Atoms with filled outer electron

shells have the largest sputtering yields since their collisions are more elastic than those of atoms with unfilled outer electron shells, thus providing more efficient momentum transfer. The sputtering yield increases across a given period of the Periodic Table [14] and has been found to be roughly inversely proportional to the binding energy of the target atoms [15]. For this reason the noble gases (He, Ne, Ar, Kr and Xe) and the noble metals Cu, Ag and Au are commonly employed in sputtering studies. Sputtering yields for Zn, Cd and Hg are higher than for Cu, Ag and Au, respectively, but the higher vapour pressures of the former limit their use at low pressures. It should be pointed out that it is the electronic configuration of the bombarding atom, rather than the ion, that is important, since the incoming ions are neutralized by electrons emitted from the cathode immediately before impact.

Roughness of the surface affects the sputtering yield because for sputtering to occur, the target atom must acquire not only sufficient energy to overcome its binding energy with its neighbours in the crystal lattice, but also acquire a velocity vector which will carry it away from the cathode and into the GD. Redeposition is more likely when the surface is rough. Surface preparation determines the roughness of the surface and can also introduce dirt and other impurities which affect the sputtering yield. In practice, a surface prepared for bombardment will always include local variations of binding energy over the surface and this will lead to variations in the sputtering yield [16]. Ion bombardment, especially at high energies and low temperatures, tends to break-up the surface and make it amorphous. This can be understood by analogy to the surface of the moon, which is covered by a dusty layer of "lunar soil" several meters thick, largely

because of the break-up of the surface rocks caused by the continual bombardment of the surface by micrometeorites and cosmic rays [17]. Thus, the most reproducible surface will be the one which has been pre-sputtered, or sputter-cleaned.

The velocity vector acquired by the target atom (and therefore, the sputtering yield) depends on the angle of incidence of the bombarding ion. The velocity vector of a target atom acquired from a normally incident ion will tend to knock the target atom farther into the cathode, rather than into the GD; this effect is known as "knock-in". The failure to observe the 10 Å periodicity of K in a depth profile of a mica crystal [18] has been attributed to "knock-in". Atoms sputtered from incident ions nearly parallel to the cathode surface will very likely be redeposited. The optimum angle of incidence is usually about 70° to 80° from the normal, the exact angle depending on a number of parameters [16]. Single crystal targets show a complex dependence of the sputtering yield on the angle of incidence for ions incident on different crystal faces [14].

The sputtering rate of a system describes the amount of sample material removed per unit time ($\mu\text{g s}^{-1}$). Fang and Marcus [19] studied in detail the dependence of sputtering rate on the discharge current, i , and gas pressure. The studies revealed a definite i^2 dependence over a range of discharge pressures. Sputtering rates will certainly vary according to the identity of the sample material. Furthermore, sputtering rates of multicomponent samples of varying lattice structures can be different.

Sigmund [20] has presented a general theory of sputtering yield, which is the number of sputtered atoms per incident ion, deriving the following equation to evaluate semiquantitatively the physical parameters affecting it. The sputtering yield (S) is given

by:

$$S = (3/4) \pi^2 (\alpha) [4M_1M_2/(M_1+M_2)^2] (E/U_0) \quad (1)$$

where α is a function of the relative masses and the angle of incidence of the incoming ion, M_1 and M_2 are the respective masses of the ion and the sputtered atom, E is the incident ion energy, and U_0 is the surface binding energy that must be overcome for sputtering to occur.

The sputtering yield is reported to be virtually independent of the temperature to within $\sim 250^\circ\text{C}$ of the melting point [13,14]. At higher temperatures there is an apparent increase in the sputtering yield which is due to vaporization. High temperatures will reduce the adsorption of low sputtering yield gaseous contaminants on the surface, will increase solid-state diffusion in the cathode and will anneal sputter-induced damage. Exposed atoms are annealed to positions of greater binding energy, making them more difficult to sputter.

The sputtering rate, q ($\mu\text{g s}^{-1}$), and the sputtering yield, S , have the following relationship:

$$S = \frac{10^{-6} q N e}{M i^*} \quad (2)$$

where N is Avogadro's number (mol^{-1}), e is the electronic charge (Coulomb), M is the atomic weight, and i^* is the ion current (ampere).

When an alloy is vaporized thermally, the depletion of the higher vapour-pressure elements at the surface is accompanied by diffusion of atoms from the bulk, and net

fractional distillation of these elements occurs. For cathodic sputtering, however, the temperature of the alloy is usually too low to permit diffusion of atoms from the bulk, and a thin layer which is depleted in the faster-sputtering elements rapidly forms near the surface [21]. It can be shown that once equilibrium is established, this altered layer should compensate for the faster sputtering rates of the depleted elements, and the composition of the sputtered material is then expected to be the same as that of the original alloy [22,23], although in some cases significant compositional differences have been reported [24,25]. The predicted correspondence between the compositions of the sputtered material and the original alloy suggest that matrix effects may not be important in spectrochemical analysis based on the sputtering technique [26,27].

There are two types of GD, the normal and the abnormal. In a normal GD, the discharge covers only a portion of the cathode surface. Increasing the discharge current increases the area of the cathode surface covered by the discharge, while the discharge voltage remains constant. Once the entire cathode surface is covered by the discharge, an increase in the discharge current causes the discharge voltage to increase as well, producing what is known as an abnormal GD. It is the abnormal GD that is analytically useful since only here is the entire cathode surface being sampled. The proportionality between the discharge current and the discharge voltage continues until thermionic emission begins. Still further increase in the discharge current results in the formation of an arc discharge. The arc discharge is a high-current, low-voltage discharge, in which cathode atoms are volatilized by the high temperature of the arc.

A GD can consist of up to eight distinct regions, depending on the exact

configuration of the discharge used [11]. The regions of interest to the analytical chemist are the cathode dark space and the negative glow (NG). GDs can exist without a NG or any of the other regions farther from the cathode, but they can never exist without a cathode dark space [28]. As electrons are accelerated away from the cathode and into the cathode dark space, they lose energy through collisions with the discharge gas and through ionization of the discharge gas. This ionization creates a large number of positive ions, producing electron multiplication and a large potential gradient which takes up almost all of the discharge voltage. This potential gradient is called the cathode fall potential. As the electrons are slowed to near thermal energies they are better able to excite the gaseous species present. The point where large numbers of these thermal electrons are first encountered marks the beginning of the NG. The NG is a region of continuing ionization and intense emission, the intensity of which is greatest just after the start of the NG. It is the NG which is of interest for atomic emission spectrometry (AES) and for GD mass spectrometry (GDMS). Positive ions are sputtered from the cathode surface but are not detectable since they are either quickly neutralized or redeposited on the cathode because of the large cathode fall potential near the cathode [29]. Atoms sputtered from the cathode diffuse away from the cathode because of concentration diffusion. A large proportion of the sputtered atoms are redeposited on the cathode surface or are deposited on the walls of the sputtering chamber. Thus, only a small fraction of the atoms sputtered are available for producing analysis signals.

The mechanism of the sputtering process is very complex since it involves not only binary collisions but also many-atom processes. The species liberated from the

cathode surface are predominantly single, ground-state, neutral atoms but may also include excited atoms, ions, and small aggregates of atoms. Some of the sputtered atoms may also aggregate as they diffuse through the discharge gas [30]. The sputtered atoms subsequently lose their energy by elastic collisions with gas atoms as they diffuse out from the cathode towards the walls of the atomizer. During transit, the sputtered atoms pass through the negative-glow region of the discharge where they may become excited or ionized by electron impact or by collisions with metastable atoms. The average time between collisions in a glow-discharge at 5 Torr and 300°K is of order of 10^{-6} sec, so an excited atom will rarely experience a collision during its lifetime (usually 10^{-7} sec). Pressure broadening is very small, and so the profile of an absorption line is expected to be close to a pure Gaussian, with a Doppler width corresponding approximately to the temperature of the gas [31].

The main processes which may occur in the plasma include [32,33]:

1. Electron impact (mainly with high energy electrons):

where * stands for an excited atom.

2. Collisions of the second kind:

3. Recombination (mainly with slow electrons):

4. Possible reactions involving water molecules in the Ar discharge:

In a GD the discharge current determines the bombarding ion flux and the discharge voltage determines the bombarding ion kinetic energy. In order for sputtering to occur the bombarding ions must have an energy greater than the threshold energy of the target cathode. For sputtering under normal incidence with Ne, Ar, Kr or Xe the threshold energy is approximately four times the heat of sublimation of the target, and is characteristic of a given combination of discharge gas and target.

The sputtering effect is more pronounced at lower pressures because of the

accompanying rise in discharge voltage ($V \propto 1/P$). Also, less redeposition would be expected at lower pressures because of the larger mean free path [34]. Normally, GD operates at a pressure such that the incident ions and sputtered atoms have a small mean free path compared to the dimensions of the tube. Ideally, optimum conditions should be the lowest possible operating pressure at the highest feasible current.

GD sputtering source has proven to be an excellent atomization source for direct analysis of major and trace elements in solid samples, such as metals [35], meteorites [36], semiconductors and alloys [37,38], as well as powder samples [39] and for solution samples after depositing and drying the sample residues on graphite or Cu surface [1,40-43]. Direct vaporization from the solid sample by sputtering in a GD source is very attractive when it is desirable to detect trace quantities without dissolving the sample and when rapid analysis is required. The representative atoms, molecules, meta-stables, ions, and photons [44] in the plasma produce several analytical options. As the material volatilized in a GD is to a large extent present as a vapour cloud of free atoms [5,7,8,32], GDs are suitable atom reservoirs for AAS [1,37,40,45-51]. The narrow Doppler widths of absorption lines in sputtered vapours makes cathodic sputtering a particularly attractive method of atomization for isotopic analysis by AAS and has permitted successful analyses to be performed on isotopes of U, Pb and B. Excellent resolution of the isotopic components can now be achieved for elements with small isotope shifts, such as Zr, using Doppler-free laser spectroscopy in a sputtered vapour [30]. This technique has also been used for the analysis of surface layers [52] and for depth profiling [53].

Atomic fluorescence (AF) can also be performed on the vapour cloud [30,31,54,55]. The fact that decay of the excited species by quenching is low at low pressure is a distinct advantage. The non-dispersive resonance fluorescence spectrometer described by Human et al. [56] makes use of one GD as the primary radiation source and a second GD in which the sample is used as cathode, as the atom reservoir. Laser-induced fluorescence with a GD as the atom reservoir has also been described [57-60]. Laser excitation of the sputtered vapours and detection of the AF offers several important advantages including sensitivity, selectivity and multi-element determination capability.

GDs are also of potential interest as atom reservoir for laser enhanced ionization techniques. Cathodic sputtering allows laser spectroscopic techniques to be applied to essentially any element and permits measurement of spectroscopic properties such as atomic lifetimes, absolute oscillator strengths and hyperfine structures, which are of importance in fields such as astrophysics, atomic physics and plasma physics, as well as in analytical atomic spectroscopy [30]. The ability of the sputtering technique to generate singly-charged ions for lifetime measurements is especially important in solar and stellar abundance work since such ions are usually the dominant species in the photosphere of hot stars such as the sun.

Discharges under reduced pressure, from the point of view of sample volatilization and excitation, can serve as a radiation source for atomic emission spectrometry (AES) [12,48,52,53,61-68]. Owing to the non-local thermal equilibrium (non-LTE) character of the discharge [32], high line-to-background intensity ratios are obtained for the analyte lines. The spectra consist mainly of very narrow lines, because

of low Doppler and pressure broadening and do not suffer significantly from interferences by molecular bands. GD optical emission spectrometry has emerged as an important and versatile technique for in-depth profiling of the composition of surface layers [69].

Apart from their use as sources for optical atomic spectrometry, GDs also have been recognized as being powerful ion sources for inorganic mass spectrometry [29,30,44,54,55,70-74]. Glow discharge mass spectrometers (GDMS) are now commercially available and are of considerable interest for trace analysis of solid samples. The technique may be applied to metals, alloys [75] and electrically non-conducting powders. Dry residues can also be analyzed [1,40-42].

A GD can be powered in the constant current, constant voltage, or constant power mode. Current control is often selected in DCGD because this holds constant the number of sputter events at the sample surface. However, the voltage changes required to maintain a constant current [76] cause a corresponding change in energy of the sputtering ions, which in turn can affect the sputter yield [44]. The flux of sputtering particles at the cathode is not equivalent to current, since some of the cathode current is carried by electrons, and some of the sputtering particles are neutral [3]. The effect of a higher GD current is significant because of the increase in the number of ions bombarding the surface which consequently increase the sputtering rate [34]. An increase in the discharge current enhances collisions of fast and slow electrons with discharge gas and sputtered atoms with a net increase in excitation and ionization of both the discharge gas and the sputtered species. The sputtering rate increases with both ion energy and flux

[76]. The dynamics of surface changes seem to be greater at larger discharge currents, perhaps partially as a result of higher-energy ions bombarding the cathode surface [34].

Some power supplies permit constant-power regulation, a mode that strikes an advantageous compromise between current and voltage control. As cathodic sputtering occurs in the region of an abnormal GD, where the voltage increases rapidly with current [77], the power (voltage $\times$ current) is a more meaningful experimental parameter than either voltage or current. Wagatsuma and Hirokawa [78] have investigated the operation of Grimm-type GD in a constant power mode for alloy analysis by AES. Marcus et al. [19] reported that the rate of cathodic sputtering with a d.c. source was directly related to the power density delivered to the cathode surface. Both continuous and pulsed (power-modulated) operation was used. Pulsed operation has the advantage of applying higher average discharge power while avoiding a significant increase in sample surface temperature and still maintaining a reasonably short analysis time. For AAS, the pulsed mode of atomization not only increases the sputtering rate but also cancels the background emission [49].

In investigating the GD as an atomization source for AAS, a study of a number of factors is necessary, such as the identity, pressure and flow rate of the sputtering gas, the cathode material and its recent surface history (preparation, cleaning, and net sputter time), and the discharge current or voltage. The type of cathode and its surface history seems to be of great importance in sputtering of solution residues, since the cathode is the matrix support for sample films exposed to subsequent sputtering in the discharge. The sputtering of solution residues is not favoured unless the ionic and atomic

bombardment sputter and clean the cathode surface efficiently. The time taken for this process varies widely from metal to metal selected as cathode [30]. Various types of cathode surface features form as a result of sputtering which can influence the reproducibility and sensitivity of analytical results, probably by affecting the net surface area and the sputtering rate of analytical residue films. Large changes in reproducibility appeared to correlate with changes in the cathode surface [34].

Cathodic sputtering has offered several promising applications: ability to generate atomic vapours of refractory elements and refractory samples; elimination of chemical interferences and quenching due to molecular species; and ability to make absorption measurements in the vacuum u.v., thereby offering potential of determining C, S and P. For the analyst, an attractive feature of sputtering is that sputtering yields are very similar from element to element; for example, they are only about five times lower for refractory elements than for the easily sputtered metals such as Ag and Cu [30]. The possibility of analyzing solid samples without prior dissolution is another attractive prospect; yet another is the development of sensitive methods for determining refractory elements [40].

One of the factors that has tended to limit the application of GD has been the requirement that the sample be electrically conductive. An insulating surface, such as provided by a NaCl matrix in solution residues, when subjected to positive ion bombardment quickly builds up a layer of positive charge. This layer acquires a potential up to the floating potential [3], repelling subsequent discharge gas ions, and thus, slowing any further sputtering from the surface. For any electrically isolated

surface, the sheath voltages developed are usually no more than 10 or 20 volts [3]. This same process occurs for nonconductive powder samples. A conductive sample may be made by mixing the nonconductive sample with a suitable conductive host matrix, e.g. Cu powder or graphite powder [79], but the mixing introduces certain problems. For example, mixing causes dilution of the sample, which decreases sensitivity; mixing also increases the likelihood of contamination. In addition, many bulk solids are not easily transformed into powders. Mixing also precludes any depth-resolved analysis. The radiofrequency glow discharge (RFGD) circumvents these problems [65]. The RF plasma is capable of sustaining a stable GD on the surface of a non-conductive electrode, thus allowing the direct atomization and subsequent excitation and ionization of non-conductive materials. The technique of RF-sputtering has been applied extensively to the deposition of thin films and etching processes and has had a great deal of application in the electronics industry [80]. Spectrochemical studies of these sources have included both optical and mass spectrometric techniques, with most effort having been extended to the latter.

Anderson et al. [81] applied an RF potential to a metal plate behind their dielectric sample which was immersed in the plasma of a low pressure DC gas discharge. Since the electron mobility is much greater than the ion mobility, and the net current to the dielectric target must be zero, the surface of the sample takes a negative DC self-bias and is sputtered. In a later extension of that work, Davidse and Maissel [66] demonstrated that a self-sustained RF induced gas discharge suitable for sputtering could be ignited using only the RF electrodes. When the cathode is alternatively biased

negatively and positively, the positive charge accumulated during one half cycle will be neutralized by electron bombardment during the following half cycle. Ion bombardment of the insulator would occur for only half of each cycle at the most but the much greater mobility of electrons in a discharge enables one to achieve almost continuous energetic ion bombardment if high enough frequencies are used. Secondary electrons, which have extremely high yields in the case of insulators, are accelerated across the positive ion sheath into the plasma and act as an additional supply of electrons for sustaining the glow [3]. At the same time the oscillatory nature of electrons in RF plasma fields and at plasma-sample and plasma-wall sheaths gives rise to efficient electron impact ionization which sustains the discharge, and this enables sputtering to be carried out efficiently. As a result, an RF discharge can operate at pressures of mTorr, lower than pressures at the Torr level required for DC discharge. To prevent redeposition of sputtered materials on the cathode surface and also to prevent formation of molecular species, RF systems are usually operated at the lower end of their operating pressure range when employed in sputtering applications [3]. The power source normally used to meet these requirements is an RF powered generator usually working at 13.56 MHz. It is a frequency allotted by international communications authorities at which one can radiate a certain amount of energy without interfering with communications. At low frequencies, there will be a series of short-lived discharges with the electrodes successively taking opposite polarities (non-continuous plasma) [3].

By adding a magnetic field normal to the plane of the cathode, plasma density ($\sim 10^{10}/\text{cm}^3$) can be increased and the glow can be made much more stable. Tuning of

the RF power supply also will be easier with the application of a magnetic field. This is a result of the tensor character of the conductivity of a magnetoplasma. Davidse and Maisel [66] found that the density of their plasma increased and tuning was easier with an applied magnetic field.

Analytical applications of cathodic sputtering in a GD have almost wholly involved the production of a steady-state atomic vapour from a bulk solid. Limitations of kinetics inherent in production of steady-state atomic vapour, as discussed in Chapter 2, result in relatively poor sensitivity and limits of detection for the steady-state mode of atomization. This is because in solid samples the analyte is more strongly bound in its three-dimensional lattice. A method that overcomes these limitations [1] uses the rapid generation of analyte atoms from the atomization of solution residues to produce a greater transient concentration of atoms in the analysis volume than is possible for the steady-state mode of atomization. Transient atomization of solution residues involves rapid kinetics of atom formation by cathodic sputtering in a GD and is a promising new technique for AAS. Steady-state and transient modes of atomization are compared in Chapter 2 from kinetics point of view.

In studies of trace metals, it is essential to have an analysis scheme which requires a minimum volume of sample and a minimum of sample handling. Atomic absorption analysis by direct deposition of solution residue on a cathode of a GD atomizer meets both requirements. While there is inconvenience associated with the manipulation of small volumes of samples and with the use of a low pressure system, the difficulties do not seem greater than those associated with the popular graphite furnace atomization

system for atomic absorption spectroscopy [82].

A GD would be quite inefficient for aqueous sample de-solvation and vaporization in comparison with atmospheric-pressure flames and plasma. Water vapour has been shown to have a detrimental effect when present in the GD [83,84]. Water vapour dissociates to form H^+ , which then carries a significant fraction of the ion current but causes no effective sputtering because of the small mass of the ion [71]. Strange et al. [85] have described aqueous sample introduction into a GD device via a particle beam interface. With such an interface, both solids and solutions may be analyzed employing the same spectrochemical source without a major change in the configuration. Any liquid sample introduction scheme must include a high efficiency de-solvation process and subsequent solvent vapour removal otherwise the water-related gaseous species in the plasma lower the metastable atom populations in the negative glow region [86].

For sample residue films deposited on the cathode surface, Cu has the advantage of a larger sputtering rate which enhances the transmission of the sample film into the discharge plasma [34]. On the other hand, this high sputter rate creates possible problems of changing surface geometry, including massive redeposition. Sample atoms may become buried beneath other sputtered and redeposited atoms of the cathode material. At the same time a nonporous material, such as Cu, offers some advantages in sensitivity because the sample residue films remain entirely on the surface. Graphite with its low sputtering rate under bombardment with Ar ions [26], does not contribute significantly to the transmission of a sample film into the discharge plasma, but does provide a simpler matrix surface, with less memory contribution than Cu. A further

advantage is relative inertness of graphite to acidic sample solutions [87].

Other factors that have an effect upon the analytical signals are the transport efficiency and the sputtering efficiency. The transport efficiency is defined as the fraction of the total number of atoms sputtered from the cathode surface that reaches the analysis volume. The sputtering efficiency is defined as the fraction of the total number of analyte atoms that are sputtered from the cathode surface and are not redeposited. For the cathodic sputtering atomizer used in this work there is a spatial separation between the cathode surface (where sputtering occurs) and the analysis volume (defined by the geometry of the beam of radiation from the hollow-cathode lamp). Therefore, the rate of atom formation at the cathode surface cannot be directly measured; only the rate of supply can be measured; the rate of supply is the rate at which the atoms are transported from the cathode surface to the analysis volume. Thus, the absorbance signal arising from the total number of atoms which enter the analysis volume may not be due to all the analyte atoms present in the original sample. If either the sputtering or the transport efficiency is less than unity, the absorbance signal will represent less than the total possible number of atoms which enter the analysis volume. It should be made clear that the rate for the supply of analyte atoms to the analysis volume, is a measure of the rate of transport of the gas-phase analyte atoms to the analysis volume and not of the rate of sputtering. Nevertheless, the rate for the supply of analyte atoms reflects changes in the rate of sputtering. The rate for the removal of analyte atoms from the analysis volume includes diffusion of analyte atoms to and adsorption of the analyte atoms onto the cathode surface and the walls of the analysis cell and removal of analyte atoms out of the

analysis volume by convection.

CHAPTER 2

Cathodic sputtering of analyte atoms in a glow discharge for atomic absorption spectrometry

2.1 Introduction

Chakrabarti et al. [46] have reported that for the analysis of solution residues by atomic absorption spectrometry (AAS) cathodic sputtering atomization has a sensitivity similar to or better than graphite furnace atomic absorption spectrometry. McCamey and Niemczyk [88], who studied the interferences in the sputter atomization of solution residues in AAS, concluded that although interferences found in the graphite furnace were reduced or eliminated when sputter atomization was used, other interferences were observed. The results of various matrix interference in AAS with the ATOMSOURCE for solution residues were reported by Headrick et al. [87].

2.2 Theory

Assuming that consecutive, first-order reactions occur during atom introduction into and their loss from the analysis volume (defined by the geometry of the beam of radiation from the hollow-cathode lamp), the reaction may be represented as [89,90]:

where A represents the analyte atoms entering the analysis volume, B the analyte atoms within the analysis volume, C the analyte atoms that have been lost from the analysis

volume; k_1 and k_2 are first-order rate constants for the introduction of atoms into and their loss from the analysis volume, respectively. It should be noted that the geometry of the atomizer, with its spatial separation of the cathode surface (where atoms are sputtered) and the analysis volume, may result in a difference between the rates of atom formation and loss at the cathode surface and the rates of introduction of atoms into and their loss from the analysis volume. This is in contrast to the situation in a graphite furnace, in which the rate of introduction of atoms into the analysis volume is identical to the rate of atom formation, since the site for atom formation is spatially the same as the analysis volume.

At all times the following equality prevails:

$$A_t + B_t + C_t = A_o \quad (2)$$

where the subscripts t and o represent the number density (since the analysis volume is constant) of the analyte atoms at any time, and of the initial number density of the analyte atoms at time $t = 0$, respectively. The rate of loss of A may be written as:

$$\frac{dA}{dt} = -k_1 A \quad (3)$$

which on integration gives

$$\ln \frac{A_o}{A} = k_1 t \quad (4)$$

Also,

$$\frac{dB}{dt} = k_1 A - k_2 B \quad (5)$$

At long times, A tends to zero, which is identified with the exhaustion of the supply of the analyte species entering the analysis volume. At this point, Equation 5 simplifies to

$$\frac{dB}{dt} = -k_2 B \quad (6)$$

or

$$\ln B = -k_2 t + C \quad (7)$$

As absorbance is proportional to the number of the absorbing atoms, B, the rate constant k_2 for atom loss can be determined from the falling edge of a plot of $\ln B$ (or $\ln$ absorbance due to B) as a function of time. This plot should be linear, yielding the rate constant k_2 from the slope.

Extrapolation of this straight line plot to zero time will give the amount of B, resulting from the complete conversion of A_0 into B, necessary to produce the decay of the signal by the diffusion process alone. Equation 5, however, shows that the rate of formation of B is equal to the difference between the rate of conversion of species A into species B and the rate of loss of species B by diffusion. The ratio of the extrapolated absorbance to the experimental absorbance at any time t is proportional to the number of the analyte species entering the analysis volume. Equation 4 suggests that a plot of the natural logarithm of this difference versus time should be linear, with a slope equal to the rate constant k_1 for the entry of atoms into the analysis volume.

If the kinetic parameters are evaluated, the shape of the absorbance profile can then be determined by solving Equation 5. Using Equation 4, the following solution for Equation 5 is obtained.

$$B_t = \frac{k_1}{k_1 - k_2} A_o (e^{-k_2 t} - e^{-k_1 t}) \quad (8)$$

The number of atoms in the analysis volume B_t , which is initially zero, at first increases and then reaches a maximum when dB/dt becomes zero, and the system is then said to have reached a stationary state. Absorbance by analyte atoms will be used as a measure of B , recognizing that the absorbance is proportional to the analyte atom number density and the latter is proportional to B , since the analysis volume is constant.

The following two cases are of special interest [91]. Their derivation was given in the reference cited.

