

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

ATOMIZATION OF SYNTHETIC AND REAL SAMPLES

USING HEATED GRAPHITE ATOMIZERS

FOR ATOMIC ABSORPTION SPECTROSCOPY.

A thesis presented in partial fulfilment of  
the requirements for the degree of

Master of Science

in Chemistry

at Massey University

MARK WILLIAM PRITCHARD