Case 1. If $k_2 \gg k_1$, $dB/dt = 0$, and the system is said to have reached a steady state. Therefore,

$$B = A_o \frac{k_1}{k_2} \quad (9)$$

and B is therefore much less than A_o ; hence, the steady-state system gives poor relative sensitivity. This mode of atomization requires that the total number of analyte atoms which enter the analysis volume, A_o , greatly exceeds the rate of atomization multiplied by the total duration (time) of atomization. This mode will be called the "steady-state atomization". Steady-state systems are useful for the purpose of quantitative determination when the total number of analyte atoms entering the analysis volume A_o

is relatively high, so that even with $k_2 \gg k_1$, a measurable analyte signal is obtained.

Note that for a constant rate of introduction of atoms,

$$B = A_o \frac{k_1}{k_2} \quad (9)$$

and therefore, a steady-state signal is obtained regardless of the relative values of k_1 and k_2 , provided that the total number of atoms which enter the analysis volume, A_o , greatly exceeds the rate of atomization multiplied by the total duration (time) of atomization, and the ratio of k_1/k_2 remains constant. This is true for the direct atomization of solid samples by cathodic sputtering in a GD.

Case 2. If $k_1 \gg k_2$, $B \equiv A_o$ and B reaches its maximum possible value, giving the maximum possible peak-height absorbance. This mode of atomization requires that the total number of analyte atoms, A_o , must enter the analysis volume in a relatively short time. The absorbance signal rises extremely rapidly to attain a peak value and then decays exponentially. This mode will therefore be called "transient atomization".

CHAPTER 3

Study of atomization of Au, Fe and Mg from a sodium chloride matrix by cathodic sputtering in a glow discharge for atomic absorption spectrometry

3.1 Experimental

3.1.1 Apparatus

A laboratory-constructed atomizer (Figure 3.1a) was used [48]. The atomizer was mounted in the usual position of the burner assembly in a Varian-Techtron model AA-5 atomic absorption spectrophotometer, and was operated as part of the atomic absorption spectrophotometer. The absorbance and the discharge voltage were recorded simultaneously using a Nicolet Model 201, two-channel digital oscilloscope. The hollow-cathode lamps used were manufactured by Westinghouse.

A comparative study of the power supply and gas-control system supplied with the commercially available ATOMSOURCE cathodic sputtering atomizer for AAS with those previously used in our laboratory-constructed cathodic sputtering atomizer for AAS [48] was done. The limitations of the ATOMSOURCE power supply and the gas control system were discussed previously by Chakrabarti *et al.* [40]. Henceforth, the ATOMSOURCE power supply with its gas control system will be referred to as the

Figure 3.1a - Schematic diagram of the laboratory-built atomizer.

apparatus for the transient mode of atomization, and the model MDX-1K power supply (Advanced Energy Industries Inc., Fort Collins, CO, U.S.A.) with the laboratory-constructed gas control system will be referred to as the apparatus for the pulsed mode of atomization.

The transient mode of atomization experiments used the ATOMSOURCE power supply, which was capable of either current or voltage regulation, and was used in the current regulation mode. This power supply had a maximum output of 300 mA at 1500 V, giving a maximum output of 450 W; however, because of limitations in the ATOMSOURCE gas control system the useable power was often considerably less. The microprocessor controlling the power supply allowed for discharges of 1 s and multiples thereof. The ATOMSOURCE controlled the pressure by varying the Ar gas flow rate; the result was a high and variable flow rate of the Ar discharge gas over which the operator had no control. The atomizer pressures quoted for this equipment were those read from the ATOMSOURCE controller, the actual pressure in the atomizer was slightly different. A laboratory-constructed power supply [92] for the hollow-cathode lamp modulated at 843 Hz and a synchronous detection system with a laboratory-constructed lock-in amplifier having a time constant variable from 2 to 104 ms were used. A time constant of 2 ms was used for this work. Other experimental conditions are given in Tables 3.1 and 3.2.

The pulsed mode of atomization experiments used the MDX-1K power supply and the laboratory-constructed gas-control system [48]. This apparatus was used in order to achieve fine control of the power and of the duration of the discharge and to control the

Table 3.1 Experimental conditions for DC-sputtering with the ATOMSOURCE power supply.

Analyte	Wavelength (nm)	Spectral bandpass (nm)	Analyte mass (ng)	Hollow-cathode lamp current (mA)
Au	242.8	1	5	6
Fe	248.3	0.5	5	6
Mg	285.2	1	0.1	1

Table 3.2 Discharge parameters for DC-sputtering of solution residues with the ATOMSOURCE power supply.

Preburn time	2 sec
Preburn DC current	220 mA (Au, Mg), 150 mA (Fe)
Preburn running gas pressure	8 Torr
Burn time	2 sec
Burn stabilization time	46 sec
Burn DC current	0.0 mA
Burn running gas pressure	8 Torr
Flush gas pressure	12 Torr
Flush time	10 sec
Standby flush gas pressure	8 Torr
Vacuum target gas pressure	550 Torr
Maximum time to vacuum	30 sec
Time to reach running gas pressure	10 sec
Maximum time to reach positive gas pressure	10 sec
Minimum voltage	250 volt
Maximum voltage	1500 volt
Minimum current	4 mA
Maximum current	250 mA

pressure and the flow rate of the discharge gas independently. This apparatus was described in detail by Hutton *et al.* [48]. For these experiments, the hollow-cathode lamp was modulated at 1 kHz and a time constant of 1 ms was used for the lock-in amplifier, model SR530 (Stanford Research System Inc., U.S.A.) of the detection system. Other experimental conditions for these experiments are given in Table 3.3.

3.1.2 Gas control system

Ar gas (99.997% pure) was used as sputter gas. Insufficient purity of carrier gas manifests itself in excessive heat development in the sample, even at fairly low power dissipation [12]. A moisture trap (Chromatographic Specialities, model No. MT120-4) was used to remove water from the sputtering gas. The sputtering gas was then passed through a particulate filter (Matheson Gas Products, Canada, model 6183) to remove particulate matter. For experiments in which independent control of gas flow rate and pressure was required, a laboratory-built gas control system [48] was employed (Figure 3.1b). The gas flow rate was regulated using a Nupro fine-regulating needle valve and was measured using the flow rate transducer of a mass flow controller (Sierra Instrument, model No. 740-05-2). A digital voltmeter (Keithley Instruments model 190) which displayed the gas flow rate was employed. This transducer was capable of measuring up to five standard litres per minute (SLPM) of gas. The gas was then admitted into the chamber through a 6.3 mm compression fitting mounted on the top of the chamber. The gas pressure was monitored on the outlet side using a Pirani gauge (Granville-Phillips Convectron Gauge, model No. 275). The gauge was calibrated for both N₂ and Ar gases. The gas pressure was controlled by throttling the vacuum line using a Whitey ball

Table 3.3 Experimental conditions for DC-sputtering with the MDX-1K power supply

Analyte	Wavelength (nm)	Spectral band pass (nm)	Analyte mass (ng)	Hollow-cathode lamp current (mA)	Ar gas flow rate (SLPM)	Ar gas pressure (Torr)	Power (W)
Au	242.8	0.33	5	4.5	0.5	8	160
Fe	248.3	0.33	5	5	0.5	10	70
Fe	248.3	0.33	5	5	0.5	10	330

Figure 3.1b - Schematic diagram of the gas control apparatus.

valve and a Whitey regulating valve in a parallel configuration. The ball valve was used for coarse control of the gas pressure while the regulating valve gave fine control. Although there is no direct indication of the gas pressure in the discharge chamber, the gas pressure measured using the Pirani gauge can be a useful guide. A two stage vacuum pump (Edwards High Vacuum, model E2M5) fitted with an oil mist filter (Edwards High Vacuum, model EMF10) and a fore-line trap eliminated the back diffusion of pump oil vapour into the sputtering cell.

For measurements in which independent control of gas pressure and flow rate was not essential the gas delivery/pumping system of the ATOMSOURCE (Analyte Corp., Grants Pass OR) was used.

3.1.3 Test solutions and reagents

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions were prepared as follows. For Fe (1000 $\mu\text{g/mL}$), the metal was dissolved in 50% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. For Au, the stock solution (1000 $\mu\text{g/mL}$, prepared by dissolving pure gold in aqua regia), was supplied by Harleco (Philadelphia, PA, U.S.A.). For Mg (1000 $\mu\text{g/mL}$), MgO (Baker Analyzed Reagent, 94.1% pure) was dissolved in 10% (v/v) nitric acid (ULTREX) and the solution was diluted with ultrapure water. A 10% (w/v) NaCl stock solution was prepared by dissolving pure NaCl (BDH) in ultrapure water. Ultrapure water of resistivity 18.3 M Ω cm was obtained directly from a Milli-Q2 Water Purification System (Millipore Corp., Canada). All test solutions were prepared by serial dilution of the above stock solutions with ultrapure water immediately prior to determination.

3.1.4 Procedure

Blocks of pure copper and pyrolytic graphite were used as cathodes. The cathodes were polished (working surface only) to 400 grit with an electric polishing machine, then cleaned with ethanol, and air-dried. The clean, dry cathode was then clamped to the atomizer. Two L-brackets were attached to the outer surface of the cathode plate. These L-brackets were positioned perpendicular to each other so that one corner of the square, removable cathode was placed at the intersection of the L-brackets, making the position of the cathode reproducible. Prior to every atomization cycle, the cathodes were sputter-cleaned to ensure a reproducible sputtering surface and to create a circular cavity into which the test solution was pipetted (the effective surface area of the cathode was defined by the sputtered region provided by the ATOMSOURCE sampling orifice). The cathode was then detached from the atomizer and laid flat with the prepared surface facing up. A 1 μL volume of the test solution was then pipetted in the centre of the cavity with a Hamilton microsyringe, fitted with a Chaney adaptor, model No. 7105 NCH, part No. H88004 (Chromatographic Specialities). The test solution was then air-dried outside the atomizer and the cathode re-clamped to the atomizer.

Whenever the ATOMSOURCE power supply was used, the following gas flushing sequence was used as a part of the run mode. The atomizer pressure was maintained at 10 Torr of Ar gas for 10 s; the atomizer was evacuated to less than 100 mTorr, then re-pressurized to the pre-selected operating pressure. When the atomizer reached the operating pressure, the glow discharge was automatically initiated. The oscilloscope and

spectrophotometer were triggered manually just prior to the initiation of the discharge. In all cases, blanks were run to ensure that there was no sample carry-over from run to run and to subtract blank absorbance from the gross absorbance to obtain the net absorbance.

For the MDX-1K apparatus the following procedure was adopted. The cathode was clamped to the cathode plate of the atomizer and the gas solenoid on the vacuum line was opened, evacuating the cell to less than 100 mTorr. When this pressure was attained the gas solenoid on the Ar gas inlet was opened and the fine-regulating needle valve was adjusted to give the desired Ar gas flow rate. When the desired flow rate of the Ar gas was attained the valve on the vacuum line was adjusted to give the desired pressure. The oscilloscope and the function generator that controlled the power supply were then triggered simultaneously, and plots of the absorbance signal intensity versus time were obtained together with the corresponding voltage.

The mean peak height or mean peak area was obtained from 4 to 7 replicate samplings of each solution sample. Typical uncertainties were about 10%. The error bars in the figures represent one standard deviation for 4 to 7 measurements. Since sputtering is an inefficient process, most of the power input to the system appears finally as heating of the target [3]. Nevertheless, in all experiments, the temperature was kept low enough, by the cooling system, to prevent significant thermal vaporization, oxidation or diffusion of sample.

Before deposition of the sample solution on a freshly-surfaced cathode, the cathode was sputtered for 1 minute using the same experimental conditions as used for

the subsequent determination, in order to create a circular cavity into which the sample solution was pipetted. This circular cavity, which was approximately 5 mm in diameter, had 6 depressions (craters) corresponding to the 6 gas jets used for the introduction of the Ar discharge gas into the atomizer. A pre-sputtering time of 1 minute was found to give the best compromise between having a cavity so deep that a long time was required to re-surface the cathode, and having the cavity so shallow that the sample solution was inadequately contained, resulting in sample spread and consequent poor sensitivity and reproducibility. The cathode did not have to be re-surfaced after every run because the discharge itself "sputter-cleaned" the cathode surface; the cathode was therefore re-surfaced periodically as required.

3.2 Results and Discussion

3.2.1 Parametric evaluation

Figure 3.2 shows the variation in the peak-height and the peak-area absorbances with Ar gas pressure for DC-sputtered solution residue of 5 ng Au at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply (pulsed mode of atomization). Figure 3.2 shows that there is an optimum Ar gas pressure of 8 Torr at which Au atoms show maximum absorbance. At Ar gas pressures higher than 8 Torr, the absorbance decreases which is most probably due to redeposition of sputtered materials which prevents the arrival of analyte atoms in the analysis volume. At the same time, the voltage which determines the sheath voltage at the cathode surface decreases as the gas pressure increases (Figure 3.3); therefore, Ar ions travel a too short

Figure 3.2 - Variation of peak-height and peak-area absorbances with Ar gas pressure for DC-sputtered solution residue of 5 ng Au at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply. (O), Peak-height absorbance; (■), peak-area absorbance.

Figure 3.3 - Cathode potential as a function of Ar gas pressure in DC-sputtering of solution residue of 5 ng Au at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply.

distance in the accelerating field of cathode sheath to gain enough kinetic energy and consequently the sputtering yield decreases [93]. An experiment with similar discharge conditions was performed for 5 ng Au in the presence of 300 ng NaCl and the results are shown in Figure 3.4.

Generally, optimum discharge gas pressure depends on the sputtering gas, the cathode material and the analyte [3]. The number of ionizing collisions, which sustain the discharge, increases with increasing discharge gas pressure. The discharge gas ions have a smaller energy distribution at low pressures, because of the longer mean free path. Consequently, the sputtering yield becomes small at the lower end of discharge gas pressure range. At high discharge gas pressures, on the other hand, materials sputtered from the sample may collide with discharge gas atoms on their way to the analysis volume, and the collision frequency will increase with increasing discharge gas pressure. The result of this collision is redeposition of the sputtered atoms. Therefore, the optimum discharge gas pressure is a compromise between an increase in ionizing collisions and a decrease in redeposition of analyte atoms. Hence, the discharge gas pressure that gives the maximum number of sputtered atoms in the GD must be determined experimentally.

Figure 3.5 shows the variation in the peak-height and the peak-area absorbances with the Ar gas flow rate for 5 ng Au, DC-sputtered from a solution residue, using MDX-1K power supply. For this experiment, the Ar gas pressure and power were held constant at 8 Torr and 160 W, respectively. An Ar gas flow rate of 0.5 SLPM, gives the maximum absorbance. At the Ar gas flow rates lower than 0.5 SLPM, the transport

Figure 3.4 - Variation of peak-height and peak-area absorbances with Ar gas pressure for DC-sputtered solution residue of 5 ng Au in the presence of 300 ng NaCl at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply. (○), Peak-height absorbance; (■), peak-area absorbance.

Figure 3.5 - Variation of peak-height and peak-area absorbances with Ar gas flow rate for DC-sputtered solution residue of 5 ng Au at constant power and constant Ar gas pressure of 160 W and 8 Torr, respectively, using MDX-1K power supply. (O), Peak-height absorbance; (■), peak-area absorbance.

efficiency of sputtered atoms into the analysis volume and consequently the measured absorbances are small. At Ar gas flow rates higher than 0.5 SLPM, the decrease in absorbance is probably due to a decrease in residence time of atoms within the analysis volume. Figure 3.6 shows a similar experiment for 5 ng Au in the presence of 300 ng NaCl.

Figure 3.7 shows the variation in the peak-height and the peak-area absorbances of 5 ng Au DC-sputtered from solution residues, using MDX-1K power supply, as a function of discharge power at constant Ar gas flow rate and pressure of 0.5 SLPM and 8 Torr, respectively. Decrease in absorbance at high power was probably due to massive redeposition of Cu cathode atoms (with high sputtering rate) which buried the analyte atoms [34]. At the same time, with increasing applied power, high-energy Ar ions penetrated further into the cathode lattice, but dissipated their energy in collisions too deep into the lattice to cause sputtering. Hence, the sputtering rate was reduced [14]. It was not possible to increase the power further because of arcing problems. A similar experiment was performed for 5 ng Au in the presence of 300 ng NaCl (Figure 3.8). Comparison of Figure 3.7 with Figure 3.8 shows that the threshold energy (defined as that ion energy below which no sputtering occurs [14]) for sputtering of Au is lower in the presence of NaCl.

3.2.2 Study of NaCl matrix interference using

ATOMSOURCE and MDX-1K power supplies

Matrix interferences were studied with one analyte and one matrix species, using

Figure 3.6 - Variation of peak-height and peak-area absorbances with Ar gas flow rate for DC-sputtered solution residue of 5 ng Au in the presence of 300 ng NaCl at constant power and constant Ar gas pressure of 160 W and 8 Torr, respectively, using MDX-1K power supply. (O), Peak-height absorbance; (■), peak-area absorbance.

Figure 3.7 - Variation of peak-height and peak-area absorbances with discharge power for DC-sputtered solution residue of 5 ng Au at constant Ar gas flow rate and pressure of 0.5 SLPM and 8 Torr, respectively, using MDX-1K power supply. (O), Peak-height absorbance; (■), peak-area absorbance.

Figure 3.8 - Variation of peak-height and peak-area absorbances with discharge power for DC-sputtered solution residue of 5 ng Au in the presence of 300 ng NaCl at constant Ar gas flow rate and pressure of 0.5 SLPM and 8 Torr, respectively, using MDX-1K power supply. (○), Peak-height absorbance; (■), peak-area absorbance.

a fixed mass of analyte element and an increasing mass of the matrix species. With the ATOMSOURCE power supply, the gas flow rate could not be controlled and the power supply was used in its constant current mode. For controlling gas flow rate and pressure independently and for applying a constant discharge power, the MDX-1K power supply with the laboratory-built flow rate control was used.

Figure 3.9 shows the percent peak-height recoveries of 5 ng Fe DC-sputtered from solution residues deposited on Cu cathodes, in the presence of different amounts of NaCl using the transient (ATOMSOURCE power supply) and the pulsed (MDX-1K power supply, power = 70 W) mode of atomization. It can be seen from Figure 3.9 that the presence of even small amounts of NaCl interferes with the AAS signal when the transient mode of atomization is used. In contrast to this, the presence of up to 500 ng NaCl [$\log(\text{mass of NaCl/ng}) = 2.7$] does not interfere with the AAS signal when the pulsed mode of atomization is used. It seems that using a constant power mode of atomization, such as that provided by MDX-1K power supply, is more reliable than the constant current mode such as that provided by ATOMSOURCE power supply. Generally, the constant power mode strikes an advantageous compromise between current and voltage control. As cathodic sputtering occurs in the region of an abnormal GD, where the voltage increases rapidly with the current, the power is a more meaningful experimental parameter than either voltage or current.

It should be mentioned that a "false matrix effect" also leads to a decrease in peak-height absorbance. This effect is the reduction of signal due to the dilution of the analyte atoms in the solution residue deposited on the cathode surface by the matrix

Figure 3.9 - Percent peak-height and peak-area recoveries of 5 ng Fe from solution residues with NaCl matrix, DC-sputtered from Cu cathode. (O), ATOMSOURCE power supply; (■), MDX-1K power supply (power = 70 W). For experimental conditions see Tables 3.1 and 3.3.

components [94]. The solution residues form a deposit the thickness of which depends on the absolute amount of matrix components. If the same amount of analyte is deposited on the cathode surface from two samples, each having very different amounts of matrix components, the effect of the matrix components is to dilute the analyte. Thus, an increase in matrix components (such as NaCl) will lead to a decrease in the number of analyte atoms available for the sputtering per unit surface per unit time. In other words, the sputtering process is expected to remove analyte from a thick deposit more slowly than from a thin layer of the same mass of analyte spread over a much larger surface area [95].

The dilution effect on peak-height absorbance is negligible if the total amount of solution residue is insufficient to build up deposits of considerable thickness, or if the sputtering rate is increased by changing discharge conditions such as gas pressure, gas flow rate, applied power, type of cathode material or discharge gas.

Figure 3.9 also shows the peak-area recoveries of 5 ng Fe, DC-sputtered from solution residues (see the peak-height recoveries shown in Figure 3.9) as a function of the NaCl matrix mass. As it is shown in Figure 3.9, up to 500 ng NaCl [$\log(\text{mass of NaCl/ng}) = 2.7$] does not interfere with 5 ng Fe in solution residues when MDX-1K is used as the power supply.

Figure 3.10 shows the variation of the negative sheath voltage at the cathode surface, with the mass of the NaCl matrix in Fe solution residues at Ar gas pressure of 8 Torr and DC current of 150 mA, using ATOMSOURCE power supply. As seen from Figure 3.10, the sheath voltage becomes more positive as the mass of NaCl is increased.

Figure 3.10 - Variation of the cathode sheath voltage with increasing mass of NaCl matrix in DC-sputtering of Fe solution residue using ATOMSOURCE. For experimental conditions see Table 3.1.

This condition provided less energetic sputter ions which resulted in less atomization of Fe in the presence of increasing amounts of NaCl matrix, and consequently, decreased the recoveries. It is therefore concluded that the recovery is improved by applying higher power. These results are similar to the results obtained by Riby and Harnly [96] on the effect of the concentration of NaCl on the discharge voltage profile for hollow anode-furnace atomization non-thermal excitation spectrometry (HA-FANES). In their experiments a graphite furnace was used for sample atomization, and a GD formed by a central coaxial graphite cathode was used for sample excitation. Riby and Harnly [96] found that as the concentration of NaCl was increased, the discharge voltage decreased until the discharge was entirely shorted.

Figure 3.11 shows the peak-height and the peak-area recoveries of 5 ng Fe, DC-sputtered from solution residues deposited on copper cathodes, in the presence of different masses of NaCl, using the pulsed mode of atomization, with discharge powers of 70 and 330 W. The lower power of 70 W was chosen as being typical of the lower power available with the ATOMSOURCE power supply as opposed to the MDX-1K power supply. Figure 3.11 shows that the peak-area recoveries of Fe increase when higher power is used. Using the higher power allows for the quantitative determination of Fe in the presence of 1000 ng NaCl, whereas only up to a maximum of 500 ng NaCl can be tolerated at the lower power. The greater peak-area recovery probably suggests that the interference is at least partly the result of incomplete sample atomization at the lower power of 70 W (ATOMSOURCE), as opposed to the higher power of 330 W (MDX-1K). These results also confirm that the peak-area absorbance gives better

Figure 3.11 - Percent peak-height and peak-area recoveries of 5 ng Fe from solution residues with NaCl matrix, DC-sputtered from Cu cathode for different applied powers using MDX-1K power supply. For experimental conditions see Table 3.3. (○), 330 W; (■), 70 W.

accuracy than the peak-height absorbance for the analysis of real samples using cathodic sputtering atomization. This is because peak-area absorbance is not subject to the variations which affect the peak-height absorbance as a result of changes in the kinetics of sample atomization and entry into the analysis volume, whereas peak-height absorbance is subject to these variations.

Figure 3.12 shows the peak-area and peak-height recoveries of 5 ng Au, DC-sputtered from solution residues deposited on copper cathodes, in the presence of different masses of NaCl using the transient and the pulsed mode of atomization. This figure shows that the interference of NaCl is less severe with Au than with Fe (see Figure 3.9). Figure 3.12 also shows the superiority of the peak-area over the peak-height recovery, and the superiority of the pulsed over the transient mode of atomization. In all cases, discharge voltage profiles similar to those of Chakrabarti *et al.* [40] were observed, suggesting that the mechanism of the interference was similar for the transient and the pulsed modes of atomization. As discussed by Headrick *et al.* [97], the interference was probably the result of the sputtering of large amounts of the matrix ions into the discharge; the matrix ions disrupted the discharge by carrying a considerable portion of the discharge current while being much less efficient than Ar^+ ions in sputtering. Build-up of a positive surface charge on the surface of the cathode by the non-conducting matrix might also play a role in the observed interference by making it difficult for the discharge to become established. To eliminate these effects, matrix interferences were studied using RF-sputtering (Chapter 7). In a similar experiment but using inductively-coupled plasma mass spectrometry (ICP-MS) the recoveries of Au in

Figure 3.12 - Percent peak-height and peak-area recoveries of 5 ng Au from solution residues, with NaCl matrix, DC-sputtered from Cu cathode. (O), ATOMSOURCE power supply (70 W); (■), MDX-1K power supply (160 W). For experimental conditions see Tables 3.1 and 3.3.

the presence of different amounts of NaCl were found to be very poor; the recoveries for 5 ng Au in the presence of 10, 100 and 1000 ng NaCl were found to be 0.31, 0.02 and 0.06 percent, respectively, with a relative standard deviation of about 3%.

Kinetic modelling was performed for sputtering of solution residues of 5 ng Au, in the both absence and presence of different masses of NaCl, using the ATOMSOURCE. Experimental and theoretical absorption profiles are shown in Figure 3.13. Theoretical absorption data were calculated using a procedure shown in the Appendix. Kinetic modelling was performed assuming that consecutive, first order reactions occur during formation and introduction of atoms into and their loss from the analysis volume, as done by Chakrabarti et al. [1]. In Table 3.4, k_1 and k_2 are the first order rate constants for analyte atoms formation in and loss from the analysis volume, respectively. t_{max} is the time required to attain the maximum absorbance. Table 3.4 shows that there is no significant difference between the transport rates of Au atoms from the analysis volume, in the presence and in the absence of NaCl.

Figure 3.14 shows the percent peak-height and peak-area recoveries for Fe, Mg and Au atomized from a Cu cathode in a matrix of NaCl. Figure 3.14 indicates that in DC-sputtering in the presence of less than 500 ng NaCl [$\log(\text{mass of NaCl/ng}) = 2.7$], the percent recoveries of Au are better than those of Fe and Mg. The percent recoveries (for both peak area and peak height) of Au, Fe and Mg are smaller the higher the melting points of their chloride salts are. This can be related to sputtering yield as melting point is a measure of the surface binding energy. Melting points of AuCl_3 , FeCl_3 and MgCl_2 are 254 (decomposes), 306 and 714 °C, respectively.

Figure 3.13 - Comparison of the theoretical and the experimental absorbance profiles of Au sputtered from solution residues with various concentrations of NaCl matrix deposited on the Cu cathode using ATOMSOURCE. (●) Experimental profile. Lines are calculated absorbances. For theoretical results see Table 3.4.

Table 3.4 Rate constants for transient atomization of Au solution residue, deposited on Cu surface, sputtered in the presence of various masses of NaCl using ATOMSOURCE power supply.

Sample sputtered	k_1/ms^{-1} (± 20)	k_2/ms^{-1} (± 5)	t_{max}/ms
5 ng Au	240	30	10
5 ng Au + 10 ng NaCl	240	30	10
5 ng Au + 300 ng NaCl	200	40	10
5 ng Au + 1000 ng NaCl	200	40	10

Figure 3.14 - Percent peak-height and peak-area recoveries of Au, Fe and Mg solution residues sputtered from NaCl matrix. For experimental conditions for each element see Table 3.1.

Figure 3.15a shows the percent peak-height recovery of 5 ng Au as a function of Ar gas pressure in the presence of 300 ng NaCl using MDX-1K power supply. The Ar gas flow rate and the applied power were 0.5 SLPM and 160 W, respectively. This figure shows that peak-height recovery at first increased with increasing Ar gas pressure, probably as a result of an increase in the atomization yield of Au atoms. Figure 3.15b shows that with increasing pressure of Ar gas the discharge voltage decreases. In the presence of NaCl, this decrease is more pronounced. The discharge current for sputtering of Au in the presence of NaCl increased with increasing pressure of Ar (Figure 3.16) which is thought to be a possible reason for improvement in the recovery. Since NaCl provides a nonconductive matrix, it is most probable that secondary ions are responsible for changing the current, as the cathode current includes a secondary electron component [3]. When particles such as ions, electrons, photons and neutral atoms (both ground state and metastable) strike a surface, one of the possible results is that an electron is ejected. These electrons, known as secondary electrons, are accelerated across the positive ion sheath into the plasma and are responsible for maintaining the electron supply and sustaining the GD. The yield of secondary electron emission depends on the energy of the bombarding particle and is strongly dependent on the condition of the surface. Insulators, such as NaCl residue, generally have extremely high values for the yield of secondary electrons [3,98]. Similar observations are seen in deposition processes in the removal of the layer of metal oxide that is inevitably on the surface of the target. The removal of the metal oxide is accompanied by a corresponding change (usually decrease) in the discharge current. This is explained by the difference

Figure 3.15a - Variation of peak-height recovery with Ar gas pressure for DC-sputtered solution residues of 5 ng Au in the presence of 300 ng NaCl from a Cu cathode at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply.

Figure 3.15b - Cathode potential as a function of Ar gas pressure in DC-sputtering of solution residues of Au at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply. (●) For 5 ng Au. (◇) For 5 ng Au in the presence of 300 ng NaCl.

Figure 3.16 - Variation of discharge current with Ar gas pressure for DC-sputtered solution residues of Au from a Cu cathode at constant power and constant Ar gas flow rate of 160 W and 0.5 SLPM, respectively, using MDX-1K power supply. (●) For 5 ng Au. (◇) For 5 ng Au in the presence of 300 ng NaCl.

in the secondary electron coefficient of metal and metal oxide [3].

Variations of the secondary electron emission yield with surface condition, such as provided by the presence of NaCl in Au solution residue, are quite important in DC-sputtering where the magnitude of the yield plays a role in determining the voltage-current characteristics of the discharge [3,99]. By increasing current, there will be an increase in sputter ion flux which consequently leads to an increase in sputtering yield. The result shows that the voltage-current relationship in the discharge can be changed by varying the gas pressure while maintaining the same power input, and also that secondary electrons have an important role in cathodic sputtering in a glow discharge.

Figure 3.17 shows the effect of Ar gas pressure on the percent recovery of 5 ng Fe, sputtered from a Cu cathode in the presence of 1000 ng NaCl using MDX-1K power supply. Ar gas flow rate and applied DC power were 0.2 SLPM and 100 W, respectively. Figure 3.17 shows that the peak-area recovery is independent of gas pressure. The results also show that the residence time of sputtered Fe atoms in the analysis volume not only depends on NaCl matrix but also on discharge gas pressure.

Figure 3.18 shows the percent peak-height recovery for DC-sputtering of 5 ng Au as a function of Ar gas flow rate, using MDX-1K power supply, in the presence of 300 ng NaCl. The power and Ar gas pressure were 160 W and 8 Torr, respectively. Figure 3.18 shows that the presence of NaCl does not have a significant effect on the atomization efficiency of Au. Figure 3.19 indicates that the effect of the Ar gas flow rate on the discharge voltages of solution residues is the same with or without the NaCl matrix. This is in contrast to the effect of the Ar gas pressure on the discharge voltage

Figure 3.17 - Variation in the peak-height and peak-area recoveries with Ar gas pressure for DC-sputtered solution residues of 5 ng Fe in the presence of 1000 ng NaCl from a Cu cathode at constant power and constant Ar gas flow rate of 100 W and 0.2 SLPM, respectively, using MDX-1K power supply. (■): Peak-area recovery. (◇): Peak-height recovery.

Figure 3.18 - Variation in the peak-height recovery with Ar gas flow rate for DC-sputtered solution residues of 5 ng Au in the presence of 300 ng NaCl from a Cu cathode at constant power and constant Ar gas pressure of 160 W and 8 Torr, respectively, using MDX-1K power supply.

Figure 3.19 - Cathode potential as a function of Ar gas flow rate in DC-sputtering of solution residues of Au at constant power and constant Ar gas pressure of 160 W and 8 Torr, respectively, using MDX-1K power supply. (●) For 5 ng Au. (◇) For 5 ng Au in the presence of 300 ng NaCl.

in the presence of NaCl (Figure 3.15b). These results also show that the local changes in the Ar gas pressure, at the cathode surface, due to the effect of Ar gas flow rate is of no significance; it is known that discharge voltage at the cathode surface is pressure dependent.

The precision of the GD source for AAS of the solution residues at trace levels of Au was investigated using a series of solution residue films, each containing 5 ng Au, sputtered under optimal conditions of gas pressure and discharge current. Between each determination, the cathode was sputtered to check for any background contribution. Relative standard deviations (RSD) of 6% and 15% were obtained for peak-height and peak-area, respectively. For a similar experiment carried out with 5 ng Fe, the RSD was 5% for peak-height measurement and 17% for peak-area. For 0.1 ng Mg, the RSD for peak-height and peak-area absorbances were 19% and 24%, respectively. It seems that Mg solution residue shows poor reproducibility compared to Au and Fe. Given the large change in surface area and the dependence of sputter yield on ion bombardment angle [100], it is reasonable to expect cathode surface history to affect the sputtering. Bruhn and Harrison [34] showed a sequence of surface changes of a Cu cathode after various durations of Ar sputtering. Trapping of sample residue inside the cathode surface-cones, produced by bombarding ions, could make a nonhomogeneous surface which can influence the reproducibility of analytical results. Poor reproducibility in the absorption measurements disappeared when the cathodes were sputter-cleaned for identical times before a sample solution was deposited. Gough et al. [83] and Larkins [84] have shown the effect of water vapour on stability of sputtering and on atom production by GD

sputtering. It is therefore concluded that residual water molecules in the residue of aqueous solutions of Au, Fe and Mg salts can affect the reproducibility of results. This work suggest that peak-area absorbance is a better quantitative measure because the width of the peak changes from sample to sample and run to run, since the area of the peak often remains proportional to concentration. However, if the integration is carried too far into the wings of a peak, then the locations of the beginning and end of the peak may not be clear in the presence of noise. If the limits of integration approach the main part of the peak, more signal than noise will be rejected and the RSD of the integral will deteriorate. The influence of baseline noise on the choice of how much of a transient absorbance peak to include in the integral has been considered in detail by Piepmeyer [121].

3.2.3 Direct current sputtering of bulk solids

The atomic absorption of Fe from bulk solids (brass) using the steady-state mode of atomization was studied. The actual concentration of Fe in the brass sample was not critical as only the effects that different experimental conditions had upon the magnitude of the AA signals were of concern. The hollow-cathode lamp current was 5 mA and was modulated at 1 kHz. The wavelength chosen was 248.35 nm and spectral bandpass was set at 0.30 nm.

Figure 3.20(a) shows the variation in the absorbance of Fe with applied DC current at constant Ar gas pressure of 8 torr for different Ar gas flow rates. Within this range of Ar gas flow rate, the absorbance increased with increasing applied DC current. It is also seen from this figure that the sensitivity was highest at the Ar gas flow rate of

Figure 3.20 - Variation in the normalized absorbance and cathode potential with applied DC current for DC-sputtered Fe from brass at constant Ar gas pressure of 8 Torr and various Ar gas flow rates, using MDX-1K power supply.

0.5 SLPM. Figure 3.20(b) shows the voltage-current relationship, at constant Ar gas pressure of 8 torr, for various Ar gas flow rates. The dependency of operating voltage on discharge gas flow rate at constant current, which was also reported by other workers [48], predicts that there is a decrease in kinetic energy of sputter ions at higher discharge gas flow rate with consequent decrease in the sputtering yield of sample. According to Figure 3.20(b), the cathode voltage for an Ar gas flow rate of 0.5 SLPM is approximately equal to that for Ar gas flow rate of 0.4 SLPM, and greater than that for Ar gas flow rate of 0.6 SLPM. The absorbance results, shown in Figure 3.20(a), do not follow this trend. To explain this, it should be considered that with a gas-jet assisted atomizer the rate of atom removal from the analysis volume was affected by Ar gas flow rate [46], and consequently, the residence time of analyte atoms was highly dependent on the flow rate. At the lower gas flow rates, the transport efficiency of sputtered atoms into the analysis volume, and consequently, the measured absorbances are small. At higher Ar gas flow rates, decreases in the AA signals were observed probably because of decreasing residence time of atoms within the analysis volume.

For GD operating in an abnormal mode (as for most sputtering plasma) at a constant gas pressure, increases in discharge current must be accompanied by increases in operating voltage. Figure 3.21(a) is the plot of the variation in discharge voltage of the GD source as a function of applied DC current for various Ar gas pressures at a constant Ar gas flow rate of 0.5 SLPM. The slopes of voltage profiles are 4.6, 2.4 and 2.3 at gas pressures of 6.4, 8 and 9 Torr, respectively, which shows that at lower Ar gas pressure the dependency of voltage on discharge current is higher. Fang and Marcus

Figure 3.21 - Variation in the normalized absorbance and cathode potential with applied DC current for DC-sputtered Fe from brass at constant Ar gas flow rate of 0.5 SLPM and various Ar gas pressures, using MDX-1K power supply.

[19] also reported similar observation in sputtering of oxygen-free, hard copper (OFHC) in a planar, diode GD. High variation in the discharge voltage with DC current at low Ar gas pressures suggests the possibility of obtaining high kinetic energies by sputter ions. At low gas pressure, the thickness of the cathode sheath increases. This is because the product of the pressure and the thickness of the dark space is fairly constant for a DC discharge [3]. Sputter ions can spend a long time in the cathode sheath while passing through it and thus accumulate kinetic energy. This excess in kinetic energy of sputter ions can increase sputtering yield unless ions penetrate the crystal lattice of the sample cathode so deeply that most of their energy dissipates far from the surface of the cathode [13].

It is seen from Figure 3.21(b) that the absorbances of Fe atoms at Ar gas pressures of 6.4 and 8 Torr are higher than the absorbance at Ar gas pressure of 9 Torr. This confirms the explanation given above. But the absorbance is higher at Ar gas pressure of 8 Torr than at 6.4 Torr. To explain this, it should be considered that absorbance depends on the rate of removal of atoms from the analysis volume, which is pressure dependent and reflects the relative importance of the processes of diffusion and forced convection. Diffusion is more important at lower gas pressure and the rate of diffusion decreases with increasing gas pressure. Forced convection is more important at higher gas pressures and the rate of forced convection increases at higher gas pressure. Absorbance will be higher at higher gas pressures as long as the rate of removal of atoms from the analysis volume due to diffusion decreases and offset the increasing rate of atom removal due to forced convection [87]. Another factor to be considered is the chance

of redeposition of sputtered materials which is high at higher gas pressures. The optimum conditions should be set experimentally for each type of atomizers.

These results showed that in the abnormal glow discharge sputtering, the discharge gas flow rate should be considered for characterization of the dependence of discharge voltage and current. As Figure 3.20(b) shows, the dependence of discharge voltage on discharge current is lower at higher Ar gas flow rate. This observation can be explained by local increases in Ar gas pressure inside the atomizer at higher Ar gas flow rate. At the same time there is a gas pressure gradient near the cathode surface, believed to be due to the strong ion flux [3]. Therefore, it is concluded that the measurement of in situ gas pressure of the discharge glow is important in the characterization of sputtering.

3.3 Conclusions

Control of discharge gas flow rate and pressure is critical for studying the characteristics of sputtering. Both can affect the rate of atom removal from the analysis volume. Higher gas pressures increase redeposition of the sputtered atoms on the cathode surface. In a low-pressure GD, gas ions have a smaller energy distribution because of the longer mean free path; however, the discharge gas ion flux is also less. In order for the sputtering to occur, the discharge gas ions must have an energy greater than the threshold energy of the target cathode. Above the threshold energy the number of sputtered atoms increases exponentially at first, and then levels off, since very energetic discharge gas ions will penetrate the crystal lattice.

It was observed that less than 500 ng NaCl does not interfere in the determination of 5 ng Au. But both Fe and Mg absorption signals suffered from the presence of NaCl.

The recovery of the analyte from a NaCl matrix seems to be element-dependent, with Au giving better recovery than Fe and Mg. As metals give different recoveries in the presence of the same amount of NaCl, it seems that the matrix effect depends more on the nature of the analyte and the mass ratio of the analyte and the NaCl matrix rather than on the absolute amount of the NaCl matrix. For both pulsed and transient modes of atomization, the use of peak-area absorbance gives better recovery than peak-height absorbance. The observed interference of the NaCl matrix in the determination of metals is probably at least partly the result of incomplete atomization of the sample. The more efficient pulsed mode of atomization used with the laboratory-constructed atomizer resulted in a great improvement in the recovery over the less efficient transient mode of atomization available with the ATOMSOURCE commercial atomizer.

CHAPTER 4

Effects of discharge conditions on the sputtering and spatial distributions of analyte atoms in an RFGD atomizer for AAS

4.1 Introduction

The objectives were to evaluate the performance of a laboratory-built, demountable radiofrequency glow-discharge (RFGD) atomizer modified for use in atomic absorption spectrometry (AAS) by finding regions in the discharge that are suitable for AAS, as it is known that the composition of the GD is not homogeneous [102].

The investigation of distribution of analyte atoms in an atomizer for AAS is important for two reasons. First, the measurement of the distribution of species in a given atomizer provides a wealth of information for the investigation of fundamental processes that are occurring within the atomizer. Secondly, it has been shown theoretically that the absorbance signal is dependent not only on the number of absorbing species in the analysis volume but also on the distribution of these species [103,104].

4.2 Experimental

4.2.1 Sputtering atomizer

Figure 4.1 shows a schematic diagram of the RFGD apparatus. A similar apparatus has been described and characterized previously by Winchester et al. as an RFGD emission apparatus [63]. The apparatus consists of a hollow, stainless steel atomizer chamber ($9 \times 5 \times 5$ cm). Although no distinctly defined ground exists in the

Figure 4.1 - A schematic diagram of the RFGD apparatus. View from the top of the cell with the horizontal sampling axis lying in the plane of the paper, perpendicular to the sample surface. A: gas inlet port; B: atomizer chamber body; C: vacuum port; D: sampling orifice disk; E: sample; F: Cu disk; G: macor spacer; H: Cu rod; I: torque bolt; J: fused silica window; HCL: hollow-cathode lamp.

RF discharge (the net flow of charge to either electrode is zero), the sample is referred to as the cathode by analogy to the DC discharge. For experimental simplicity, the atomizer chamber is the grounded electrode which is made larger than the cathode so that all of the bias voltage resides on the cathode and there is no chance of sputtering of the chamber-wall materials (these act as contamination sources). By making the cathode area much smaller than the anode (chamber) area, the cathode sheaths are optimal for sputtering applications [3]. The vacuum port is located in the top-centre of the atomizer chamber. Two circular, fused silica windows (35 mm in diameter) are mounted on each side of the atomizer chamber to provide a light path for the hollow-cathode lamp radiation. An extra optical window is mounted directly opposite the sample location for optical emission purposes. The source also incorporates an easily removable sampling orifice disk (stainless steel) (Figure 4.2) equidistant from the two side windows, which facilitates our investigation, including studies of the role that limiting orifice geometry and consequently cathode area play in the characteristics of an RFGD atomic absorption source. Lazik et al. [105] used various limiting anode (orifice) diameters and thickness to evaluate their influence on plasma emission characteristics. In the present work, a sampling orifice diameter of 4.5 mm with a disk thickness of 4 mm was used. Placement of the sample into position for atomization is accomplished by using the brass torque bolt to compress the sample against a 6.5 mm i.d. Teflon O-ring, forming the necessary vacuum seal. There is a recess region (Figure 4.3) between the sample and orifice disk, provided by the arrangement of the Teflon O-ring. In the case of the RF power source, arcing across the sample and anode becomes a problem with a recess thickness of less

Figure 4.2 - Front view of the sampling orifice disk.

Figure 4.3 - Side view of the sampling orifice disk showing the recess region.

than about 0.2 mm [105]. The recess thickness in the cited source is small enough to operate at 13.56 MHz as the dark space thickness decreases with frequency. The width of the cathode dark space is typically 1 mm for usual operating conditions of the discharge so there is no chance of ion bombardment of the O-ring. This gap is also sufficiently small to prevent diffusion of the sputtered vapour into the region between the sample and the orifice disk, thereby enabling the cathode to remain electrically isolated from the rest of the atomizer chamber. A ceramic spacer, attached to the end of the bolt, provides the electrical isolation of the bolt from the sample. The RF feedthrough attached to the end of the coaxial RF power cable (RG-213U, Amphenol) is inserted into the bolt, and the male type-N connector is mated to the female connector until the Cu rod (ca. 3.1 mm in diameter) makes contact with the back of the sample. The length of this cable was kept at about 90 cm in order to avoid unnecessary impedance in the RF circuitry. The power cable used was coaxially shielded in order to reduce RF power losses resulting from radiated noise. It should be mentioned that in the design of an analytical RFGD, careful shielding of the powering cable should be considered. Plasma generators (e.g. ICP) are well known for their proficiency at broadcasting RF interference when not properly grounded and shielded. In order to minimize the RF interference, the source should incorporate coaxial shielding, extending from the power cable and sample holder to the sample surface. An additional feature of coaxial shielding is that it protects against electrical shock [106]. A disk of Cu (30 mm in diameter and 3 mm in thickness) was fastened at the tip of the Cu rod just between the Macor spacer and the sample to facilitate uniform RF power distribution over the sample cathode and

to ensure that the pressure of the sample clamp is evenly distributed across the entire sample. In addition, for sputtering of insulator materials, it is generally accepted that an insulator backed by a conducting RF powered electrode will not charge up to floating potential [3]. By using this disk, the excessive heating of the sample at high power dissipation is also prevented and fitting the sample is facilitated as well. This disk also facilitated impedance matching with the laboratory-modified impedance matching network [107] for different cathodes, as it was found that the tuning and loading compartments of the original impedance matching network were out of their ranges when cathodes such as Cu, glass, macor, or Al were used.

The atomizer was mounted on a laboratory-built XYZ Φ -adjustable platform. On the bottom of the atomizer-mount was an Al base which was securely attached to the instrument body by means of four bolts. The horizontal movement section was attached to the base, on the top of which was the vertical movement section. The rotational movement section was attached to the top of the vertical section. The atomizer chamber was attached to the rotational movement section by means of two bolts. Adjustment of the rotational position altered only the position of the atomizer relative to the light path of the hollow-cathode lamp without changing the horizontal or the vertical position of the atomizer. In this study, a fixed rotational position of atomizer was used so that the central axis of the atomizer chamber was parallel to the hollow-cathode lamp light beam. When the horizontal position was adjusted, the vertical and the rotational movement section also moved. When the height was adjusted, only the rotational movement section and the atomizer body moved along the vertical axis. All three movements were

controlled manually. Incremental linear markings at 1 ± 0.5 mm and 2 ± 1 mm intervals for horizontal and vertical movements, respectively, allowed reproducible placement of the atomizer chamber relative to the optical path. The origin of the coordinate was approximately a point on the central axis (Figure 4.3) of the sampling orifice disk and located at the cathode surface. "Horizontal distance" in figures refers to the distance of a vertical plane from the origin. This plane was on the cathode side of the atomizer and was parallel to the cathode surface. The zero horizontal distance was tuned by setting the horizontal movement section on the zero position as specified on the scale attached to the mount-base. The zero vertical distance refers to the points of the horizontal plane containing central axis of sampling orifice, which will henceforth be called the "horizontal plane". Horizontal distances were determined by setting the horizontal movement section to the positions specified on the scale attached to the mount-base. Negative distances refer to the points below the "horizontal plane", i.e. at the bottom-half of the atomizer chamber, and positive distances refer to the points at the top-half of the atomizer chamber.

4.2.2 Radiofrequency generator and impedance matching network

The RF generator and the impedance matching network employed were Model RFX 1250 (Advanced Energy) and AMNS-1500E (Plasma Therm, Inc. Kresson, N. J.), respectively. Good electrical grounding was made for proper impedance matching. The impedance matching network was an LC circuit which was tuned so that the total impedance of the network and the plasma equalled the output impedance of the RF generator (50Ω). To minimize RF interference and to avoid power losses due to the

large reactive current flowing about the circuit, the impedance matching network was mounted close to the discharge chamber, as suggested by the manufacturer, by using a three-foot long coaxial cable connector. Since the original component of the impedance matching network (AMNS-1500E) did not permit matching of the output impedance of the generator to the atomizer, the impedance matching network was modified. For tuning the impedance matching network, in order to achieve maximum power transfer and to protect the generator, a series of laboratory-built induction coils and various capacitors, connected both in series and in parallel were used. A schematic diagram of the impedance matching network is shown in Figure 4.4.

4.2.3 Discharge gas

Ar gas (99.997% purity) was used as the discharge gas. A moisture trap (Chromatographic Specialities Model No. MT120-4) was used to remove water vapour from the discharge gas. The discharge gas was then passed through a particulate filter (Matheson Gas Products). For experiments in which independent control of Ar gas flow rate and pressure was required, a laboratory-built gas control system was employed [48]. The Ar gas flow rate was regulated on the inlet line using a Nupro fine-regulating needle valve and was measured using the flow rate transducer of a mass flow controller (Sierra Instrument, model No. 740-05-2). This transducer was capable of measuring up to five standard litres per minute (SLPM) of Ar gas. The Ar gas was then admitted into the atomizer chamber through a 6.3 mm compression fitting, mounted on the top of the atomizer chamber. The pressure was monitored on the outlet side using a Pirani gauge (Granville-Phillips Convectron Gauge, Model No. 275). The gauge was calibrated for

Figure 4.4 - Modified impedance matching network. L : $2.0 \mu\text{H}$, CT : $25-500 \text{ pF}$, T : 300 Pf , CL : $7-1000 \text{ Pf}$, C : 500 Pf , LM : Loading Motor, TM : Tuning Motor, X : 50Ω coaxial cable.

both N_2 and Ar gas. The pressure was controlled by throttling the vacuum line using a Whitey ball valve and a Whitey regulating valve in a parallel configuration. The ball valve was used for coarse control of the gas pressure while the regulating valve gave fine control. A two-stage vacuum pump (Edwards High Vacuum, Model 5), fitted with an oil mist filter (Edwards High Vacuum, Model EMF10) and a fore-line trap for eliminating the back diffusion of pump oil vapour into the sputtering cell were used for pressure control. For measurements in which independent control of Ar gas pressure and flow rate was not essential, the gas delivery/pumping system of an ATOMSOURCE (Analyte Corp., Grants Pass OR) was employed.

4.2.4 Measurement system

The discharge source was mounted in the usual position of the burner assembly in a Varian-Techtron Model AA-5 AA spectrophotometer and was operated as part of the AA spectrophotometer. The absorbance profiles were recorded with a Nicolet Model 201 dual-channel digital oscilloscope. The Cu hollow-cathode lamp used was manufactured by Varian (Varian Techtron Pty. Ltd. Australia). The hollow-cathode lamp current was 4 mA and was electronically modulated at 1 kHz, and a lock-in amplifier (Stanford Research System Inc., SR530) with a time constant of 1 ms, was used. The light beam of the hollow-cathode lamp was focused to 6 mm in diameter as it passed through the atomizer chamber. The image of the light beam was 10 mm on both entrance and exit optical windows of the atomizer chamber. The wavelength chosen was the Cu I resonance line, 324.7 nm. The spectral bandpass was 1 nm. The RF generator

was used in the constant power mode, which made the parametric evaluation straightforward as there was a complex interdependence of the gas pressure, gas flow rate, current and voltage.

4.2.5 Procedure

Cathodes of oxygen-free, hard copper (OFHC) were used. The cathodes were $23 \times 23 \times 12$ mm blocks, with the 23×23 mm surface applied against the sealing O-ring. The working surface was polished to 400 grit with an electric polishing machine, then cleaned with ethanol and air dried. The cathodes were first sputter-cleaned for at least 3 min to ensure a reproducible atomization surface, as large changes in reproducibility were found with changes in the cathode surface [34]. Whenever the ATOMSOURCE control box was used, it was programmed in the flushing mode. The discharge gas pressure was maintained at 10 Torr of Ar gas for 10 s; after which the chamber was evacuated to 100 mTorr and then re-pressurized to the pre-selected operating pressure. Figure 4.5 shows the absorption profile of a clean pre-sputtered Cu surface with a sputtering time of 30 sec as a model profile at the Ar gas pressure and flow rate of 3.7 Torr and 0.1 SLPm, respectively and applied RF power of 40 W. Whenever the laboratory-built gas control system was used, the gas solenoid on the vacuum line was opened, evacuating the chamber to less than 100 mTorr. When this pressure was attained, the gas solenoid on the gas inlet was opened and the fine-regulating needle valve was adjusted to give the desired gas flow rate. When the required gas flow rate was attained the valve on the vacuum line was adjusted to give the desired gas pressure. When the discharge gas pressure reached the operating pressure,

Figure 4.5 - Absorbance versus time in the steady-state mode of RF atomization of cleaned pre-sputtered Cu cathode surface. Experimental conditions: Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 40 W; wavelength, 324.7 nm.

the oscilloscope and spectrophotometer were triggered just prior to applying the RF power. The RF generator was powered for at least 3 min to clean the Cu surface. For measuring absorbances of Cu atoms sputtered from the cleaned surface, the RF generator was powered for at least 10 s, which was sufficient for a steady-state sputtering. The RF generator output power was adjusted manually from the front panel controls of the generator, which displayed forward and reflected powers. The impedance matching network allowed the reflected power to be minimized automatically or matched manually by changing the capacitance of the loading or the tuning parts of the matching network, whenever needed. The RF generator output power can differ considerably from the actual power delivered to the discharge, owing to power losses in the transmission lines, electrical connections and the impedance matching network. The power losses have, however, been shown to be a relatively constant fraction of the total generator output power over a range of powers for at least one discharge system [108].

Sample loss rates for Cu cathode at different discharge parameters were obtained using pre-weighed Cu metal sheets ($24 \times 24 \times 2$ mm) that were sputtered for 15 min at an RF power of 30 W. The mass loss was determined by reweighing the cathodes on a microbalance (Mettler AT250) after allowing them to cool to room temperature. A similar procedure was performed for measuring sample loss rates for Al using Al sheets ($27 \times 21 \times 3.5$ mm) as cathodes.

4.3 Results and Discussion

4.3.1 Preliminary experiments

Because there was some fluctuation in the reflected RF power during the course of sputtering (less than approximately 1% of forward power), it was decided to investigate how changes in the reflected RF power of this magnitude would affect absorbance signals. The reflected RF power, displayed on the front panel of the power supply, was set up manually by changing the capacitance of loading and/or tuning components of the impedance matching network. The reproducibility and stability of the results showed that there was no significant variation in the absorbance in the 1% range of reflected powers as the relative standard deviation (RSD) associated with the absorbance measurement was about 1.1% ($n=10$), which was used as the criterion to indicate any significant variation in absorbance. Experimental conditions for comparing the reproducibilities of the results at two different levels of the reflected RF power were Ar gas pressure and flow rate of 3.7 Torr and 0.1 SLPM, respectively, at an RF power of 40 W. Absorbances of sputtered Cu atoms from a Cu cathode at zero and one percent power reflections were 0.272 ± 0.002 and 0.276 ± 0.002 , respectively.

Uncertainties associated with the positioning adjustment of the atomizer in both horizontal and vertical position propagate 1.7% RSD of uncertainty in the absorbance measurement. This uncertainty was measured by taking replicate ($n=6$) absorbance measurements of Cu for a specific location (horizontal position of 2 mm and vertical position of 6 mm) and set of discharge conditions (Ar gas pressure of 3.7 Torr, Ar gas flow rate of 0.1 SLPM and RF power of 40 W), moving the atomizer position and re-

setting it in between each measurement. Since only general trends were of interest, it was not necessary to do this for each measurement.

Clean-up of the cathode surface is a critical factor in the analytical sensitivity and reproducibility of results. The optimum pre-sputtering time (i.e., the time required to sputter a new cathode to achieve a representative surface [34]) was obtained by reading the Cu absorbance versus sputtering time at an Ar gas pressure of 3.7 Torr, Ar gas flow rate of 0.1 SLPM and applied RF power of 40 W. Figure 4.6(a) shows that the Cu absorbance increased and then remained essentially constant as a function of time, i.e. as a new layer of the Cu cathode was sputtered. After approximately 3 min, the RSD of absorbance was about 2% ($n=1365$ data points) over the following 12 min period. This variation in absorbance over the 12 min period was like the variation in the absorbance in sputtering of a cleaned surface for a short period of a few seconds (Figure 4.5). Once the Cu cathode surface was cleaned, the scatter in the absorbance value for a 10 s run was 1.8% at the discharge conditions of Ar gas pressure 3.7 Torr; Ar gas flow rate 0.1 SLPM, and applied power of 40 W. In general, pre-sputter times of 1–3 min were required to clean the surface and to achieve stable atomization rates under these moderate discharge conditions. Stabilization within 3 min of discharge initiation was also reported for non-conducting samples [105]. For the remainder of this work, a uniform pre-sputtering time of 3 min was adopted. The cathode is liable to become contaminated during the time that the system is open to air to load or unload it. When sputtering of a cathode surface is first started, the layer of metal oxide that is inevitably on the cathode surface is removed, revealing the metal [3]. The surface history of the cathode seems

Figure 4.6 - Variation in the absorbance of Cu atoms as a function of time at applied RF power of 40 W. Other experimental conditions: (a), Ar gas flow rate of 0.1 SLPM, Ar gas pressure of 3.7; (b), Ar gas flow rate of 0.4 SLPM, Ar gas pressure of 8 Torr.

to be of great significance. Large changes in reproducibility appeared to correlate with the changes in the cathode surface [34].

Figure 4.6 also illustrates an additional desirable quality of the RF GD-AAS source in its ability to operate stably over extended periods of time. Stabilization times for GD source would allow for the prompt analysis of a reasonable number of analytes in a given period of time [109]. The results show that the GD source is able to sustain a stable plasma for at least 3–15 min, which would enable the sequential AAS of samples such as metal alloys. This type of temporal stability is also important for in-depth profiling. The stability of the source is limited by the redeposition of a thin film of conducting sputtered materials within the recess region within the circumference of the O-ring seal as noted previously by Lazik and Marcus [105], effectively short-circuiting the cathode to the anode across the O-ring. The thin film of nonconducting materials such as Macor enables interchanging of samples without cleaning or replacing the O-ring.

Regardless of the duration of the sputtering time, the difference between Figures 4.5 and 4.6 is in the leading edge of the signal; Figure 4.5 has a faster rise than Figure 4.6. Although the same material and the same experimental conditions were used for both experiments, there was a significant difference between the atomization surface used to obtain them. Figure 4.6 was obtained with an unsputtered surface. Figure 4.5 was obtained by sputtering from the sputtered surface left after Figure 4.6 was obtained. The observed difference in the rate of rise of the absorbance signals between Figures 4.5 and 4.6 points to a significant feature of the sputtering of solid metals and alloys, which has

been also observed by other workers [87], that the sputtering rate and the sputtering yield depend on many factors including the physical conditions of the sputtering surface of the solid sample. A sputtered atom has to receive an energy which is sufficient to overcome its surface binding energy. The heat of sublimation provides a measure of the average binding energy. After stripping of the surface by sputtering, many atoms may be found at sites with lower numbers of nearest neighbours, such as at grain boundaries or dislocations, or an atom may be sitting on top of a filled plane. Such exposed atoms have a lower binding energy and are more readily sputtered than those from filled planes. Although sputtering is free from some of the background effects which can occur in a combustion flame, such as scatter from refractory particles and molecular absorption, some background non-atomic absorption can occur as a result of the agglomeration of sputtered atoms (clusters). However, the degree of attenuation of the incident beam depends on the matrix sputtered and is typically 0.25–1% for Cu [37].

4.3.2 Spatial Distribution of Analyte Atoms

In order to optimize AA signals, it is desirable to find a region in the atomizer chamber where the analyte atom density is the highest. Intense background emission and molecular clusters can cause some regions of the chamber to be useless for AAS. Furthermore, the GD plasma is an inhomogeneous medium, a fact which makes knowledge of the spatial distribution of sputtered neutrals critical for AAS [110]. With this goal in mind, absorbance signals were obtained at different regions within the atomizer chamber. Blocks of OFHC were sputtered under different discharge conditions and the absorbance of Cu (Cu I 324.7 nm) was measured. Horizontal profiles were

measured at horizontal distances of 11, 11.5, 12, 13, 14, 15, 17, 19, 21, 23, 26, 29, 32, 35, 38 and 41 mm from the Cu cathode surface. Vertical profiles were measured in 2 mm intervals over the vertical distances of 0-12 mm as well as 0 to -10 mm from the "horizontal plane", i.e., the plane containing the central axis of the sampling orifice (see Figure 4.3) at which the vertical distance is equal to zero.

The horizontal and vertical distributions of atoms, taken at various Ar gas flow rates, Ar gas pressures and applied RF powers are shown in Figures 4.7a-4.7d. The atom concentration is seen to be highest near the orifice disk surface and to decrease rapidly at greater horizontal distances. Similar patterns were observed vertically on either side of the "horizontal plane". It was not possible to determine the concentration gradient, if any, from cathode surface through the sampling orifice, because of geometrical constraints of the atomizer chamber. Specifically, it should be noted that the closest approach of the hollow-cathode lamp beam to the cathode surface was about 11 mm, so absorbance measurements closer than this to the cathode surface were not possible. It was not possible by AAS to know how atoms were distributed around the vertical plane (the plane which contained the central axis of sampling orifice and was normal to the hollow-cathode light beam). The fact that the concentration of sputtered atoms decreased further away from the orifice disk surface was most likely due to simple diffusion and convection processes. Aggregation of analyte atoms [30] or other atoms-consuming processes might also occur. Metal clusters in the GD have been observed experimentally [111] and may provide a possible explanation for the decreasing number of analyte atoms. Additionally, the RF potential in the negative glow (NG) region may

Figure 4.7a - Spatial distribution of Cu atoms (absorbance) inside the atomizer: Ar gas pressure, 8 Torr; Ar gas flow rate, 0.4 SLPM; applied RF power, 40 W. Maximum absorbance = 0.29.

Figure 4.7b - Spatial distribution of Cu atoms (absorbance) inside the atomizer: Ar gas pressure, 8 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 40 W. Maximum absorbance = 0.43.

Figure 4.7c - Spatial distribution of Cu atoms (absorbance) inside the atomizer: Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 40 W. Maximum absorbance = 0.38.

Figure 4.7d - Spatial distribution of Cu atoms (absorbance) inside the atomizer: Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied RF power, 55 W. Maximum absorbance = 0.39.

have a considerable role in the observed distribution as it continually changes through the NG region, whereas the glow region in the DC case is virtually field-free [63,112]. So this difference demands for similar spatial investigation of sputtered atoms by applying a direct current GD (DCGD) to the atomizer chamber at the similar and/or comparable discharge parameters, for comparison.

The sputtered atoms in the central region of the atomizer chamber are subjected to two counter currents: two Ar gas streams which direct the atoms out of this region and could make a rich reservoir of atoms above and below the "horizontal plane". The first stream is directed towards the vacuum port which pulls the atoms towards the top of the atomizer chamber, while the second one results from the influx of Ar gas and acts to push the atoms towards the bottom of the atomizer chamber. In general, Figures 4.7a-4.7d show that at the lower Ar gas flow rate the sputtered atoms are more concentrated at the top-half region of the atomizer chamber, where the vacuum port is located, in comparison with the bottom-half. This study shows how the location of the vacuum port and the Ar gas inlet affects the concentration of sputtered materials in the optical path.

Figures 4.7a and 4.7b show the distributions of ground-state Cu atoms at Ar gas flow rates of 0.4 and 0.1 SLPM, respectively, at a constant Ar gas pressure of 8 Torr and an applied power of 40 W. The absorbance of the sputtered atoms in front of the sampling orifice is decreased at the higher Ar gas flow rate. Simple geometric considerations of the source design show that the Ar gas is neither directed at the sample (cathode) surface, nor subjected to direct vacuum pumping within the confines of the sampling orifice, and consequently, the supply of atoms to the atomizer chamber remains

constant. This would suggest that the Ar gas flow rate does not show a distinct effect on the sputtering rate and on the transport efficiency of sputtered atoms within the sampling orifice. To verify this assumption, sample loss rates for Cu were determined at Ar gas flow rates of 0.4 and 0.1 SLPM at a constant pressure of 8 Torr and an applied power of 40 W. The sample loss rates were found to be $7.01 \times 10^2 \mu\text{g}/\text{min}$ (9% RSD, $n=5$) and $6.94 \times 10^2 \mu\text{g}/\text{min}$ (5% RSD, $n=5$), respectively. In a similar experiment, sample loss rates for Al were determined at Ar gas flow rates of 0.05 and 0.2 SLPM at a constant Ar gas pressure of 4 Torr and applied power of 35 W. The sample loss rate for Al was found to be about $54.0 \mu\text{g}/\text{min}$ (4% RSD, $n=5$) at both Ar gas flow rates. Mass loss rate, rather than sputter yields, were chosen because mass losses are easily measured. Before a sputter yield (in units of atoms removed per incident ion) can be calculated, discharge ion current must be estimated. Estimates of discharge ion current is not possible in RF mode and in DC mode vary from under 10% to 100% with respect to total discharge current. Further, when sputter rates are calculated with masses of cathode material lost during higher-pressure discharge, it is difficult to account for cathode atoms back-scattered onto the cathode by collisions with gas-phase atoms near the cathode [113]. This experiment suggests that the Ar gas flow rate does not appear to have a marked effect on the transport efficiency of atoms within the sampling orifice. The discharge gas flow rate could have two possible effects on the absorbances in different regions of the atomizer chamber. First, it could affect the sputtering rate if it alters the local pressure, and consequently, the DC self-bias potential. The dependence of DC self-bias potential on the gas pressure has been investigated by Winchester et al.

[63]. Secondly, it could affect the transport processes of analyte atoms through the atomizer volume. High flow rates of Ar gas would act to decrease the absorbance by decreasing the residence time of sputtered analyte atoms in all regions of the atomizer chamber as is shown in Figure 4.7a (in contrast to Figure 4.7b). This study seems to suggest the beneficial effect of the use of low and direct flow of Ar gas at the surface [67]. Such an experimental condition should help to sweep away sputtered atoms from the cathode surface, minimizing redeposition and maximizing transport efficiency of atoms through the sampling orifice, thereby increasing the analytical sensitivity of AAS. To test this idea, an experiment was done in which the inlet port of discharge gas was moved from the top of the atomizer chamber to the body of sampling orifice disk. The results of this experiment are shown in Chapter 5.

To measure any changes in the gas pressure at cathode surface due to gas flow rate, a device is needed to measure the voltage developed on cathode surface during the sputtering period for various discharge gas flow rates. Since DC self-bias depends on discharge gas pressure, pressure variation due to gas flow rate changes can be confirmed by observing changes in the DC self-bias potential (Chapter 5).

Figures 4.7b and 4.7c show the spatial distribution of ground-state Cu atoms at the Ar gas pressures of 8 and 3.7 Torr, respectively, at a constant Ar gas flow rate of 0.1 SLPM and applied power of 40 W. The Cu atoms are more extended from the orifice disk surface towards the central region of the atomizer chamber at the lower gas pressure. However, most of the sputtered atoms are still localized around the orifice disk surface as was observed in Figure 4.7a. In addition, side-on viewing of the GD plume

through the optical windows showed that the GD plume was more restricted at the Ar gas pressure of 8 Torr towards the orifice disk surface. Greater transport of Cu atoms and the extension of the discharge plume towards the central region of the atomizer chamber at the lower Ar gas pressure could be due to a reduction in the number of energy-attenuating collisions as a result of increasing the mean free-paths of Cu and Ar atoms at the low operating gas pressure. The high kinetic energy of sputtered atoms at low gas pressures definitely promotes the transport process. Greater transport of Cu atoms towards the central region (>20 mm) of the atomizer chamber at the Ar gas pressure of 3.7 Torr (Figure 4.7c) is responsible for the higher observed absorbance in this region. The definite skewing of the spatial distribution due to the vacuum pumping can also be seen more clearly here.

The maximum absorbance observed near the sampling orifice at the Ar gas pressure of 8 Torr (Figures 4.7b) is due to a number of factors. At the Ar gas pressure of 8 Torr, the plasma resides within the restricting orifice and probably provides for more efficient Ar ionizing collisions, which consequently increases the amount of sputtered atoms. Additionally, since the current is the dominant channel for increasing discharge power [63] and the root mean square ion current at the cathode increases with discharge gas pressure for a given power, the rate of sample loss should increase with increasing discharge gas pressure. Another explanation for the maximum absorbance observed near the sampling orifice at the higher discharge gas pressure could be increased localization (higher residence time) of Cu atoms in this region.

Figures 4.7c and 4.7d show the effect of different applied RF powers of 40 and

55 W on the spatial distribution of ground-state atoms at the constant Ar gas pressure of 3.7 Torr and Ar gas flow rate of 0.1 SLPM. There is not a great difference between absorbances or spatial distribution of sputtered atoms between these two applied powers, suggesting that the sputtering efficiencies are more or less equal at these two applied powers. The amount of sputtered material would be expected to increase with increasing discharge power for a given set of pressure/flow conditions. Figure 4.8 shows the absorbance of Cu as a function of applied RF power. In Figure 4.8, the Ar gas pressure and flow rate were 3.7 Torr and 0.1 SLPM, respectively. It can be seen from Figure 4.8 that there is a threshold energy of about 5 W at a pressure of 3.7 Torr, above which the sputtering rate increases in a near-linear fashion with increases in discharge power, levelling off at the highest discharge powers. The levelling effect is probably the result of a combination of factors: sample heating at high discharge powers; spatial re-orientation of the plasma; and possible discharge power losses through radiation or contact heating. Increases in discharge power are known to affect all of these factors. In terms of what is directly observable, sample heating seems to be the most likely factor. The target temperature of hundreds of degrees, which are quite likely, given the temperature of the bulk sample, are long known to have deleterious effects in secondary ion mass spectrometry (SIMS) type of sputtering of Cu targets [14]. Excessive surface heating would also be likely to contribute to the observed increased error in the measurements through sample volatilization and variations in the secondary electron yields.

General observations from Figures 4.7 are that the Ar gas flow produced less

Figure 4.8 - Absorbance of sputtered Cu atoms as a function of applied RF power at Ar gas flow rate of 0.1 SLPM and Ar gas pressure of 3.7 Torr.

turbulent conditions for the glow itself at high pressures with low Ar flow rates, as Figure 4.7b shows that the absorbance decreases monotonically from the orifice disk surface. Higher flow rates of Ar gas cause a physical disruption of the glow, restricting it near the orifice disk area. A similar observation was reported by Banks and Blades [62] for a DC jet-assisted GD source.

It can also be clearly seen that the distribution pattern of atoms is more or less symmetrical around the "horizontal plane". The population of sputtered atoms is higher at the top-half region of the chamber than at the bottom-half region. Figures 4.7b-4.7d show the general trends of atoms being transported towards the top-half region of the atomizer chamber where the vacuum port is located.

A decrease in absorbance develops in front of the sampling orifice at the vertical position of 2 mm below the "horizontal plane" for different parametric conditions, as is shown in Figure 4.9. Copper atoms are sputtered from the sample primarily as metallic atoms; however, Cu atoms clusters may also be sputtered and subsequently dissociated collisionally in the negative glow.

An equation fitted to the curves (shown in Figure 4.9) was derived from absorbance versus horizontal distance. In Figure 4.9, a constant applied power of 40 W and Ar gas flow rate of 0.1 SLPM were employed while the Ar gas pressure was varied from 8 to 3.7 Torr. This equation has the exponential form of:

$$A = A_{\max} \exp[-k_p(d-0.5)]$$

where A is absorbance, $A_{\max}$ refers to the maximum absorbance of the curve observed for each condition, d is the distance from the orifice disk surface in mm and k_p is the

Figure 4.9 - Spatial distributions of Cu atoms along horizontal distances from orifice disk surface while the atomizer is set at the vertical position of -2 mm for all parametric conditions. (▼): Ar gas pressure, 8 Torr; Ar gas flow rate, 0.4 SLPM; applied power, 40 W. (O): Ar gas pressure, 8 Torr; Ar gas flow rate, 0.1 SLPM; applied power, 40 W. (●): Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied power, 40 W. (◇): Ar gas pressure, 3.7 Torr; Ar gas flow rate, 0.1 SLPM; applied power 55 W.

concentration gradient constant, which is pressure-dependent and has the dimension of mm^{-1} . At the pressures of 8 and 3.7 Torr the values of the concentration gradient constants are 0.20 and 0.11 mm^{-1} , respectively. These results indicate that the concentration gradient and/or any process which removes analyte atoms under these conditions are pressure-dependent and this dependence is such that an increase in pressure brings about a sharp decrease in the number of analyte atoms. One of the possible processes that is responsible for the concentration gradient of atoms is the aggregation process [30], which is directly promoted by increased pressure, and its effect is more pronounced as analyte atoms are transported from the NG farther from the orifice disk surface into regions where there are fewer dissociating collisions.

The observation of an initial maximum in each of the spatial profiles is not entirely unexpected. Early studies by Stirling and Westwood [93] in the modelling of low pressure (0.1 Torr) sputter deposition systems revealed such a maximum in the AA values for Al. The position of this maximum coincided with the edge of the negative glow/dark space (NG/DS) interface, which existed ≈ 1 cm above the cathode surface for this lower pressure system. These workers [93] suggested that this was the evidence for a mechanism whereby fast ions in the dark space dissociate molecular species ejected from the cathode surface. Ferreira and Human [114] came to a similar conclusion in mapping the sputtered atom population within a Grimm-type discharge source. In this case, the higher operating pressure of the Grimm device (≈ 3 Torr) resulted in maxima located ≈ 1.5 mm above the cathode surface, again corresponding to the NG/DS interface. Obviously, the maximum absorbances found in this research do not correspond

to the NG/DS region.

Atomic absorption studies by McDonald [111] have shown that appreciable amounts of agglomeration occur at distances as much as 2 cm from the cathode surface in a flow-assisted, GD atomizer. In fact, spatially and temporally-resolved measurements for Cu cathode sputtering have shown maxima of the type illustrated in this chapter at distances of < 2 cm from the sample (cathode) surface [111]. No single AA experiment has in fact covered the entire spatial distance up to 3 cm with the resolution of the order of 1 mm. Studies in both DC and RF GD-MS have indicated that substantial populations of dimeric species (M_2^+ and $M\text{Ar}^+$) do indeed exist at regions removed from the interfacial region, with their relative intensities decreasing at distances farther into the plasma [73,115]. This would suggest that collisions within the NG may have a cumulative effect in dissociating such species. While more detailed study of these types of spatial distribution is in order, it would appear that a sequence whereby two maxima occur may be possible; the first resulting from dissociation of sputtered molecules in the region of the NG/DS interface, and the second from dissociation due to successive collisions with discharge gas atoms.

Figure 4.10 shows the absorbance of Cu atoms, sputtered from a Cu sheet, as a function of both Ar gas pressure and Ar gas flow rate at a constant applied power of 35 W while the atomizer was set up at the vertical distance of zero and at the horizontal distance of 12 mm. At constant pressure, the absorbance values reach a maximum at an Ar gas flow rate of approximately 0.2 SLPM and then decrease. The occurrence of flow rate maxima indicate a trade off between atom transport by diffusion and by convection

Figure 4.10 - Absorbance of Cu atoms as a function of Ar gas pressure and flow rate at a constant applied RF power of 35 W. (○): Ar gas flow rate, 0.1 SLPM. (◆): Ar gas flow rate, 0.2 SLPM. (□): Ar gas flow rate, 0.3 SLPM. (▲): Ar gas flow rate, 0.4 SLPM. (▼): Ar gas flow rate, 0.5 SLPM. (●): Ar gas flow rate, 0.6 SLPM. (◇): Ar gas flow rate, 0.7 SLPM. (■): Ar gas flow rate, 0.8 SLPM.

(due to the pumping system). Higher flow rates act to decrease the number of analyte atoms in the analysis volume. No results for high flow rates at low pressures could be obtained because of limitations in the ability of the vacuum pump associated with the apparatus. But it is clear that there is always a tendency for absorbance to decrease with increasing flow rate at a constant pressure and power beyond the point of the maximum (≈ 0.2 SLPM). In addition, Figure 4.10 shows the dependence of absorbance on Ar gas pressures. A decrease in the Ar gas pressure at a constant Ar gas flow rate brings about a maximum in absorbance. This occurs approximately at an Ar gas pressure of 5 Torr for Ar gas flow rates of less than 0.4 SLPM. Decreases in the absorbance at Ar gas pressures in excess of 5 Torr is probably the result of increased redeposition of sputtered atoms as shown by the Cu sample loss rates presented in Table 4.1. Table 4.1 also presents the mean free-path of Cu atoms corresponding to each Ar gas pressure on the assumption that the size and consequently the mean free path of Cu atom is approximately the same as for Ar atom. The mean free path (in cm) for Ar has been estimated from kinetic theory of gases to be $[2.0 \times 10^{16} \sigma p]^{-1}$ where p is the gas pressure in Torr and σ is the cross-section (in cm^2) for atom collision, which is $6.46 \times 10^{-16} \text{ cm}^2$ for Ar atom [76]. In a similar experiment, sample loss rate for Al was determined at Ar gas flow rate of 0.05 SLPM and various Ar gas pressures using an applied RF power of 35 W; the results are shown in Table 4.2. At pressures less than the optimum, the amount of discharge current for a given power drops substantially as was shown in Figure 3.16 for DCGD. Thus, optimum pressure provides a compromise between ionizing collisions (i.e. discharge current) and redeposition of analyte atoms.

Table 4.1 Sample weight loss rates and mean free-paths of Cu atoms at different Ar gas pressures. Cu atoms were sputtered at applied RF power of 30 W. ATOMSOURCE gas control box was used for controlling the discharge gas pressure.

Ar gas pressure (Torr)	Mean free-path (μm)	Sample weight loss rate ($\mu\text{g min}^{-1}$)
2	390	380
4	190	685
5	160	670
6	130	430
10	80	400

Table 4.2. Sample weight loss rate in RF-sputtering of Al cathode at various Ar gas pressures for Ar gas flow rate of 0.05 SLPM and an applied power of 35 W.

Ar gas pressure (Torr)	Sample weight loss rate ($\mu\text{g}/\text{min}$)
3	71 ± 2
4	54 ± 2
5	9 ± 1

Ideally, this optimum pressure should be the lowest possible operating pressure at the highest feasible current. Hence, the pressure that provides the maximum number of sputtered atoms in the GD must be determined experimentally.

Figure 4.11a shows absorbance of Cu atoms as a function of applied RF power, using the ATOMSOURCE control box for controlling the discharge gas. In this experiment, the Ar gas pressure was 8 Torr. It should be mentioned again that the ATOMSOURCE control box does not permit independent control of the Ar gas flow rate and pressure. Figure 4.11a shows that there is a threshold energy of about 10 W at an Ar gas pressure of 8 Torr, above which the sputtering increases linearly at first and then exponentially owing to the more rapid, steady-state sputtering at higher powers. This curve eventually levels off, since very energetic sputter ions will penetrate the crystal lattice of the cathode. Absorbance of sputtered Cu atoms as a function of applied RF power at Ar gas flow rate of 0.2 SLPM and Ar gas pressure of 5 Torr is shown in Figure 4.11b. As it is seen from Figures 4.11a, 4.11b and 4.8, the threshold energy is lower at lower Ar gas pressure and the precision of measurement decreases with increasing applied power. This is because the discharge becomes unstable at higher powers which limits the range of applied power. It is expected that a reduction in the absorbance will be observed at still higher applied powers because of energy dissipation (as heat) of penetrated sputter ions far from the cathode surface.

The results presented in this study illustrate the existence of spatial inhomogeneities within the atomizer chamber and energetic regions within the glow which indicate the necessity of the adjustable optical mount. It is shown that the most

Figure 4.11a - Absorbance of Cu atoms as a function of applied RF power at constant Ar gas pressure, with ATOMSOURCE control box for sputter gas control. Ar gas pressure, 8 Torr.

Figure 4.11b - Absorbance of Cu atoms as a function of applied RF power at Ar gas flow rate of 0.2 SLPM and Ar gas pressure of 5 Torr.

useful region for AAS of Cu atoms and ions is around the sampling orifice disk. The results of this study are consistent with those of many DCGD systems and seem to support the notion that the RF discharge acts as a DC discharge [3].

This study seems to support the desirability of having the vacuum port directly opposite the orifice disk location. Such a design will help to pull away sputtered atoms from the sampling orifice, increasing the population of sputtered atoms by controlling the convection process (due to vacuum pumping), increasing the number density of analyte atoms and the analytical sensitivity of AAS.

4.4 Conclusions

The results show that the GD plasma is an inhomogeneous medium so that the sampling position is critical for atomic absorption and other atomic spectrometric methods. It was seen that the distribution pattern of atoms is more or less symmetrical around the horizontal plane (the plane containing central axis of the sampling orifice). It is not feasible by AAS to know how analyte atoms are distributed within the sampling orifice and around the vertical plane (the plane containing the central axis of sampling orifice normal to the hollow-cathode light beam). The population of sputtered atoms is higher at the top-half region of the chamber than at the bottom-half, with a general trend for atoms to be transported towards the top-half of the chamber where the vacuum port is located. Independent control of Ar gas flow rate and pressure was found to be critical in determining the spatial distribution of Cu atoms within the atomizer chamber. The surface history of the cathode seems to be of great importance. Large changes in

reproducibility appeared to correlate with the changes in the cathode surface.

CHAPTER 5

Effects of anode dimensions and location of the inlet port of discharge-gas on the spatial distributions of Cu atoms in an RFGD Atomizer for AAS

5.1 Introduction

One of the main problems with cathodic sputtering in a glow discharge (GD) for atomic absorption spectrometry (AAS) is the transport of the sputtered atoms from the cathode surface to the analysis volume. The sputtered neutral particles leave the surface and enter the analysis volume by concentration diffusion. Therefore, there exists the possibility that the analyte atoms may redeposit on the cathode surface. The redeposition of analyte atoms is an extremely undesirable side-effect of the cathodic sputtering process. At an Ar gas pressure of 1.5 Torr it has been estimated that as much as 95% of the sputtered atoms are redeposited [34]. At higher discharge gas pressures the amount of redeposition increases. This results in only a small fraction of sputtered atoms being available to produce the analytical signal. Therefore, the atomizer must be designed so to reduce the problem of redeposition.

The existence of concentration gradients of sputtered atoms [107] and molecular analyte species, such as MAr^+ and M_2^+ [110], makes the knowledge of the spatial distribution of analyte atoms important in determining the optimum sampling location within the atomizer chamber. Knowledge of the spatial distribution of the sputtered analyte atoms may also shed light on analyte transport patterns and mechanisms.

The spatial distributions of Cu atoms as a function of discharge conditions, such as the pressure, the flow rate of the Ar discharge gas and the applied RF power, have been reported in Chapter 4. The results showed that the spatial distribution of the sputtered atoms in the atomizer chamber is largely determined by the locations of the vacuum port and the discharge-gas inlet port in the atomizer chamber. The existence of concentration gradients inside the atomizer chamber suggested that the vicinity of the sampling orifice disk should be a good atom reservoir for AAS. However, the atomizer design (used in Chapter 4) did not permit measurement of the atomic absorption of the sputtered atoms inside the orifice of the sampling orifice disk.

In this work a laboratory-built RF atomizer was used to study the spatial distribution of Cu atoms sputtered from a Cu cathode by AAS for various discharge conditions. The laboratory-built RF atomizer was modified by changing the location of the discharge-gas inlet port to evaluate the effect of the location on the spatial distribution of sputtered Cu atoms [107]. The effect of varying the thickness and the inside diameter of the sampling orifice disk on the absorbance of sputtered Cu atoms was also investigated.

5.2 Experimental

5.2.1 Sputtering atomizer

It was shown in Chapter 4 that most sputtered analyte atoms are localized inside the orifice of the sampling orifice disk and it was physically impossible to investigate these analyte atoms using AAS because of the atomizer chamber design used in Chapter

4. To make these atoms available for measurement by AAS, the location of the discharge-gas inlet port was shifted from the top of the atomizer chamber (used in Chapter 4) to the body of the sampling orifice disk. Schematic diagrams of the modified sampling orifice disk are shown in Figures 5.1a and 5.1b. The radiofrequency generator and the impedance matching network used for this study have been described in Chapter 4.

5.2.2 Direct current self-bias monitor

Because of the inherent difference between mobility of the electron and the discharge gas ion, a negative potential develops at the cathode surface as a result of the application of an RF power. This potential, called DC self-bias potential, is of particular importance in evaluation and application of RF-sputtering systems. It can be used to assess many analytical properties of RF discharge such as sputtering, excitation and ionization efficiencies as it influences the energies of both incident ions and the secondary electrons ejected from the cathode surface. Furthermore, the DC self-bias potential is largely dependent on the discharge gas pressure within the cathode fall region of the discharge and consequently reflects changes in the local gas pressure near the cathode surface due to directed gas flow on the cathode surface [67]. Also, because power losses are common in RF-powered discharge system, the DC self-bias potential measurement can sometimes be more useful for determining the actual power delivered to a plasma [105]. Therefore, a laboratory-built DC self-bias monitor was used (Figure 5.2) to study the DC self-bias potential. This device was inserted in the circuit between the impedance matching network and the atomizer. The laboratory-built DC self-bias monitor blocks

Figure 5.1a - Front view of the sampling orifice disk with the Ar gas inlet port.

Figure 5.1b - Side view of the sampling orifice disk with the Ar gas inlet port.

Figure 5.2 - A schematic diagram of the laboratory-built DC self-bias monitor.

the RF current but attenuates the DC current by a factor of 21.95 which was determined by the voltage divider used in its network. The inductor ($16.6\ \mu\text{H}$) blocks RF current because of the induced magnetic field which opposes changes in current. Capacitors block DC current but have low impedance for any residual RF current.

5.2.3 Gas control system

Schematic diagram for gas flow rate control system is shown in Chapter 3 (Figure 3.1). The discharge gas admitted into the atomizer chamber through a 6.3 mm compression fitting mounted either on the top of the atomizer chamber body, as described in Chapter 4, or through a similar compression fitting mounted on the sampling orifice disk, as is described in this chapter (Figure 5.1).

5.2.4 Test solutions and reagents

The Au stock solution ($1000\ \mu\text{g/mL}$) was supplied by Harleco (Philadelphia, PA, U.S.A.), and was prepared by dissolving the metal in dilute aqua regia. All test solutions were prepared by serial dilution of the above stock solution with ultrapure water immediately prior to determination. Ultra-pure water of resistivity $18.3\ \text{M}\Omega\ \text{cm}$ was obtained direct from a Milli-Q2 Water Purification System (Millipore Corp.).

5.2.5 Procedure

Cathodes of oxygen-free, hard copper (OFHC) were used. The cathode surface was prepared as described in Chapter 4 (section 4.2.5). A uniform pre-sputtering time of 3 min was adopted as the optimum time required to sputter the polished cathode surface to achieve a representative and reproducible surface. All absorbance data were recorded for atoms sputtered from such a cleaned surface.

For analysis of solution residues, prior to every atomization cycle, the cathode was sputter-cleaned to ensure a reproducible atomization surface and to produce a circular depression (cavity) into which the test solution was pipetted (the effective surface area of the cathode is defined by the sputtered region provided by the sampling orifice). The cathode was then detached from the atomizer and laid flat with the prepared surface facing up. A 1 μ L volume of the test solution was then pipetted in the centre of the cavity with a Hamilton microsyringe, fitted with a Chaney adaptor, Model No. 7105 NCH, part No. H88004 (Chromatographic Specialities). The test solution was then air-dried outside the atomizer and the cathode re-clamped to the atomizer. The measurement system has been described in Chapter 3.

5.3 Results and Discussion

5.3.1 Effect of the location of the inlet port of discharge-gas on the number density of Cu atoms

It has been shown [107] that a large fraction of the sputtered atoms are probably localized within the confines of the sampling orifice disk. Measurement of the AA signal inside the orifice of the sampling orifice disk is physically impossible because of the design of the atomizer chamber. To circumvent the above problem the location of the discharge-gas inlet port was changed from the top of the atomizer chamber (unmodified atomizer) to the body of the sampling orifice disk (modified atomizer) as shown in Figures 5.1a and 5.1b. Figure 5.1a shows that the sputter gas is introduced into the atomizer chamber through three small gaps (1.8 mm in width) located in the sampling

orifice 3 mm from, and in a direction parallel to, the sample surface. Gas channels are directed at an angle of 180 degrees with respect to the sample surface. Such introduction of the sputter gas can form a barrier, preventing the diffusion of sputtered atoms back onto the cathode surface; also, the sputter gas flow aids in the transport of sputtered materials to the analysis volume. Gas jets do not produce any crater on the burning spot produced on the cathode surface. When the discharge-gas inlet port is mounted on the sampling orifice disk, the discharge gas inside the sampling orifice does not remain static (Chapter 4). When the discharge gas is static, increased local gas pressure inside the sampling orifice disk can redeposit the sputtered atoms on the surface of the orifice as well as on the recess region between the arrestor and the cathode surface (Figure 5.1b). This was confirmed by the visual observation that the negative glow (NG) was extended in the direction of the discharge gas flow. Mounting the discharge-gas inlet port on the sampling orifice disk creates a convective flow of the discharge gas from the sampling orifice disk into the atomizer chamber, where the sputtered atoms can be detected by AAS. For a static DCGD, at a discharge gas pressure of 0.1 Torr, 90% of the sputtered material diffuses back to the cathode surface and is redeposited [5]. A convective flow of the discharge gas has been shown [37,46,47,116] to entrain the sputtered atoms effectively into the analysis volume. This convective flow of the discharge gas greatly reduces sample redeposition on the surfaces of the cathode, the sampling orifice disk and the teflon O-ring, and sweeps the sputtered atoms into the analysis volume. Minimizing sample redeposition also decreases the possibility of arcing between the cathode and the anode, resulting in greater stability of the GD.

Using the modified atomizer (in which the discharge-gas inlet port was shifted from the top of the atomizer chamber to the body of the sampling orifice disk), it was observed that the NG was extended in the direction of the convective flow of the discharge gas relative to the unmodified atomizer. Confirmation that the sputtered atoms are efficiently swept from the sampling orifice disk into the atomizer chamber is given in Figures 5.3a and 5.3b. These figures compare the absorbance of Cu atoms sputtered from a Cu cathode as a function of horizontal distance (at a fixed vertical distance of -4 mm) for various discharge conditions for the modified and the unmodified RF atomizers. Figure 5.3a gives the absorbance as a function of the horizontal distance for both the atomizers at an Ar gas pressure of 3.7 Torr and an Ar gas flow rate of 0.1 SLPM. Figure 5.3b gives the absorbance of sputtered Cu atoms as a function of the horizontal distance for both the atomizer types at an Ar gas pressure of 8 Torr and Ar gas flow rates of 0.1, 0.4 and 0.6 SLPM. Figures 5.3a and 5.3b show that for all of the discharge conditions investigated, the absorbance is much greater (up to 45 times) for the modified RF atomizer, having the discharge-gas inlet port on the body of the sampling orifice disk, than for the unmodified RF atomizer having the discharge-gas inlet port on the top of the atomizer chamber. It seems that the flow of the discharge gas effectively blocks any sample atoms, sputtered with an ejection velocity sufficient to carry it beyond the gas stream, from returning to the cathode surface [116]. Also, the absorbance varied with the discharge conditions and the region within the atomizer chamber that was sampled.

Figure 5.3a - Absorbance of Cu atoms measured along the horizontal axis for Ar gas flow rate of 0.1 SLPM at the fixed vertical position of -4 mm. The applied RF power and Ar gas pressure were 40 W and 3.7 Torr, respectively. Discharge-gas inlet port was located on: (▽), top of the atomizer chamber; (●), sampling orifice disk.

Figure 5.3b - Absorbance of Cu atoms measured along the horizontal axis for various Ar gas flow rates at the fixed vertical position of -4 mm. The applied RF power and Ar gas pressure were 40 W and 8 Torr, respectively. Discharge-gas inlet port was located on: (∇ , $\circ$, $\times$), top of the atomizer chamber; ($\bullet$, $\blacksquare$, $\blacktriangle$), sampling orifice disk.

5.3.2 Effect of the anode geometry on the number density of Cu atoms

The effect of the inside diameter of the sampling orifice disk (anode) on the absorbance of Cu atoms sputtered from a Cu cathode using the unmodified RF atomizer is shown in Figure 5.4. Several sampling orifice disks 2 mm thick with inside diameters of 2, 4, 6, and 8 mm were used. The discharge conditions used for this experiment were an Ar gas flow rate of 0.2 SLPM, an Ar gas pressure of 5 Torr and an applied RF power of 40 W. Absorbances were measured at a vertical distance of 0 mm and a horizontal distance of 15 mm from the cathode surface. As can be seen from Figure 5.4, the absorbance of the sputtered Cu atoms increased with increasing inside diameter of the sampling orifice disk. This result was expected since increasing the inside diameter of the sampling orifice disk allows a larger area of the cathode surface to be sputtered. Parker and Marcus [109] also reported a similar observation, and suggested a simple path-length dependence to explain these results. However, Figure 5.5 shows that the sample weight loss is inversely related to the sampling orifice diameter at orifice diameters equal to or higher than 4 mm.

Figure 5.4 also shows the change in the signal-to-noise ratio (S/N) with increasing inside diameter of the sampling orifice disk. When larger diameter O-rings are employed the recess region area becomes larger, allowing the discharge to extend into this region. Under this condition, the area of the cathode that is sputtered is extended out to the inner diameter of the teflon O-ring. In studies of the emission characteristics of an RF GD-AES source, Lazik and Marcus [105] reported that periodic changes in the position of the NG occurs relative to the cathode surface and focusing optics as a result of the

Figure 5.4 - Effect of sampling orifice disk diameter (disk thickness of 2 mm) on the absorbance of Cu atoms, RF-sputtered from a Cu cathode. Experimental conditions: Ar gas flow rate, 0.2 SLPM; Ar gas pressure, 5 Torr; applied RF power, 40 W. (□): Signal-to-noise ratio. (●): Absorbance.

Figure 5.5 - Effect of the sampling orifice diameter (disk thickness of 2 mm) on sample weight loss rate of Cu atoms when unmodified atomizer was used. Experimental conditions: Ar gas flow rate, 0.2 SLPM; Ar gas pressure, 5 Torr and applied RF power, 40 W.

plasma "wandering" in and around the recess region. This situation gives rise to uncertainties in absorbance (Figure 5.6), and consequently, a decrease in the signal-to-noise ratio, as shown in Figure 5.4. As can be seen from Figure 5.4, the best S/N was obtained with a sampling orifice disk with an inside diameter of 4 mm. Figure 5.5 shows that the rate of sample weight loss reaches a maximum with a sampling orifice diameter of 4 mm. The inside diameter of the sampling orifice disk was therefore set at 4 mm for the remainder of this study. As shown in Figure 5.5, the rate of sample weight loss is smaller for a sampling orifice disk diameter of 2 mm. It was observed that the teflon O-ring was sputtered when the 2 mm sampling orifice diameter was used, thereby reducing the power efficiency for sputtering of the sample cathode. It was also found that the rate of sample weight loss for the 2 mm sampling orifice diameter was too small to be measured reliably. The rate of sample weight loss shown in Figure 5.5 was instead calculated by comparison of the absorbance with that observed for larger sampling orifice disk diameters.

The effect of the thickness of the sampling orifice disk on the absorbance and signal-to-noise ratio of Cu atoms sputtered from a Cu cathode using the unmodified RF atomizer is shown in Figure 5.7a. Data for Figure 5.7a were obtained for sampling orifice disks of 4 mm inside diameters and 2, 4, 6, and 8 mm thicknesses. It should be noted that for the unmodified RF atomizer it was not possible to make a sampling orifice disk with a thickness less than ≈ 2 mm because of the teflon O-ring groove (i.d., ≈ 6.5 mm; o.d., ≈ 11.5 mm; depth, ≈ 1.5 mm) which is made around the orifice of the sampling orifice disk, as shown in Figure 5.1a. The discharge conditions that were used

Figure 5.6 - AA signals of Cu atoms RF-sputtered from a Cu cathode for sampling orifice disk thicknesses: (a), 8 mm, absorbance = 0.8240; (b), 6 mm, absorbance = 0.2640; (c), 4 mm, absorbance = 0.0405; (d), 2 mm, absorbance = 0.0020. Experimental conditions: Ar gas flow rate, 0.2 SLPM; Ar gas pressure, 5 Torr; applied RF power, 40 W.

Figure 5.7a - Effect of the sampling orifice disk thickness (orifice diameter of 4 mm) on the absorbance of Cu atoms, RF-sputtered from a Cu cathode. Experimental conditions: Ar gas flow rate, 0.2 SLPM; Ar gas pressure, 5 Torr; applied RF power, 40 W. (□): Signal to noise ratio. (●): Absorbance.

for this experiment were an Ar gas flow rate of 0.2 SLPM, an Ar gas pressure of 5 Torr and an applied RF power of 40 W. Since the origin of the horizontal and vertical coordinates was at the cathode surface, the distance of the cathode surface from the atomizer chamber increased with increasing thickness of the sampling orifice disk. Consequently, the coordinates of each sampling point in the atomizer chamber is changed with changes in the thickness of the sampling orifice disk. This experiment was done in such a manner as to probe a specific region of the atomizer chamber regardless of the thickness of the sampling orifice disk. The region of the atomizer chamber for this experiment is specified by a vertical distance of 0 mm and a horizontal distance of 15 mm (for a sampling orifice disk thickness of 4 mm). It should be noted that the closest approach of the beam of radiation of the hollow-cathode lamp to the cathode surface is approximately 11 mm when a sampling orifice disk of 4 mm thickness is used; it is therefore not possible to make absorbance measurements nearer than this to the cathode surface. The closest approach of the beam of radiation of the hollow-cathode lamp to the cathode surface is a function of the thickness of the sampling orifice disc. By using sampling orifice discs of 2, 4, 6 and 8 mm thickness the closest approach of the beam of radiation from the hollow-cathode lamp to the cathode surface are 9, 11, 13 and 15 mm, respectively.

Figure 5.7a shows that the absorbance of Cu atoms, RF-sputtered from a Cu cathode is inversely related to the thickness of the sampling orifice disk. This is because the distance of the region of the atomizer chamber investigated from the cathode surface increased with increasing thickness of the sampling orifice disk. A decrease in the

concentration of Cu atoms is therefore expected as a result of the concentration gradient at larger distances from the cathode surface and increasing deposition of the sputtered materials. When a sampling orifice disk of 8 mm thickness was used it was observed that the NG was confined within the boundary of the sampling orifice disk and the atomic absorption signal of sputtered Cu atoms disappeared. The above suggests complete redeposition of the sputtered atoms on the surface of the sampling orifice and/or of the sample cathode, which prevents the transport of sputtered atoms into the atomizer chamber. The rate of sample weight loss as a function of the sampling orifice disk thickness, as shown in Figure 5.7b is less when the disk is 2 mm thick. It was observed that the NG is less confined or less dense in the sampling orifice disk when a sampling orifice disk of 2 mm thickness was used. The diffuse NG for the 2 mm sampling orifice disk is indicative of a lower flux of Ar^+ ions, as evidenced by the decreased rate of sample weight loss in Figure 5.7b. Figures 5.7a and 5.7b suggest that the transport efficiency of the sputtered atoms into the atomizer chamber should be higher when a sampling disk thickness of 2 mm was used, as a higher absorbance was obtained when this sampling disk was used.

Although a sampling orifice disk thickness of 2 mm gave the best signal-to-noise ratio, (Figure 5.7a), it was not possible to make a discharge-gas inlet port on the body of such a disk in the modified RF atomizer. A sampling orifice disk with a thickness of ≈ 4 mm was therefore used with a discharge-gas inlet port located on its body to study the spatial distribution of the sputtered atoms inside the atomizer chamber. The thickness of the sampling orifice disk is crucial because it affects both sample weight loss and the

Figure 5.7b Effect of the thickness of the sampling orifice disk (orifice diameter of 4 mm) on sample weight loss rate of Cu atoms when the unmodified atomizer was used. Experimental conditions: Ar gas flow rate, 0.2 SLPM; Ar gas pressure, 5 Torr and applied RF power, 40 W.

transport of the sputtered atoms into the atomizer chamber, where the sputtered atoms are studied by atomic absorption spectrometry.

5.3.3 Spatially-resolved measurement of absorbance

Spatially-resolved measurements of the absorbance of the sputtered Cu atoms from a Cu cathode were made in order to permit optimization of the sampling location for various discharge conditions and to provide information on transport patterns of analyte atoms and mechanisms of analyte atom formation and loss. Horizontal absorbance profiles were measured for horizontal distances of 11 to 41 mm from the cathode surface. Vertical absorbance profiles were measured at 2 mm intervals for vertical distances from -10 to +12 mm relative to the horizontal plane. The uncertainty in the absorbance measurements due to re-positioning of the atomizer was determined by repetitively taking absorbance measurements ($n=6$) for a specific location and set of discharge conditions, moving the atomizer position and resetting the atomizer position between each measurement. Uncertainty in the absorbance measurements due to re-positioning of the atomizer was 1.7% relative standard deviation (RSD). Since only general trends were of interest, it was not necessary to repeat this for each measurement. It should be noted that with the gas control system used, low pressure can only be obtained by using a low flow rate of the discharge gas. At an Ar gas flow rate of 0.4 SLPM, for example, it was not possible to get a pressure of 4 Torr. The same was true for pressures of 4 and 5.4 Torr at an Ar gas flow rate of 0.6 SLPM. Hence, the effect of the gas flow rate on spatial distribution of sputtered Cu atoms was measured only at pressures above ≈ 6.6 Torr for a full range of gas flow rate, i.e. 0.1–0.6 SLPM.

Figure 5.8 shows the spatially-resolved measurements of absorbance of the sputtered Cu atoms for the modified RF atomizer. The discharge conditions for Figure 5.8 were: Ar gas flow rate, 0.4 SLPM; Ar gas pressure, 8 Torr; and applied RF power, 40 W. Because virtually the entire volume of the atomizer chamber was examined the results can be interpreted as measurements of concentration gradients of the sputtered Cu atoms. As previously mentioned, it was not possible to measure the absorbance of sputtered Cu atoms inside the orifice of the sampling orifice disk by AAS because of the geometrical constraints of the atomizer chamber. For the 4 mm thick sampling orifice disk used for these measurements, the closest approach of the beam of the radiation from the hollow-cathode lamp to the surface of the cathode was 11 mm.

Figure 5.8 shows that the absorbance of the sputtered Cu atoms was slightly greater above the horizontal plane than below. This is expected since the vacuum pump generates a net gas flow towards the vacuum port located on the top of the atomizer chamber. Figure 5.8 also shows that the absorbance increases with increasing horizontal distance and decreases with increasing vertical distance both above and below the horizontal plane. This observation is supported by Gough [37], who showed that in his DC-sputtering cell the atoms were concentrated in the centre of the sputtering chamber where the gas speed was high since the effect of lateral diffusion was relatively small. The centre of our atomizer chamber was the intersection of the central axes of the atomizer chamber and the sampling orifice disk. These results suggest that under these conditions of discharge, forced convection controls the analyte distribution in the horizontal direction, and that diffusion largely controls the analyte distribution in the

Figure 5.8 - Spatial distribution of Cu atoms (absorbance) inside the atomizer chamber of the modified RF atomizer. Experimental conditions: Ar gas flow rate, 0.4 SLPM; Ar gas Ar gas pressure, 8 Torr; applied RF power, 40 W. This is a side-view of the sample (cathode) and the sampling orifice disk. The horizontal plane is perpendicular to both the sample (cathode) surface and the plane of the paper at the vertical position of 0 mm.

vertical direction, although convection due to the vacuum pump is also evident.

Figure 5.8 also shows that the absorbance along the horizontal axis was virtually constant at or just above the vertical distance of 0 mm in the vicinity of the horizontal plane possibly because the flow of Ar gas and the pulling effect of the vacuum pump balance the rate of the supply of atoms into this zone with the rate of loss of atoms to the walls of the atomizer chamber. This suggests that the optimum vertical distance for absorbance measurement is at or slightly above the vertical position of 0 mm, where the absorbance is large and is least dependent on the horizontal position of the atomizer. This is in agreement with the findings of Kim and Piepmier [47], who reported that the centre of their sputtering chamber was a good region for stable operation and for obtaining precise measurements. The results also suggest that it may be advantageous to move the location of the vacuum port from the top of the atomizer chamber to a position opposite the sampling orifice disk, as suggested in the previous chapter. This would eliminate the forced convection of the sputtered atoms in the vertical direction and confine losses from the horizontal plane to those resulting from diffusion. This should result in an increase in the AAS signal because a larger fraction of the sputtered atoms would be available for measurement because of reduced analyte redeposition onto the top and bottom walls of the atomizer chamber.

Figure 5.9 shows the effect of Ar gas flow rate on the spatial distribution of sputtered Cu atoms from a Cu cathode when the modified RF atomizer was set at the vertical position of 0 mm for a fixed applied RF power of 40 W at an Ar gas pressure of 5.4 Torr. The absorbance generally increased when Ar gas flow rate was increased

Figure 5.9 - Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas pressure of 5.4 Torr and an applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for Ar gas flow rates: (a), "closed valve" (≈ 0 SLPM); (b), 0.1 SLPM; (c), 0.2 SLPM; (d), 0.3 SLPM; (e), 0.4 SLPM.

from 0 SLPM to 0.1 SLPM. The increase in absorbance can be explained by the increased efficiency with which the sputtered atoms are swept from the sampling orifice into the analysis volume, as defined by the size of the beam of radiation from the hollow-cathode lamp. At flow rates above 0.1 SLPM the absorbance generally decreases.

Figure 5.10 shows the effect of Ar gas flow rate on the rate of loss of sample (Cu) weight, using the modified RF atomizer. Figure 5.10 shows that there are no significant changes in the rate of sample (Cu) weight loss with increasing Ar gas flow rate at the pressure of 5.4 Torr, so the decrease in absorbance in Figure 5.9 was probably due to the decreased residence time of the sputtered Cu atoms in the analysis volume. The decrease in the absorbance near the rear wall of the atomizer chamber for all discharge conditions in Figure 5.9 could be explained by the fact that the rear wall of the atomizer chamber, which was opposite the discharge-gas inlet port, was an important site for analyte atom redeposition in this configuration of the discharge-gas inlet port.

Figure 5.11 shows the effect of Ar gas pressure on the spatial distribution of sputtered Cu atoms from a Cu cathode along the horizontal axis at an Ar gas flow rate of 0.2 SLPM when the modified RF atomizer was set at the vertical position of 0 mm for a fixed applied RF power of 40 W. Figure 5.11 shows that at pressures of 5.4 Torr and higher there was an overall decrease in the absorbance with increasing horizontal distances, with the decrease being particularly steep near the rear wall of the atomizer chamber at a horizontal distance of 41 mm. This can be explained by the decrease in the diffusion rate of the sputtered atoms with increasing pressure, leading to increased

Figure 5.10 - Effect of Ar gas flow rate on rate of weight loss of the sample (Cu) at an applied RF power of 40 W and Ar gas pressures of: (a), 5.4 Torr; (b), 8 Torr. The modified RF atomizer was used.

Figure 5.11 - Horizontal distribution of Cu atoms inside the atomizer chamber at an applied RF power of 40 W and Ar gas flow rate of 0.2 SLPM when the modified atomizer was set at the vertical position of 0 mm for Ar gas pressures: (a), 4 Torr; (b), 5.4 Torr; (c), 6.6 Torr; d, 8 Torr.

redeposition of the sputtered atoms. At a pressure of 4 Torr the effect of diffusion appeared to have become insignificant, as no significant changes in absorbance was observed along the horizontal axis.

Figure 5.12 shows the rate of sample (Cu) weight loss for various Ar gas pressures at Ar gas flow rates of 0.2 SLPM, 0.4 SLPM, and 0.6 SLPM, at RF power of 40 W. Curve (a) in Figure 5.12 shows that at an Ar gas flow rate of 0.2 SLPM, the rate of sample (Cu) weight loss had a maximum at ~ 5.8 Torr. The initial increase in the rate of the sample (Cu) weight loss was probably due to the increased efficiency with which the sputtered Cu atoms were transported away from the cathode surface by the flowing Ar gas. The subsequent decrease at pressures above ~ 5.8 Torr was probably the result of increased redeposition of the sputtered Cu atoms with increasing pressures.

Figure 5.13 shows the effect of pressure on the spatial distribution of sputtered Cu atoms from a Cu cathode along the horizontal axis at an Ar gas flow rate of 0.4 SLPM when the modified RF atomizer was set at the vertical position of 0 mm for a fixed applied RF power of 40 W. Figure 5.13 shows an initial increase in absorbance for all gas pressures used in this experiment (compared to Figure 5.11). A possible explanation for this could be changes in the dimensions of the NG. It is known [62] that when the direction of mass transport of the sputtered atoms and the discharge gas is the same (as is in this study), the NG is extended with increasing discharge-gas flow rate.

Figure 5.14 shows the effect of pressure on the spatial distribution of sputtered Cu atoms along the horizontal axis at an Ar gas flow rate of 0.6 SLPM when the modified RF atomizer was set at the vertical position of 0 mm for a fixed applied RF

Figure 5.12 - Effect of Ar gas pressure on sample (Cu) weight loss rates at an applied RF power of 40 W, and at Ar gas flow rates of: (a), 0.2 SLPM; (b), 0.4 SLPM; (c), 0.6 SLPM. The modified RF atomizer was used.

Figure 5.13 - Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas flow rate of 0.4 SLPM and an applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for Ar gas pressures: (a), 5.4 Torr; (b), 6.6 Torr; (c), 8 Torr.

Figure 5.14 - Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas flow rate of 0.6 SLPM and applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for Ar gas pressures: (a), 6.6 Torr; (b), 8 Torr.

power of 40 W. Figure 5.14 shows two maxima in the absorbance: the first maximum is what would be expected if the absorbance maximum is related to increased dissociation of non-atomic species of analyte due to the extension of the NG at the higher Ar gas flow rate. Figure 5.14 also shows that for the higher Ar gas pressure of 8 Torr the position of the absorbance maximum is shifted closer to the cathode surface as NG is less extended at the higher Ar gas pressure. The lesser absorbance of curve (b) at the higher Ar pressure of 8 Torr compared to curve (a) at the Ar pressure of 6.6 Torr can be explained by a combination of increased analyte atom redeposition and by the small rate of sample (Cu) weight loss as shown in curve (c) of Figure 5.12. The second absorbance maximum in Figure 5.14 at a greater horizontal distance could be due to gas flow perturbation and/or its influence on atom-molecule reactions in the plasma.

Figure 5.15 shows the effect of the Ar gas flow rate on the spatial distribution of sputtered Cu atoms from a Cu cathode along the horizontal axis for a pressure of 8 Torr when the modified RF atomizer was set at the vertical position of 0 mm for a fixed RF power of 40 W. At the Ar gas flow rates of 0.2 SLPM and lower (curves a-c), the absorbance decreased rapidly with increasing horizontal distance, probably because of inefficient transport of the sputtered atoms away from the cathode surface and into the analysis volume. Inefficient transport of the sputtered atoms into the atomizer chamber at Ar gas flow rates of 0.2 SLPM and lower provides a higher population of atoms near the sampling orifice; hence, a higher absorbance was observed in this region. The decrease in absorbance at the Ar gas flow rate of 0.4 SLPM suggests that at the high Ar gas pressure of 8 Torr the increased Ar gas flow rate was more than cancelled by the

Figure 5.15 - Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas pressure of 8 Torr and an applied RF power of 40 W when the modified atomizer was set at the vertical position of 0 mm for Ar gas flow rates: (a), "closed valve" (≈ 0 SLPM); (b), 0.1 SLPM; (c), 0.2 SLPM; (d), 0.4 SLPM; (e), 0.6 SLPM.

decrease in atom residence time due to forced convection. This is in agreement with the results of Chakrabarti et al. [46], who found that for their DC-sputtering atomizer at 8 Torr the rate of supply of atoms to the analysis volume was almost constant for Ar gas flow rates of 0.4 SLPM and below, while the rate of atom removal increased steadily; above 0.4 SLPM the rate of supply of atoms to the analysis volume increased rapidly. Sample weight loss results at Ar gas pressure of 8 Torr and various Ar gas flow rates (Figure 5.10) show that the Ar gas flow rate does not have a significant effect on the amount of materials sputtered from the cathode surface at this pressure. In general, Figure 5.15 shows that in the range of 23-29 mm at the centre of the atomizer chamber, the variation in absorbance (slope) as a function of distance along the horizontal axis is a minimum for Ar gas flow rates of ≥ 0.2 SLPM. This suggests that at Ar gas flow rate of ≥ 0.2 SLPM the centre region of the atomizer chamber could be a better region for AAS in order to increase the precision of the measurement.

The increase in absorbance from 0.4 SLPM to 0.6 SLPM shown in Figure 5.15 may result from an increase in the rate of supply of atoms to the analysis volume. As discussed previously, the rate of supply of atoms to the analysis volume increases rapidly at Ar flow rates above 0.4 SLPM, such that it would more than compensate for a decrease in residence time [46]. Therefore, an increase in absorbance of Cu atoms such as that seen in Figure 5.15 at an Ar flow rate of 0.6 SLPM is expected.

Changes in the local pressure within the sampling orifice disk with changes in the Ar flow rate may also be responsible for the increase in absorbance of Cu atoms at an Ar flow rate of 0.6 SLPM as seen in Figure 5.15. Chakrabarti et al. [46] also showed

that the sputtering efficiency increased with increasing pressure. In a DC glow discharge, changes in the sputtering rate resulting from changes in the local pressure at the cathode surface can be detected by plotting a graph of discharge voltage versus discharge current. Such a plot tends to flatten with both increasing gas flow rate and gas pressure, as shown by Banks and Blades [116]. In an RFGD, changes in the local gas pressure at the cathode surface can be detected by measuring changes in the DC self-bias potential. Winchester et al. [63] showed that the DC self-bias potential becomes more negative with decreasing gas pressure. The DC self-bias potential is affected by the ratio of the cathode to anode surface areas, the gas pressure, the discharge gas, the electrode spacing and the applied RF power, which are all kept constant in this experiment. To measure possible changes in the DC self-bias potential with Ar gas flow rate, the laboratory-built device as shown in the schematic diagram in Figure 5.2, was used. Figure 5.16 shows the effect of Ar gas flow rate on the DC self-bias potential for the modified RF atomizer at various Ar gas pressures for a fixed applied RF power of 40 W. Figure 5.16 shows that at higher Ar gas pressures the Ar gas flow rate does not significantly affect the DC self-bias potential, as shown by the linear regression lines (dashed lines) in Figure 5.16. These results show that at an Ar gas pressure of 8 Torr there was no significant increase in the local Ar gas pressure within the sampling orifice disk, which could help explain the increase in absorbance observed at an Ar gas flow rate of 0.6 SLPM in Figure 5.15. Figure 5.16 shows that the DC self-bias potential tends to flatten with increasing Ar gas pressure. The results of this study are therefore consistent with those of other DCGD systems [105]. This observation is supported by

Figure 5.16 - DC self-bias potential, (—), developed at the cathode surface of the modified RF atomizer at a fixed applied RF power of 40 W as a function of Ar gas flow rate for Ar gas pressures: (a), 4 Torr; (b), 5 Torr; (c), 6 Torr; (d), 7 Torr; (e), 8 Torr. (---), linear regression lines.

Banks and Blades [116], who showed that the voltage tends to become constant with increasing discharge gas flow rate and pressure. They also noted that the gas pressure differential between the gas pressure at the sample surface and that at the metering port was much greater at lower discharge gas pressures. It is therefore concluded that there is no change in the local discharge gas pressure within the sampling orifice disk with variation in the Ar gas flow rate at an Ar gas pressure of 8 Torr, which could be responsible for the general increase in absorbance at the Ar gas flow rate of 0.6 SLPM in Figure 5.15.

A general equation which fitted data drawn in Figure 5.16 has been derived. This equation has the following form:

$$V = (2.7) [23.8(8.3 - P)F^2 + (0.2 + F)P^2 - 28.9(0.95 - F)P + 305.2(1.1 - F)]$$

where V is DC self-bias potential in volt, F is gas flow rate in SLPM and P is gas pressure in Torr. The contour plots for the theoretical data, obtained from the above equation, and the experimental data are shown in Figures 5.17 for comparison.

Figure 5.18 shows the effect of the location of the discharge gas inlet port on DC self-bias potential at different Ar gas flow rate for an Ar gas pressure of 8 Torr and an applied RF power of 40 W. The results show that the best location for the discharge gas inlet port is at the body of the sampling orifice disk as the DC self-bias potential becomes more negative by an average of 13 volts when discharge gas inlet port was shifted from the top of the atomizer chamber to the body of the sampling orifice disk.

Figure 5.19 shows the horizontal distribution of Cu atoms for various Ar gas flow rates at an Ar gas pressure of 8 Torr when the vertical position of the atomizer was fixed

Figure 5.17 - The values (from 340 to 519) are DC self-bias potentials (in volt) developed at the Cu cathode surface for various Ar gas flow rates and pressures at an applied RF power of 40 W. (a), experimental data; (b), theoretical data. Equation (3) was used for calculation.

Figure 5.18 - Effect of location of the Ar gas inlet port on DC self-bias at various Ar gas flow rate for an Ar gas pressure of 8 Torr and an applied RF power of 40 W. Discharge gas inlet port located: (O), at the body of sampling orifice disk; (●) at the top of the atomizer chamber.

Figure 5.19 - Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas pressure of 8 Torr and an applied RF power of 40 W when the atomizer was set at the vertical position of -4 mm for Ar gas flow rates: (○), "closed valve"; (□), 0.1 SLPM; (●), 0.4 SLPM; (■), 0.6 SLPM.

at -4 mm. The "closed valve" in this experiment refers to the minimum discharge gas flow rate that was possible with the present equipment, which could not be read with the gas flow-meter. Absorbances measured along the horizontal axis with "closed valve" show the approximate transport profile of atoms due to diffusion. At an Ar gas flow rate of 0.1 SLPM, a general increase in absorbance was seen which was probably because of an increase in the transport efficiency of sputtered atoms due to convection. At the Ar gas flow rate of 0.4 SLPM, a general decrease in absorbance was observed, probably because of decrease in the residence time of atoms with increasing gas flow rates. At the Ar gas flow rate of 0.6 SLPM, a general decrease in absorbance would therefore be expected. However, the general increase in absorbance along the horizontal axis observed at Ar gas flow rate of 0.6 SLPM was contrary to what was expected. This could result from the fact that the NG could be extended to a greater extent such that non-atomic species would spend more time within the NG, which would result in increase in their atomization efficiency via collisional dissociation.

Figure 5.20(a) shows the effect of the applied RF power on the spatial distribution of the sputtered Cu atoms along the horizontal axis when the modified RF atomizer was set at the vertical position of -4 mm for an Ar gas pressure of 8 Torr and an Ar gas flow rate of 0.4 SLPM. Figure 5.20(a) shows an increase in the absorbance of the sputtered Cu atoms at all horizontal distances when the applied RF power was increased. An RF power of 70 W seems to provide a uniform horizontal distribution of sputtered atoms at horizontal distances greater than 20 mm, which should result in the best precision. Figure 5.20(b) shows the result of the same experiment as Figure 5.20(a)

Figure 5.20 - Horizontal distribution of Cu atoms inside the atomizer chamber at an Ar gas flow rate of 0.4 SLPM and an Ar gas pressure of 8 Torr for various RF powers when the modified atomizer was set at the vertical position of: (a), -4 mm; (b), 0 mm.

except that the vertical position of the atomizer was set on the 0 mm.

It seems that the position of the absorbance maxima near the cathode surface depends on both the discharge gas pressure and flow rate. The lower the discharge gas flow rate or the higher the discharge gas pressure, the greater the shift of the absorbance maximum towards the cathode surface. If an absorbance maximum was sometimes not observable, it was because of a complete shift of the absorbance maximum toward the cathode surface, not accessible for measurement, making its observation impossible by AAS.

Table 5.1 shows the distances of the observed maxima from the cathode surface for various discharge conditions at a vertical position of 0 mm.

5.3.5 Analysis of residues of aqueous solutions

A preliminary test was done for sputtering of residues of aqueous solutions. A polyethylene orifice disk with an orifice diameter of 33 mm was used on the back of the sampling orifice disk. This disk was positioned so that the inner wall of its orifice touched the four corners of the square removable cathode, making the position of the cathode reproducible. Various experimental conditions were tested in order to obtain optimum conditions. These optimum conditions as well as the other experimental conditions are summarized in Table 5.2. No absorbance was measured at Au masses less than 500 ng. Absorbance was measured at various regions within the atomizer chamber. Higher absorbance was measured at the vertical position of 0 mm and at a distance of 12 mm from cathode surface. The analytical sensitivity in terms of characteristic mass (defined as mass/0.0044 absorbance) for Au was 32 ng. The accepted convention has

Table 5.1. Distance of the absorbance maximum from the cathode surface at various discharge conditions for the vertical position of 0 mm.

Ar gas pressure/Torr	Ar gas flow rate/SLPM		
	0.2	0.4	0.6
4	15 mm	N/A	N/A
5.4	< 10 mm	19 mm	N/A
6.6	N/A	N/A	19 mm
8	< 10 mm	< 10 mm	15 mm

N/A: Data are not available.

Table 5.2. Experimental conditions for sputtering of Au atoms from solution residue deposited on a Cu cathode.

Analyte mass of Au taken	500 ng
Ar gas flow rate	0.2 SLPM
Running Ar gas pressure	7 Torr
Spectral band pass	1 nm
Absorption line wave length	242.8 nm
Hollow cathode lamp current	6 mA
Sampling orifice thickness	2 mm
Sampling orifice diameter	4 mm
Applied RF power	40 W

been followed for reporting the analytical sensitivity in terms of characteristic mass as in graphite furnace atomic absorption spectrometry [87]. A relative standard deviation of 17% ($n=7$) was obtained for the measurement.

5.4 Conclusions

The results of this study have shown that the location of the discharge gas inlet port for cathodic-sputtering atomizers has a great effect on the AAS signal. The best location for the discharge gas inlet port has been found to be on the sampling orifice disk, such that the mass flow of the sputtered atoms and the forced convection of the discharge gas are in the same direction, thereby allowing the sputtered atoms to be efficiently entrained and transported into the analysis volume of the atomizer chamber with the flowing discharge gas. The optimum inside diameter of the sampling orifice disk for the modified RF atomizer was found to be 4 mm. Maxima in the absorbance as a function of the horizontal distance may be related to the dimensions of the negative glow; low gas pressures and high gas flow rates provide more complete dissociation of any analyte sputtered as clusters or molecules in an extended negative glow. The distribution of sputtered atoms is highly inhomogeneous and varies greatly with differing discharge conditions. Since it is impractical to optimize both the discharge conditions and the atomizer position for each analysis, atomic absorption spectrometric measurements with this RF-sputtering atomizer should be made in the region of the atomizer chamber at or just above the horizontal plane (i.e., the plane containing the central axis of the sampling orifice), perpendicular to the optical windows and the

cathode surface, at which the vertical distance is equal to zero. For this region, the variation in absorbance with horizontal distance is minimal, which should result in the best precision. This region also gives optimum to near-optimum analytical sensitivity, which should also give the best limits of detection with this RF-sputtering atomizer.

The optimum discharge conditions for AAS are not the same for different regions of the atomizer chamber. This will make the work with solution residues difficult as a transient signal is produced. An atomizer chamber with a smaller volume, at least with a diameter as large as the focused hollow cathode light beam, is necessary for solution residues to be analyzed by AAS.

CHAPTER 6

A laboratory-built RFGD atomizer for atomic absorption spectrometry of some nonconductive materials (silica)

6.1 Introduction

One of the factors that has tended to limit the application of glow discharges (GD) has been the requirement that the sample be electrically conductive. An insulating surface subjected to positive ion bombardment, will quickly build up a positive charge layer. This layer obtains a potential up to the floating potential [3], repelling discharge gas ions and thus slowing any further sputtering from the surface. The radiofrequency glow discharge (RFGD) circumvents this problem. The use of RF-sputtering has been shown to permit direct analysis of nonconducting solids [63].

Radiofrequency GD operates at pressures of mTorr, lower than the pressures required for DC discharge. In order to avoid gas phase scattering and consequently to prevent redeposition of sputtered analyte atoms on the cathode surface, RF systems are usually operated at the lower end of their operating pressure range when employed in sputter deposition applications [3]. The power source normally used to meet this requirement is an RF generator working at 13.56 MHz.

The objective of this research is to evaluate the performance of a laboratory-built RFGD atomizer for atomic absorption spectrometry of nonconductive materials (silica).

6.2 Experimental

6.2.1 Sputtering atomizer

A new laboratory-constructed RF-atomizer (Figure 6.1) was used. The atomizer chamber was that of another atomizer constructed earlier in this laboratory for DC-sputtering [48], which was modified for RF-sputtering as follows. The entire body of the atomizer chamber as well as the accelerator were grounded. An RF feed-through attached to the end of a coaxial RF power cable (RG-213U, Amphenol Canada), was inserted into a bolt and a male type-N connector was mated to a female connector until a copper rod 3.2 mm in diameter made contact with the back of the sample cathode. The length of the cable was kept short (about 90 cm) in order to avoid unnecessary impedance in the RF circuitry. The cable was shielded coaxially in order to reduce power losses. A copper disk 22 mm in diameter and 1.5 mm in thickness was fastened to the tip of the copper rod just between the macor spacer and the sample. The advantages of this disk were discussed in Chapter 4.

The atomizer body was shielded with an Al box having a wall thickness of 2 mm. This box had 5 circular holes: two parallel holes for passing the hollow-cathode lamp light beam through the atomizer chamber, one hole for inserting the vacuum line tube, one hole for the discharge gas inlet tube, and one hole for inserting the brass torque bolt. Al foil was used to cover the latter three holes to reduce any stray RF emission and to prevent interference of the RF discharge with other electronic devices, especially the hollow-cathode lamp power supply, detector, and recorder. Canadian government guidelines [117] for exposure times and levels for workers in the frequency range 10

Figure 6.1 - A schematic diagram of the RFGD atomizer.

MHz–1 GHz limit the maximum emitted field strength (equivalent power density) to 1 mW/cm² for continuous exposure. The regulatory test of the field strength of the RF power emitted by this RF generator made by Health and Welfare Canada found that the field strength of the RF power under the experimental conditions of this research presented no health hazards.

An interesting feature of this laboratory-built RF atomizer design is that it allows a comprehensive comparison of DCGD and RFGD systems, because the geometry of the RF design is completely comparable with the DC design. Such comparison may prove that the analytical characteristics of RFGD and DCGD devices are not very different and studies reported previously show that this is indeed the case [106,110]. The radiofrequency generator, impedance matching network, and detection system have been described in Chapter 4. The discharge gas control system has been described in Chapter 3.

6.2.2 Measurement system

A schematic diagram for the instrumental system is shown in Figure 6.2. The atomizer was mounted in the usual position of the burner assembly in the Varian-Techtron Model AA-5 AA spectrophotometer (described earlier) and was operated as part of the AA spectrophotometer. The absorbance profiles were recorded with a Nicolet Model 201 dual channel digital oscilloscope. The hollow-cathode lamp was manufactured by Perkin-Elmer. The optimum hollow-cathode lamp (Si) current for analytical sensitivity was 10 mA. The hollow-cathode lamp was electronically modulated at 1 kHz, with a time constant of 1 ms used on the lock-in amplifier. The light beam of

Figure 6.2 - A schematic diagram of the instrumental system.

the hollow-cathode lamp was focused to 6 mm in diameter as it passed through the atomizer chamber. The image of the light beam was 10 mm on both entrance and exit optical windows of the atomizer chamber. The wavelength and the spectral bandpass were 251.6 nm and 1 nm, respectively. The RF generator was operated in the constant power mode.

6.2.3. Standard reference materials

Multi-component glass (NBS SRM #1412) was used as a standard reference material.

6.2.4 Procedure

Quartz in the form of disks of 25.5 mm in diameter and 2.5 mm in thickness (which was also used as windows of the atomizer) was tested for Si as an unknown sample. The cathode was first sputter-cleaned to ensure a reproducible atomization surface, since large changes in reproducibility were found with changes in the cathode surface [34]. The laboratory-built gas control system (described earlier in Chapter 3) was used. The gas solenoid on the vacuum line was opened, evacuating the chamber to approximately 100 mTorr. When this pressure was attained, the gas solenoid on the discharge gas inlet was opened and the fine-regulating needle valve was adjusted to give the desired gas flow rate. When the desired gas flow rate was attained the valve on the vacuum line was adjusted to give the desired gas pressure. When the gas pressure attained the operating pressure, the oscilloscope and spectrophotometer were triggered just prior to applying the RF power. For measuring absorbances of Si atoms sputtered from the sputtered-cleaned surface, the RF generator was powered for at least 5 s, which

was sufficient for a steady-state sputtering. The RF generator output power was adjusted manually from the front panel of the generator, which displayed forward and reflected powers.

6.3 Results and discussion

Table 6.1 shows the effect of backing materials on AA signal of Si atoms. RF-sputtered from the quartz surface of the unknown sample at Ar gas pressure and flow rate of 3.7 torr and 0.2 SLPM, respectively. The applied RF power was 100 W. The results show that the presence of a conductive backing cathode is important for sputtering of Si atoms. The sputtering is independent of the type of the conductive backing material. The effect of all the backing materials shown in Table 6.1 is statistically not very different as long as one uses a conductive backing material.

In Figure 6.3, Ar gas pressure was held constant at 5.3 Torr and the absorbance of sputtered Si atoms was measured while the RF power was varied for Ar gas flow rates of 0.1, 0.2, 0.3 and 0.4 SLPM. As the RF power was increased, the absorbance of Si atoms increased as a result of the increase in sputtered material from the sample (quartz) surface. Radiofrequency powers more than 400 W could not be applied on the atomizer used for this work as the impedance matching network could not tune the impedances of the atomizer and the power supply assemblies. Also, Ar gas flow rates more than 0.4 SLPM could not be achieved for Ar gas pressure of 5.3 Torr because of limitations in the capacity of the vacuum pump used with the apparatus. The results show an optimum Ar gas flow rate of 0.2 SLPM for these conditions. It is expected that more Si atoms

Table 6.1. Effect of backing material on AAS signal of RF-sputtered Si atoms from the unknown sample (quartz) at Ar gas pressure and flow rate of 3.7 Torr and 0.2 SLPM, respectively, and an RF power of 100 W.

Backing Material	Dimensions of the backing material Length × Width × Thickness (mm)	Absorbance
None	-	0.10 ± 0.01
Copper	23 × 23 × 0.5	0.14 ± 0.01
	23 × 23 × 1	0.13 ± 0.01
	23 × 23 × 6	0.15 ± 0.02
	23 × 23 × 11	0.13 ± 0.01
	40 × 35 × 11	0.14 ± 0.02
Tantalum	23 × 23 × 0.5	0.14 ± 0.01
	35 × 21 × 0.5	0.14 ± 0.01
Steel	23 × 23 × 1	0.16 ± 0.02
Graphite	23 × 23 × 6	0.16 ± 0.01
Brass	23 × 23 × 1	0.13 ± 0.01
Macor	23 × 23 × 4	$(4.0 \pm 1.0) \times 10^{-3}$
Aluminum	23 × 23 × 6	0.15 ± 0.02
Zinc	23 × 23 × 6	0.14 ± 0.01

Figure 6.3 - Absorbance of RF-sputtered Si atoms sputtered from a quartz sample surface as a function of RF power for various Ar gas flow rates at a fixed Ar gas pressure of 5.3 Torr: (▽), 0.1 SLPM; (○), 0.2 SLPM; (●), 0.3 SLPM; (□), 0.4 SLPM.

will be sputtered from the sample surface at higher RF powers, and the absorbance-power curve would finally level off, followed by a drop-off as a result of penetration of discharge gas ions into the interior of the cathode lattice, and consequently, of dissipation of energy of discharge gas ions in the depth of the cathode lattice.

Figure 6.4 shows the absorbances of sputtered Si atoms as a function of Ar gas flow rate for different Ar gas pressures at an applied RF power of 400 W. For all the pressures tested, the absorbance reaches a maximum plateau at an Ar gas flow rate of 0.2 SLPM. The spread of the plateau of the maximum absorbance depends on the Ar gas pressure. Hutton et al. [48] have reported a similar levelling-off for absorbances of Cu and Cr atoms, DC-sputtered from steel, and Ni atoms, DC-sputtered from brass, at an Ar gas pressure of 10 Torr and a DC power of 300 W. These authors have reported a decrease in absorbance at high Ar gas flow rates, but they have not shown the effect of the Ar gas pressure on the spread of the plateaux of the maximum absorbances.

Figure 6.4 shows that at higher Ar gas pressures the plateaux of the maximum absorbances cover a greater range of higher flow rates of the discharge gas. This observation reflects the relative importance of diffusion and convection effects on the residence time of atoms in the analysis volume. Diffusion of atoms in the analysis volume is more important at lower discharge gas pressures; the rate of diffusion decreases with increasing gas pressure. For Ar gas flow rates more than 0.2 SLPM, if the decrease in residence time due to convection is more than increase in residence time due to diffusion, a decrease in absorbance, similar to that observed at Ar gas pressure of 5.3 torr, is expected. On the other hand, if the decrease in residence time due to

Figure 6.4 - Absorbance of RF-sputtered Si atoms as a function of Ar gas flow rate for various Ar gas pressures at a fixed applied power of 400 W: (Δ), 5.3 Torr; (○), 6 Torr; (●), 7 Torr; (□), 8 Torr; (×), 9 Torr; (■), 10 Torr.

convection is more or less equal to the increase in residence time due to diffusion, the absorbance will remain unchanged, as was observed at Ar gas pressure of 10 Torr.

From Figure 6.4, it is also reasonable to conclude that the transport efficiency of atoms to the analysis volume was at a maximum and redeposition of sputtered atoms was at a minimum for an Ar gas flow rate of 0.2 SLPM. The fact that the absorbance of Si atoms remained essentially constant as Ar gas flow rate was increased from 0.2 to 0.4 SLPM, at the Ar gas pressure of 10 Torr, also reflects an increase in the transport efficiency (defined as the fraction of the total number of analyte atoms sputtered from the cathode surface that reach the analysis volume) with increasing discharge gas flow rate. This effect offsets the decrease in the residence time and the dilution of analyte atoms in the analysis volume due to higher flow rates, as described by Pavski et al. [118].

Figure 6.5 shows the absorbance of Si atoms sputtered from a quartz surface at an Ar gas flow rate of 0.2 SLPM as a function of Ar gas pressure for various applied RF powers. It should be noted that the Ar gas pressure of 3.7 Torr was the lowest pressure which could be attained at the Ar gas flow rate of 0.2 SLPM. As seen from Figure 6.5, the absorbance decreases with increasing Ar gas pressure because of increased redeposition of sputtered materials. The results indicate that still higher absorbances could be obtained at Ar gas pressures lower than 3.7 Torr as RF discharge can operate at lower pressures than its DC counterpart. That is because secondary electrons, which have extremely high yields in the case of insulators, are accelerated across the positive ion sheath into the plasma and act as an additional supply

Figure 6.5 - Absorbance of Si atoms, RF-sputtered from a quartz surface at a fixed Ar gas flow rate of 0.2 SLPM as a function of Ar gas pressure for various applied powers: (○), 100 W; (●), 200 W; (▽), 300 W; (▼), 400 W.

of electrons for sustaining the glow discharge [3].

Figure 6.6 shows the results of an experiment performed using the same discharge conditions as used for Figure 6.5 except that the Ar gas flow rate was 0.3 SLPM. A decrease in absorbances was observed similar to that in Figure 6.5.

Figure 6.7 shows the absorption profiles for Si atomization from a quartz sample at Ar gas flow rate of 0.2 SLPM, applied RF power of 100 W and Ar gas pressure of 3.7 Torr. Figure 6.7(a) was obtained using an unsputtered surface. Figure 6.7(b) was obtained by sputtering from the sputter-cleaned surface left after Figure 6.7(a) was obtained. The difference in the rise time of the leading edges of the absorbance profiles shown in Figure 6.7 illustrates a significant feature of the sputtering of solid samples, as previously observed in DC sputtering of solid metals and alloys [13]. The sputtering rate and the sputtering yield depends critically on the physical conditions of the sputtering surface of the solid sample. As explained by Wehner [13], a sputtered atom has to receive an energy which is sufficient to overcome its surface binding energy. The heat of sublimation provides a measure of the average binding energy. After stripping of the surface by sputtering, either DC or RF, many atoms may be found at sites with lower numbers of nearest neighbour, such as at grain boundaries or dislocations, or on top of a filled plane. Such exposed atoms have a lower binding energy and are more readily sputtered than those from filled planes. Roughness of the cathode surface also affects the sputtering yield, because for sputtering to occur, the target atom must acquire not only sufficient energy to overcome its binding energy with its neighbours in the crystal lattice, but also acquire a velocity vector which will carry it away from the cathode and

Figure 6.6 - Absorbance of Si atoms, RF-sputtered from a quartz surface at a fixed Ar gas flow rate of 0.3 SLPM as a function of Ar gas pressure for various applied powers: (○), 100 W; (●), 200 W; (▽), 300 W; (▼), 400 W.

Figure 6.7 - Absorption profiles for Si atomization of a quartz sample at a fixed Ar gas flow rate of 0.2 SLPM and a fixed RF power of 100 W and an Ar gas pressure of 3.7 Torr. (a), during sputter-cleaning; (b), from a sputter-cleaned surface.

into the GD. Redeposition is more likely when the surface is rough. Surface preparation determines the roughness of the surface and can also introduce dirt and other impurities which affect the sputtering yield. A surface which has not been sputter-cleaned will always include local variations of binding energy over the surface and this will lead to variations in the sputtering yield [16]. Thus, the most reproducible surface will be the one which has been sputter-cleaned.

Figure 6.8 shows the AA signal from RF-sputtered Si atoms from a quartz sample and from the hollow-cathode lamp light beam under the pulsed mode of atomization. Experimental conditions were Ar gas pressure and flow rate of 3.7 Torr and 0.2 SLPM, respectively. A pulsed RF-power of 100 W with a duty cycle of 58% ("ON" time and "OFF" time were 5.5 and 4 sec, respectively) was used. This experiment was performed to check the stability of the hollow-cathode lamp light beam during a long period of atomization such as that required for depth profiling by AAS. The pulsed mode of atomization provides a correction for the AA signal by probing changes in the hollow-cathode lamp light beam. The pulsed mode of operation has the advantage of applying higher average discharge power, thereby avoiding a significant increase in the sample surface temperature while still maintaining a reasonably short analysis time. For AAS, the pulsed mode of atomization not only increases the sputtering rate but also cancels the background emission [49]. By applying the pulsed mode of atomization, it is possible to obtain higher analytical sensitivity as a result of increased rate of sputtering. Winchester and Marcus [119] have studied the effects of a pulsed GD on the emission intensities of Cu lines. They have reported anomalies in the temporal emission intensity

184

Figure 6.8 - AA signal of RF-sputtered Si atoms from a quartz sample as well as the hollow-cathode lamp light absorption under the pulsed mode of atomization with a duty cycle of 58% at an Ar gas flow rate of 0.2 SLPM, an RF power of 100 W and an Ar gas pressure of 3.7 Torr.

for some analyte emission lines.

The rate of weight loss of quartz at an Ar gas pressure of 3.7 Torr, Ar gas pressure of 0.2 SLPM and an applied RF power of 100 W was $31.4 \pm 1.4 \mu\text{g}/\text{min}$. At the same condition a macor sample was found to have a rate of weight loss of $6.70 \mu\text{g}/\text{min}$. Kinetic analysis of the RF-sputtered Si atoms from quartz showed similar results (Table 6.2) for both first-order (Equation 1) and normalized zero-order sputtering rate constants (Equation 3). Zero-order sputtering rate constant was normalized to the mass of the sample, thus the normalized zero-order sputtering rate constant is defined by the ratio of zero-order sputtering rate constant (Equation 2) to initial sample weight. This experiment was performed in order to test the effect of physical parameters of the sample, such as dimensions, on the rate of RF sputtering. For a first-order rate process,

$$\ln(W_t/W_0) = -k_1 t \quad (1)$$

where k_1 is the first-order rate constant in sec^{-1} , t is time in second, W_t is the sample weight at time t and W_0 is the sample weight at $t = 0$. For a zero-order rate process,

$$\Delta W/\Delta t = k_0 \quad (2)$$

where k_0 is the zero-order rate constant in gram sec^{-1} and ΔW is the sample weight loss (in gram) after a time of Δt seconds. For the normalized zero-order rate process,

$$k_N = k_0/W_0 \quad (3)$$

where k_N is the normalized zero-order rate constant in sec^{-1} . The result of this study shows that the zero-order and the first-order process are indistinguishable.

Figure 6.9 shows the absorbance of Si atoms sputtered from a multi-component glass containing 16.53 % Si, as a function of applied RF power. The Ar gas flow rate

Table 6.2. Kinetic analysis for RF-sputtered Si atoms from a quartz sample at Ar gas flow rate and Ar gas pressure of 0.2 SLPM and 3.7 Torr, respectively, and an applied RF power of 100 W.

Order of the rate process	Rate constant
First order, s^{-1}	$(3.1 \pm 0.2) \times 10^{-7}$
Zero order, g/s	$(5.2 \pm 0.2) \times 10^{-7}$
Normalized zero order, s^{-1}	$(3.1 \pm 0.2) \times 10^{-7}$

Figure 6.9 - Absorbance as a function of applied RF power for sputtered Si atoms from the surface of the Multi-Component Glass (NBS SRM # 1412) at Ar gas flow rate and Ar gas pressure of 0.2 SLPM and 3.7 Torr, respectively.

and Ar gas pressure were 0.2 SLPM and 3.7 Torr, respectively. It was not possible to apply RF powers more than 140 W for sputtering of this sample as the sample was fragile and broke under higher applied RF power.

The analytical sensitivity of the steady-state atomization mode is presented in terms of characteristic concentration (concentration/0.0044 absorbance). The accepted convention for AAS using a flame atomizer-burner [87] was followed for reporting the analytical sensitivity in terms of characteristic concentration. Calculation showed that the analytical sensitivity of RF atomization for determination of Si in the Multi-Component Glass (NBS SRM #1412) was 1.05 percent by weight.

6.4 Conclusions

The result of this study show that the laboratory-built RF atomizer holds promise for analysis of nonconductive samples. This technique can also determine metals in non-conductive residues of solutions deposited on a cathode surface such as Cu or graphite described in Chapter 7. The results suggest several modifications for the atomizer and the gas control system to improve analytical sensitivity. As high powers increase both sputtering yield and atomization efficiency, a pulsed mode of atomization may help to increase analytical sensitivity while using lower powers which are not only more suitable and safe but also applicable to the laboratory-built atomizer described in this chapter.

CHAPTER 7

Removal of sodium chloride matrix interferences in the determination of gold and iron in solution residues by GD-AAS

7.1 Objective

The objective of this research was to investigate the matrix interferences by sodium chloride in the quantitative determination of Au and Fe by atomic absorption spectrometry with atomization by cathodic sputtering in a glow discharge. Sodium chloride was chosen as the matrix for two reasons: 1) it is a major constituent of sea waters and interferes with the determination of trace elements in sea waters by inductively coupled plasma mass spectrometry, and by graphite furnace atomic absorption spectrometry; 2) sodium chloride has been found to interfere with the quantitative determination of Au and Fe (also, of Ag and Pb by CSGD) in a previous study [97] from this laboratory. This chapter presents the results of this investigation.

7.2 Experimental

7.2.1 DC-sputtering apparatus

These experiments were performed using a laboratory-built atomizer modelled after the ATOMSOURCE atomizer [48], which was supplied with the ATOMSOURCE power supply and its other accessories (manufactured by Analyte Corp., Grants Pass, OR, U.S.A.). It was mounted in the usual position of the burner assembly in a Varian-Techtron model AA-5 atomic absorption spectrophotometer and was operated as part of

the AA spectrophotometer.

For experiments done without controlling Ar gas flow rate (the experimental conditions have been given in Table 3.1), the ATOMSOURCE power supply was used, which was capable of operation under either the direct-current or the voltage regulation mode. The ATOMSOURCE was used in the current regulation mode. The ATOMSOURCE and hollow-cathode lamp power supplies have been described in Chapter 3. The hollow-cathode lamps were manufactured by Westinghouse. The absorbance and the discharge voltage were recorded simultaneously with Nicolet Model 201 two-channel digital oscilloscope.

For experiments carried out with fine control of the discharge duration, and the discharge gas flow rate, the laboratory-built apparatus was used [48]. For these experiments, the ATOMSOURCE power supply was disconnected from the atomizer. The power supply used was a 1 kW High Z DC Magnetron, Model MDX-1K, manufactured by Advanced Energy Industries Inc., Fort Collins, CO, U.S.A.. The MDX-1K power supply has a rated output of 1 A at 1000 V for a maximum power output of 1000 W. The power supply permits current, voltage, or power regulation. The entire apparatus for this study was composed of four basic units: the "new atomizer" modelled after the ATOMSOURCE, the system for the discharge gas flow rate and pressure control, the power supply (MDX-1K), and the measurement system. A detailed description of the MDX-1K apparatus was provided by Hutton et al. [48]. In this apparatus, the hollow-cathode lamp power supply was modulated at 1 kHz and a time constant of 1 ms was used on the lock-in amplifier (Stanford Research System Inc.,

U.S.A., model SR530). Other experimental conditions for this experiment have been given in Table 3.3.

7.2.2 RF-sputtering apparatus

A schematic diagram of the laboratory-built RFGD source has been given in Figure 6.1. The atomizer was mounted in the usual position of the burner assembly in a Varian-Techtron Model AA-5 atomic absorption spectrophotometer and was operated as part of the AA spectrophotometer. The hollow-cathode lamp power supply was modulated at 1 kHz and a time constant of 1 ms was used on the lock-in amplifier. Other experimental conditions are given in Table 7.1. The radiofrequency generator and impedance matching network have been described in Chapter 4. A schematic diagram for the laboratory-built DC self-bias monitor has been given in Figure 5.2. The discharge gas was Ar.

7.2.3 Test solutions and reagents

Chemically pure metals or their salts were used to prepare standard solutions. Stock solutions were prepared as follows. For Fe (1000 $\mu\text{g/mL}$), the metal was dissolved in 50% (v/v) nitric acid (ULTREX) and the solution diluted with ultrapure water. For Au, the stock solution (1000 $\mu\text{g/mL}$, prepared by dissolving pure gold in aqua regia), was supplied by Harleco (Philadelphia, PA, U.S.A.). The triton-X solution was prepared to contain $\approx 0.1\%$ v/v triton-X (octylphenoxy polyethoxyethan) by diluting the triton-X (Sigma Chemical Company) with ultrapure water. Triton-X was used as a surfactant, to reduce the surface tension between test solution and the cathode surface, so as to spread the test solutions evenly all over the cavity. Ultrapure water of resistivity 18.3

Table 7.1 Experimental conditions for RF-sputtering of Au and Fe atoms from solution residues on a Cu cathode

Analyte	Wavelength (nm)	Spectral bandpass (nm)	Analyte mass (ng)	Hollow-cathode lamp current (mA)	Ar gas flow rate (SLPM)	Ar gas pressure (Torr)	Power (W)
Au	242.8	1	5	6	0.2	5	150
Fe	248.3	0.1	5	6	0.4	5	100

M Ω cm was obtained direct from a Milli-Q2 Water Purification System (Millipore Corp., Canada). All test solutions were prepared by serial dilution of the above stock solutions immediately prior to determination. Cu (99%) and pyrolytic graphite were used as cathodes for deposition of solutions on them.

7.2.4 Procedure

The procedure used has been described in Chapter 3. For the RF-sputtering experiments, gas pressure and flow rate adjustment was the same as for the MDX-1K apparatus. The RF power supply then triggered to set the impedance matching network during the production of circular cavity on the cathode surface and prior to every atomization cycle. For every atomization cycle, the oscilloscope and the RF power supply were triggered simultaneously and the absorption signal was obtained together with the corresponding DC self-bias voltage as a function of time. The mean peak height or mean peak area of at least four replicate depositions of test solutions was taken for each solution sample.

Before deposition of the sample solution on a freshly-surfaced (sputter-cleaned) cathode, the cathode was sputtered for 1 minute using the same experimental conditions as used for the subsequent determination, in order to create a circular cavity (Figure 7.1) into which the sample solution was pipetted. This circular cavity, which was approximately 5 mm in diameter, had 6 depressions (craters) corresponding to the 6 gas jets used for the introduction of the Ar discharge gas into the atomizer. A pre-sputtering time of 1 minute was found to give the best compromise between having a cavity so deep that a long time was required to resurface the cathode, and having the cavity so shallow

Figure 7.1 - Depression profiles produced by six gas-jets on the cathode surface.

that the sample solution was inadequately contained, resulting in sample spread and consequent poor sensitivity and reproducibility. The cathode did not have to be resurfaced after every run because the discharge itself "sputter-cleaned" the cathode surface; the cathode was therefore resurfaced periodically as required.

7.3 Results and Discussion

Figure 7.2 shows the atomic absorption signals for 500 ng Fe, RF-sputtered from solutions deposited into different locations inside the circular cavity of a graphite cathode. The experimental conditions are given in Table 7.2. The highest sensitivity was obtained when the solution was pipetted exclusively into the 6 depressions formed by the gas jets (Figure 7.2(a)). This was expected since these depressions were formed because the sputtering was most intense where the gas jets impinged on the cathode surface. The lowest sensitivity was obtained when the sample solution was pipetted exclusively into the centre of the circular cavity and not at all into the 6 depressions (Figure 7.2(c)). Since the centre of the cavity was at a higher level than the 6 depressions, it followed that this was where the sputtering was the least intense. The sensitivity obtained by pipetting the sample solution such that it covered all but the outer edge of the cavity (Figure 7.2(b)) was intermediate but relatively high. This was because most of the sample solution was contained in, and thus was dried in the 6 depressions, where the sputtering was the most intense. This observation is supported by the results of Banks and Blades [116], who reported a reduction in the redeposition of sputtered material in the depressions, where the gas-jet flow of Ar impinged on the sample surface.

Figure 7.2 - Atomic absorption signals of Fe given by RF-sputtered solution residues deposited in various locations of the cavity of pyrolytic graphite cathode. Deposition locations are: (a), inside the craters only; (b), the entire cavity; (c), only at the centre of the cavity. Experimental conditions are given in Table 7.2.

Table 7.2 Experimental conditions for RF-sputtering of Fe from solution residues deposited on a graphite cathode

Wavelength (nm)	Spectral bandpass (nm)	Analyte mass (ng)	Hollow-cathode lamp current (mA)	Ar gas flow rate (SLPM)	Ar gas pressure (Torr)	Power (W)
248.3	0.2	500	6	0.4	5	150

Therefore, redeposited sputtered material must have buried that fraction of the solution residue which was still not sputtered, requiring a longer sputtering time, without changing other discharge conditions, similar to that observed in the present study for the sputtering of solution residues located off the depressions (Figure 7.2(c)).

In practice, the sample solution was distributed evenly over the circular cavity (Figure 7.2(b)). The reason for this was that it was generally very difficult to pipette the sample solution so that it was deposited only in the 6 depressions. The surface tension of the sample solution, particularly with copper cathodes, was often such that the sample solution readily spread out over the entire circular cavity and outside it as well if sufficient care was not exercised, thus precluding any attempt to localize the distribution of the solution residues on the cathode surface. The reason that a graphite cathode was used for this particular experiment despite the lower sensitivity given by graphite cathodes compared to copper cathodes [26], was that the sample solutions readily spread on copper cathodes and could not be localized as easily as on graphite cathodes. Even with graphite cathodes it was sometimes found necessary to reduce the surface tension of the sample solution by adding 0.02% Triton X-100 surfactant to it. Poor precision in the peak-height absorbance was found when we attempted to localize the sample solution in the 6 depressions as opposed to distributing the sample solution evenly over the circular cavity: 15% RSD as opposed to 5% RSD for Fe ($n=4$). It thus seems that the nature of distribution of the sample residues on the cathode surface has a significant effect on the sensitivity and the precision of the determination. Even distribution of the sample solution over the entire circular cavity was found to give high sensitivity and

good precision, and which also resulted in the best limits of detection. Other experimental results (not shown) also showed that gas-jets improved the sensitivity of the measurement. It was observed that the peak-height and the peak-area absorbances were drastically decreased when the accelerator was removed from the atomizer (no gas-jets): this is in agreement with the results of Banks and Blades [61] and of Kim and Piepmeier [47].

The shape of the signal was independent of the position of the solution residue when the residue and cathode material had high sputtering rates. A similar observation was reported by Daughtrey et al. [120] in the study of the effects of sputtering in a hollow-cathode discharge by scanning electron microscopy. They indicated that a solution residue deposited on a cathode cavity surface was subject to varying degrees of release by sputtering depending upon its location.

The precision of the results of Au determination in Au solution residues at trace levels was investigated using a series of solution residues. Each solution residue contained 5 ng Au and was DC-sputtered under the identical experimental conditions of gas pressure, applied power, and discharge current, using the ATOMSOURCE power supply. The experimental conditions have been given in Table 3.1. Between each experiment, the cathode was checked for any background contribution. An RSD of 6% was obtained for peak-height measurement and of 15% for peak-area measurement. For a similar experiment, using 5 ng Fe, the RSD was 5% for peak-height and 17% for peak-area measurement. Given the large change in surface area and the dependence of sputter rate on ion bombardment angle [100], it is reasonable to expect the cathode surface

history to affect the results. Bruhn and Harrison [34] reported a sequence of surface changes of Cu after various times of Ar sputtering. Trapping of sample residues inside the cathode surface-cones produced by bombarding ions could produce a nonhomogeneous surface microstructure, which can affect the reproducibility of analytical results. Poor reproducibility in the absorption measurements was eliminated when the cathodes were sputter-cleaned for identical times before a sample solution was deposited.

Gough et al. [83] and Larkins [84] have shown the effect of water vapour on the stability of the sputtering process and on atom production by GD sputtering. Water vapour is dissociated in the discharge and the resulting hydrogen ions contribute to the discharge current. These ions, however, do not contribute significantly to the sputtering yield, since the sputtering yield for hydrogen ion bombardment is very low, because of its low mass. Water vapour may nevertheless cause considerable changes in current density and thus affect the sputtering yield and reproducibility [76]. Therefore, any residual water in the residues of aqueous solutions of Au and Fe salts may affect the reproducibility.

7.3.1 The NaCl matrix interferences in the DC-sputtering

Figures 7.3a-7.3d shows the absorption profiles of Fe, DC-sputtered (ATOMSOURCE power supply) from solution residues deposited on a copper cathode, as a function of the mass of NaCl added to the solution. The voltage profiles, related to these signals, are also shown in these figures. Experimental conditions have been listed in Table 3.1. Figure 7.3a shows the absorption profile for 5 ng Fe atomized from a Cu cathode. Figures 7.3b-7.3d are absorption profiles for 5 ng Fe, sputtered from a

Figure 7.3a - (a) absorbance profile; (b) the related discharge voltage, for sputtering of 5 ng Fe solution residues using ATOMSOURCE. Experimental conditions: Ar gas pressure, 8 Torr; discharge current, 150 mA.

202

Figure 7.3b - (a) absorbance profile; (b) the related discharge voltage, for sputtering of 5 ng Fe + 500 ng NaCl Fe solution residues using ATOMSOURCE. Experimental conditions: Ar gas pressure, 8 Torr; discharge current, 150 mA.

203

Figure 7.3c - (a) absorbance profile; (b) the related discharge voltage, for sputtering of 5 ng Fe + 1000 ng NaCl solution residues using ATOMSOURCE. Experimental conditions: Ar gas pressure, 8 Torr; discharge current, 150 mA.

204

Figure 7.3d - (a) absorbance profile; (b) the related discharge voltage, for sputtering of 5 ng Fe + 5000 ng NaCl solution residues using ATOMSOURCE. Experimental conditions: Ar gas pressure, 8 Torr; discharge current, 150 mA.

Cu cathode in the presence of 500 ng, 1000 ng and 5000 ng NaCl, respectively. The results show that the dilution of analyte in the residue by the NaCl matrix decreases the peak height but does not change the peak area.

Figures 7.3a-7.3d also show the voltage profiles in DC-sputtering of Fe from solution residues with and without NaCl matrix, in relation to the absorbance signals shown in these figures. Discharge voltage profiles are similar to those obtained by Headrick et al. [97]. As discussed by these authors, the interference is probably the result of the sputtering of large amounts of the ionic matrix in the discharge. These ions disrupt the discharge by carrying a significant portion of the discharge current while being much less efficient than the Ar ions at sputtering. These results are similar to the results obtained by Riby and Harnly [96] on the effect of the concentration of NaCl on the discharge voltage profile for hollow anode-furnace atomization non-thermal excitation spectrometry (HA-FANES). They used a graphite furnace for sample atomization, while a GD formed by a central coaxial graphite cathode was used for sample excitation. Riby and Harnly [96] found that as the concentration of NaCl was increased, the discharge voltage decreased until the discharge was entirely shorted. These results seem to be related to the presence of large numbers of electrons resulting in a low voltage arc instead of a stable GD. The appearance of an AA signal of Fe in the presence of the high concentration of NaCl, as shown in Figure 7.3d, coincides with the steep rise in the discharge voltage as the NaCl was removed by sputtering, and the discharge current was again carried by Ar ions instead of electrons. Build-up of a positive surface charge on the surface of the cathode by the non-conducting NaCl matrix might also have played a

role in the observed interference by making it difficult for the discharge to become established. Radiofrequency or ion beam sputtering can be used to eliminate interferences caused by differences in the sample conductivity, but the later is expensive and has a limited throughput.

7.3.2 The NaCl matrix interferences in the RF-sputtering

Figure 7.4 shows the peak-height and the peak-area recoveries of 5 ng Fe, RF-sputtered from solution residues deposited on a copper cathode, as a function of the mass of NaCl; other experimental conditions are given in Table 7.1. Figure 7.5 shows the peak-height and the peak-area recoveries of 5 ng Au, RF-sputtered from solution residues deposited on a copper cathodes, as a function of the mass of NaCl; other experimental conditions are given in Table 3.1. Contrary to what was observed for the DC-sputtering, Figures 7.4 and 7.5 show that for the RF-sputtering there is essentially no difference between the peak-height and the peak-area recoveries, and that the use of RF-sputtering allows quantitative determination of Fe and Au in the presence of large amounts of NaCl without the interferences that are observed with the DC-sputtering. In Figure 7.6, atomic absorption signals of Fe, RF-sputtered in the presence and in the absence of NaCl, are shown with their related DC self-bias voltages. The DC self-bias voltage profiles in Figure 7.6 are undisturbed by the presence of the NaCl matrix, in contrast to the disruption observed in Figures 7.3b-7.3d. Probably, this suggests an absence of interference by the NaCl matrix ions with the RF-sputtering of Fe.

Table 7.3 compares the minimum mass of NaCl matrix which was found to interfere with the peak-height and the peak-area absorbance of Au and Fe for the various

Figure 7.4 - Percent peak-height and peak-area recoveries of 5 ng Fe from solution residues with NaCl matrix. (○), DC-sputtering mode; (■), RF-sputtering mode. Experimental conditions are shown in Table 3.1 for DC-sputtering and in Table 7.1 for RF-sputtering.

Figure 7.5 - Percent peak-height and peak-area recoveries of 5 ng Au from solution residues with NaCl matrix. (○), DC-sputtering mode; (■), RF-sputtering mode. Experimental conditions are shown in Table 3.1 for DC-sputtering and in Table 7.1 for RF-sputtering.

Figure 7.6 - Absorbance signals and their related DC self-bias voltage profiles for Fe, RF-sputtered from solution residues containing various masses of NaCl matrix. (a), 5 ng Fe; (b), 5 ng Fe with 10 μg NaCl. Experimental conditions are shown in Table 7.1.

Table 7.3 Minimum mass, in ng, of NaCl matrix which gives less than 100% recoveries of peak-height and peak-area of 5 ng of Fe and Au in GD-AAS with Cu as the cathode.

Sputtering mode	Mass of NaCl in Fe solution residue, ng		Mass of NaCl in Au solution residue, ng	
	Peak-height measurement	Peak-area measurement	Peak-height measurement	Peak-area measurement
DC, transient (ATOMSOURCE) DC, pulsed (MDX-1K) RF	5	5	50	500
	500	1000	500	500
	10 ⁴	10 ⁴	10 ⁵	10 ⁵

sputtering systems investigated in this work. Severe interferences were found for Au and Fe in the presence of NaCl using the transient mode of atomization (ATOMSOURCE). The use of pulsed mode of atomization (MDX-1K) was found to be much less subject to this interference, and had the added benefit of having a high sensitivity [46]. The use of RF-sputtering further reduced the interference to the point where only the highest mass of NaCl used still interfered. For example, for 5 ng Au, up to 10^5 ng NaCl can be tolerated without interference. This is equivalent to a concentration of 10% NaCl, which is greater than its concentration in sea water. In summary, the use of the pulsed mode of atomization reduces the NaCl interference, the use of RF-sputtering effectively eliminates it.

Figure 7.7 shows typical AA signals, and their related DC self-bias voltage profiles of RF-sputtered Au from solution residues with and without NaCl matrix. Experimental conditions were Ar gas flow rate and pressure of 0.2 SLPM and 5 Torr, respectively, with an applied RF power of 100 W.

Figure 7.8a shows the variations in the peak-height absorbance, and its related DC self-bias voltage, with Ar gas pressure for RF-sputtered solution residue of 5 ng Au at an RF power and Ar gas flow rate of 100 W and 0.2 SLPM, respectively. This figure shows an optimum Ar gas pressure of 5 Torr for absorbance of Au atoms. At Ar gas pressures higher than 5 Torr, the absorbance of Au atoms decreases, most probably as a result of redeposition of the sputtered materials. Figure 7.8a also shows that the voltage, which determines the sheath voltage at the cathode surface, decreases as Ar gas pressure increases. Thus, at high Ar gas pressures, Ar ions travel too short a distance

Figure 7.7 - (a) typical AA profiles; (b) the related discharge voltages, for RF-sputtering of 5 ng Au solution residue, with and without 5000 ng NaCl, deposited on a Cu cathode. Experimental conditions were Ar gas pressure and flow rate of 5 Torr and 0.2 SLPM, respectively, and the discharge power was 100 W.

Figure 7.8a - Variations in the peak-height absorbance and its related DC self-bias voltage as a function of Ar gas pressure, for 5 ng Au, RF-sputtered from solution residue, at a fixed power and a fixed Ar gas flow rate of 100 W and 0.2 SLPM, respectively. (O), Peak-height absorbance; (●), DC self-bias voltage.

in the accelerating field of the cathode sheath and do not gain enough kinetic energy. Consequently the sputtering rate decreases [93].

Figure 7.8b shows the variations in the peak-height absorbance, and its related DC self-bias voltage, as a function of Ar gas flow rate, for 5 ng Au, RF-sputtered from solution residue at Ar gas pressure and RF power of 5 Torr and 100 W, respectively. An optimum Ar gas flow rate of 0.2 SLPM, corresponding to maximum absorbance of Au atoms, is deduced from the results. At Ar gas flow rates lower than 0.2 SLPM, the transport efficiency of Au atoms into the analysis volume, and consequently, the measured absorbances are small. It should be mentioned that the analysis volume is spatially separated from the cathode surface in the atomizer used for this study. At Ar gas flow rates higher than 0.2 SLPM, decreases in the AA signals are the result of decrease in the residence time of Au atoms within the analysis volume.

Figure 7.8c shows the variations in the peak-height absorbance, and its related DC self-bias voltage, as a function of discharge power, for 5 ng Au, RF-sputtered from solution residue at Ar gas flow rate and pressure of 0.2 SLPM and 5 Torr, respectively. At RF powers more than 250 W, the variation in the peak-height absorbance seems to be less than that observed for lower RF powers, as seen from the slope of the curve. It is probably because high-energy Ar ions penetrate further into the cathode lattice with increasing applied power, and dissipating their energy in collisions too deep inside the crystal lattice to transmit a disturbance back to the surface, resulting in a reduction in the sputtering rate [14]. It was not possible to get results at RF powers higher than 300 W because of arcing observed across the electrodes at these powers.

Figure 7.8b - Variations in the peak-height absorbance and its related DC self-bias voltage as a function of Ar gas flow rate for 5 ng Au, RF-sputtered from solution residue at an Ar gas pressure and applied RF power of 5 Torr and 100 W, respectively. (○), Peak-height absorbance; (●), DC self-bias voltage.

Figure 7.8c - Variations in the peak-height absorbance and its related DC self-bias voltage as a function of discharge power, for 5 ng Au, RF-sputtered from solution residue at a fixed Ar gas flow rate and pressure of 0.2 SLPM and 5 Torr, respectively. (○), Peak-height absorbance; (●), DC self-bias voltage.

Tables 3.3 and 7.1 show that optimum Ar gas pressures and flow rates for the RF-sputtering of Fe and Au are less than those for DC-sputtering. This is probably because the oscillation of ions in the RF field increases the collision frequency required for atomization of clusters or molecules in the gas phase which consequently allows the use of a lower pressure. Since at lower gas pressures the redeposition rate decreases then a lower gas flow rate is necessary to transport atoms from the cathode surface into the analysis volume.

Figure 7.9 shows the analytical calibration curves for determination of Fe in the presence of the matrix formed from a NASS-3 solution. The experimental conditions are shown in Table 7.4.

7.4 Conclusions

The distribution of the sample solution residue on the cathode surface has a significant effect on the sensitivity and the precision of determination of Au and Fe in aqueous solutions. An even distribution of the sample solution over the entire circular cavity was found to give high sensitivity and good precision.

Control of discharge parameters, gas flow rate, gas pressure, and applied power is critical for obtaining a good yield of sputtering of solution residues. These parameters can affect the sputtering rate as well as the rate of atom transport to and atom removal from the analysis volume.

The laboratory-built RF atomizer shows very little matrix interference by NaCl matrix with Au and Fe solution residues. Less than 500 ng NaCl causes no interference

Figure 7.9 - Analytical calibration curves for determination of Fe in a matrix of NASS-3. For experimental conditions see Table 7.4.

Table 7.4 Experimental conditions used for the determination of Fe spiked in NASS-3 matrix.

Cathode	Spectral bandpass (nm)	Wavelength (nm)	Hollow-cathode lamp current (mA)	Ar gas pressure (Torr)	Ar gas flow rate (SLPM)	Applied RF power (W)
Cu	0.5	248.3	6	5	0.4	100

in DC-sputtering of 5 ng Au, but does interfere in the case of Fe. 10 μg and 100 μg NaCl matrices do not interfere with the determination of Fe and Au, respectively, in solution residues.

Appendix

k_1 and k_2 calculation procedure

Maximum absorbance, $A_{\max}$, and its corresponding time, $t_{\max}$, are found after selecting t_0 which is the time that $A = 0$. Fitting a theoretical curve to an experimental one depends on how precisely t_0 is selected. Exact fitting to the experimental points must be considered cautiously as k_1 can be altered significantly if t_0 , which is obtained from the noisy part of the signal, is displaced. The absorbance vs. time for $A > A_{\max}$ is linear for a kinetically first order process. The slope and the intercept of the linear portion give k_2 and A_0 , respectively:

$$k_2 = \text{slope}$$

$$\text{Ln}(A_0) = \text{intercept}$$

k_1 is calculated using the following equation:

$$t_{\max} = \frac{1}{k_1 - k_2} \text{Ln} \left(\frac{k_1}{k_2} \right)$$

and the following equation was used for finding the theoretical curve:

$$A_t = \frac{k_1}{k_1 - k_2} A_0 (e^{-k_2 t} - e^{-k_1 t})$$

t_0 is redefined and the procedure is repeated if the theoretical and experimental data do not fit well.

References

- 1 C. L. Chakrabarti, K. L. Headrick, P. C. Bertels and M. H. Back, J. Anal. At. Spectrom., **3**, 713 (1988).
- 2 B. J. Russell and A. Walsh, Spectrochim. Acta, **10B**, 883 (1959).
- 3 B. N. Chapmann, *Glow Discharge Process*, Wiley, New York, 188 (1980).
- 4 J. A. McHugh, *Methods and Phenomena: Their Applications in Science and Technology*. Vol. 1, S. P. Wolsky and A. W. Czanderna, eds., Elsevier, New York (1975).
- 5 A. von Hippel, Ann. Phys., **80**, 672 (1926).
- 6 T. Baum, Z. Phys., **40**, 686 (1927).
- 7 G. K. Wehner, Adv. Electron. Electron Phys., **7**, 239 (1955).
- 8 J. R. Woodyard and C. B. Cooper, J. Appl. Phys., **35**, 1107 (1964).
- 9 R. V. Stuart and G. K. Wehner, J. Appl. Phys., **35**, 1819 (1964).
- 10 M. Kaminsky, *Atomic and Ionic Impact Phenomena on Metal Surface*, Springer, Berlin (1965).
- 11 P. J. Slevin and W. W. Harrison, Appl. Spectrosc. Rev., **10**, 201 (1975).
- 12 P. W. J. M. Boumans, Anal. Chem., **44**, 1219 (1972).
- 13 G. K. Wehner, *Methods and Phenomena: Their Applications in Science and Technology*, Vol. 1, S. P. Wolsky and A. W. Czanderna, eds. Elsevier, New York (1975).
- 14 G. Carter and J.S. Colligon, *Ion Bombardment of Solids*, Elsevier, New York

- (1968).
- 15 R. Kelly and N. Q. Lam, Radiat. Eff., **19**, 39 (1973).
 - 16 B. Navinsek, Prog. Surf. Sci., **7**, 49 (1976).
 - 17 H. L. Levin, *Contemporary Physical Geology*, Saunders College, Philadelphia (1981).
 - 18 P. Staib, Radiat. Eff., **18**, 217 (1973).
 - 19 D. Fang and R. K. Marcus Spectrochim. Acta, **43B**, 1451 (1988).
 - 20 P. Sigmund, Phys. Rev., **184**, 383 (1969).
 - 21 E. Gillam, J. Phys. Chem. Solids, **11**, 55 (1959).
 - 22 W. L. Patterson and G. A. Shinn, J. Vac. Science Technol., **4**, 343 (1967).
 - 23 S. D. Dahlgren, E. D. McClanahan, J. W. Johnston and A. G. Graybeal, J. Vac. Science Technol., **7**, 398 (1970).
 - 24 G. S. Anderson, J. Appl. Phys., **40**, 2884 (1969).
 - 25 W. T. Ogar, N. T. Olson and H. P. Smith, J. Appl. Phys., **40**, 4997 (1969).
 - 26 N. Laegreid and G. Wehner, J. Appl. Phys., **32**, 365 (1961).
 - 27 D. Rosenberg and G. K. Wehner, J. Appl. Phys., **33**, 1842 (1962).
 - 28 E. Nasser, *Fundamentals of Gaseous Ionization and Plasma Electronics*, Wiley, New York (1971).
 - 29 W. W. Harrison, K. R. Hess, R. K. Marcus and F. L. King, Anal. Chem., **58**, 341A (1986).
 - 30 P. Hannaford and A. Walsh, Spectrochim. Acta, **43B**, 1053 (1988).
 - 31 D. S. Gough, P. Hannaford and A. Walsh, Spectrochim. Acta, **28B**, 197 (1973).

- 32 J. A. C. Broekaert, J. Anal. At. Spectrom., **2**, 537 (1987).
- 33 Y. Mei and W.W. Harrison, Anal. Chem., **65**, 3337 (1993).
- 34 C. G. Bruhn and W. W. Harrison, Anal. Chem., **50**, 16 (1978).
- 35 J. B. Ko, Spectrochim. Acta, **39B**, 1405 (1984).
- 36 T. Shimamura, T. Takahashi, M. Honda and H. Nagai, J. Anal. At. Spectrom., **8**, 453 (1993).
- 37 D. S. Gough, Anal. Chem., **48**, 1926 (1976).
- 38 O. Dessenne, A. Quentmeier, and H. Bubert, Fresenius' J. Anal. Chem., **346**, 340 (1993).
- 39 G. Ehrlich, U. Stahlberg, V. Hoffmann and H. Scholze, Spectrochim. Acta, **46B**, 115 (1991).
- 40 C. L. Chakrabarti, K. L. Headrick, J. C. Hutton, Z. Bicheng, P. C. Bertels and M. H. Back, Anal. Chem., **62**, 574 (1990).
- 41 G. Absalan, C. L. Chakrabarti, K. L. Headrick, Canadian Journal of Applied Spectroscopy, **41**, 51 (1996).
- 42 K. D. Ohls, J. Flock and H. Loepp, Fresenius' J. Anal. Chem., **342**, 924 (1992).
- 43 G. Absalan, C. L. Chakrabarti, K. L. Headrick and M. H. Back, Paper No. 57, presented at *40th Canadian Spectroscopy Conference*, Halifax, Nova Scotia, Canada, 8-10 August, 1994.
- 44 W. W. Harrison and B. L. Bentz, Prog. Analyt. Spectrosc., **11**, 53 (1988).
- 45 C. L. Chakrabarti, K. L. Hearick, J. C. Hutton, B. Marchand and M. H. Back, Spectrochim. Acta, **44B**, 385 (1989).

- 46 C. L. Chakrabarti, K. L. Headrick, J. C. Hutton, P. C. Bertels and M. H. Back, Spectrochim. Acta, **46B**, 183 (1991).
- 47 H. J. Kim and E. H. Picpmeier, Anal. Chem., **60**, 2040 (1988).
- 48 J. C. Hutton, C. L. Chakrabarti, P. C. Bertels and M. H. Back, Spectrochim. Acta, **46B**, 193 (1991).
- 49 M. R. Winchester, S. M. Hayes and R. K. Marcus, Spectrochim. Acta, **46B**, 615 (1991).
- 50 C. L. Chakrabarti, G. Absalan, K. L. Headrick, M. H. Back and R. K. Marcus, Paper No. 646, presented at *21th Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies*, St. Louis, Missouri, U.S.A., 2-7 October, 1994.
- 51 G. Absalan, C. L. Chakrabarti, K. L. Headrick and M. H. Back, Paper No. 55, presented at *40th Canadian Spectroscopy Conference*, Halifax, Nova Scotia, Canada, 8-10 August, 1994.
- 52 V. Hoffmann, Fresenius' J. Anal. Chem., **346**, 165 (1993).
- 53 W. Fischer, A. Naoumidis, H. Nickel, Fresenius' J. Anal. Chem., **346**, 144 (1993).
- 54 M. G. Benjamin, W. Smith and J. D. Winefordner, Anal. Chem., **62**, 157 (1990).
- 55 P. L. Larkins, Spectrochim. Acta, **39B**, 1365 (1984).
- 56 H. G. C. Human, N. P. Ferreira, R. A. Kruger and L. R. P. Butler, Analyst, **103**, 469 (1978).

- 57 B. W. Smith, N. Omenetto and J. D. Winefordner, Spectrochim. Acta, **39B**, 1389 (1984).
- 58 B. M. Patel and J. D. Winefordner, Spectrochim. Acta, **41B**, 469 (1986).
- 59 J. C. Travis, G. C. Turk, R. L. Watter, J. L. Yu, and J. L. Blue, J. Anal. At. Spectrom., **6**, 261 (1991).
- 60 O. S. Lunyov and S. V. Oshemkov, Spectrochim. Acta, **47B**, 71 (1992).
- 61 P. R. Banks and M. W. Blades, Spectrochim. Acta, **44B**, 1117 (1989).
- 62 P. R. Banks and M. W. Blades, Spectrochim. Acta, **46B**, 501 (1991).
- 63 M. R. Winchester, C. Lazik and R. K. Marcus, Spectrochim. Acta, **46B**, 483 (1991).
- 64 F. Paschen, Ann. Phys., **50**, 901 (1916).
- 65 M. R. Winchester and R. K. Marcus, J. Anal. At. Spectrom., **5**, 575 (1990).
- 66 P. D. Davidse and L. I. Maissel, J. Appl. Phys., **37**, 574 (1966).
- 67 C. Lazik, and R. K. Marcus, Spectrochim. Acta, **48B**, 863 (1993).
- 68 S. Caroli and A. Alimonti, Spectrochim. Acta, **38B**, 625 (1983).
- 69 A. Bengtson, A. Eklund, M. Lundholm and A. Saric, J. Anal. At. Spectrom., **5**, 563 (1990).
- 70 J. W. Coburn and W. W. Harrison, Appl. Spectros. Rev., **17(1)**, 95 (1981).
- 71 W. W. Harrison, *Glow Discharge Mass Spectrometry*, in: *Inorganic Mass Spectrometry*, Eds. F. Adams, R. Gijbels and R. van Grieken, Chap. 3, p. 85. Wiley, New York (1988).
- 72 Y. Shao and G. Horlick, Spectrochim. Acta, **46B**, 165 (1991).

- 73 D. C. Duckworth and R. K. Marcus, J. Anal. Atom. Spectrom., **7**, 711 (1992).
- 74 S. A. McLuckey, G. L. Glish, D. C. Duckworth and R. K. Marcus, Anal. Chem., **64**, 1606 (1992).
- 75 N. Jakubowski, D. Stuewer and W. Vieth Anal. Chem., **59**, 1825 (1987).
- 76 W. D. Westwood, Prog. Surf. Sci., **7**, 71 (1976).
- 77 W. Grimm, Spectrochim. Acta, **23B**, 433 (1968).
- 78 K. Wagatsuma and K. Hirokawa, Anal. Chem., **56**, 2024 (1984).
- 79 M. Dogan, K. Laqua and H. Massmann, Spectrochim. Acta, **27B**, 65 (1972).
- 80 G. N. Jackson, Thin Solid Films, **5**, 209 (1970).
- 81 G. S. Anderson, Wm. N. Mayer and G. K. Wehner, J. Appl. Phys., **33**, 2991 (1962).
- 82 J. M. Brackett and T. J. Vickers, Spectrochim. Acta, **37B**, 841 (1982).
- 83 D. S. Gough, P. Hannaford and R. M. Lowe, Anal. Chem., **61**, 1652 (1989).
- 84 P. L. Larkins, Spectrochim. Acta, **46B**, 291 (1991).
- 85 C. M. Strange and R. K. Marcus, Spectrochim. Acta, **46B**, 517 (1991).
- 86 K. R. Hess and W.W. Harrison, Anal. Chem., **60**, 691 (1988).
- 87 K. L. Headrick, Ph.D. Thesis, Chap. 5, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada.
- 88 D. A. McCarney and T. M. Niemczyk, Appl. Spectros., **34**, 692 (1980).
- 89 K. Ohls, Fresenius Z. Anal. Chem., **327**, 111 (1987).
- 90 R. LeHouillier, Project: 88-CR-12, Centre de Recherches Minerales, Sainte-Foy, Quebec (1989).

- 91 K. J. Laidler, *Chemical Kinetics*, 3rd Edition, Harper and Row, New York (1987).
- 92 S. B. Chang and C. L. Chakrabarti, *Prog. Anal. Atom. Spectrosc.*, **8**, 83 (1985).
- 93 A. J. Stirling and W. D. Westwood, *J. Appl. Phys.*, **41**, 742 (1970).
- 94 J. Tseng and J. C. Williams, *Anal. Chem.*, **63**, 1933 (1991).
- 95 S. Caroli, O. Senfonte and P. D. femmine, *Analyst*, **108**, 196 (1983).
- 96 P. G. Riby and J. M. Harnly, *J. Anal. At. Spectrom.*, **8**, 945 (1993).
- 97 K. L. Headrick, C. L. Chakrabarti, Z. Bicheng and B. Marchand, *Spectrochimica Acta*, **49B**, 975 (1994).
- 98 E. W. McDaniel, *Collision Phenomena in Ionized Gases*, Wiley, New York and London (1964).
- 99 A. J. T. Holmes and J. R. Cozens, *J. Phys. D Appl. Phys.*, **7**, 1723 (1974).
- 100 G. K. Wehner, *J. Appl. Phys.*, **30**, 1762 (1959).
- 101 R. E. Sturgeon, S. S. Berman, A. Desaulniers and D. S. Russell, *Anal. Chem.*, **51**, 2364 (1979).
- 102 N. P. Ferreira, J. A. Strauss and H. G. C. Human, *Spectrochim. Acta*, **38B**, 899 (1983).
- 103 A. Kh. Gilmudinov, T. M. Abdullina, S. F. Gorbachev and V. L. Makarov, *Spectrochim. Acta*, **47B**, 1075 (1992).
- 104 J. C. Hutton, Ph.D. Thesis, p. 49, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada.
- 105 C. Lazik and R. K. Marcus, *Spectrochim. Acta*, **47B**, 1309 (1992).

- 106 R. K. Marcus, J. Anal. At. Spectrom., **8**, 935 (1993).
- 107 G. Absalan, C. L. Chakrabarti, J. C. Hutton, M. H. Back, C. Lazik and R. K. Marcus, J. Anal. At. Spectrom., **9**, 45 (1994).
- 108 C. M. Horwitz, J. Vac. Sci. Technol. **A1**, 1795 (1983).
- 109 M. Parker and R. K. Marcus, Applied Spectroscopy, **48**, 623 (1994).
- 110 D. C. Duckworth and R. K. Marcus, Anal. Chem., **61**, 1879 (1989).
- 111 D. C. McDonald, Anal. Chem., **54**, 1057 (1982).
- 112 M. Dogan, K. Laqua and H. Massmann, Spectrochim. Acta, **26B**, 631 (1971).
- 113 Z. Shi, T. H. Woodrum, K. Dehghan, S. Brewer and R. Sacks, Applied Spectroscopy, **46**, 749, (1992).
- 114 N. P. Ferreria and H. G. C. Human, Spectrochim. Acta, **36B**, 215 (1981).
- 115 F. L. King, A. L. McCormack and W. W. Harrison, J. Anal. At. Spectrom., **3**, 883 (1988).
- 116 P. R. Banks and M. W. Blades, Spectrochim. Acta, **47B**, 1203 (1992).
- 117 Safety Code-6, Recommended Safety Procedures for the Installation and Use of Radio Frequency and Microwave Devices in the Frequency Range of 10 MHz-300 GHz, Health Protection Branch, Health and Welfare Canada, 1979.
- 118 V. Pavski, C. L. Chakrabarti, J. C. Hutton and M. H. Back, Spectrochim. Acta, **48B**, 413 (1993).
- 119 M. R. Winchester and R. K. Marcus, Anal. Chem., **64**, 2067 (1992).
- 120 E. H. Daughtrey Jr., D. L. Donohue, P. J. Slevin and W. W. Harrison, Anal. Chem., **47**, 683 (1975).

- 121 E. H. Piepmeier, Anal. Chem., **48**, 1296 (1976).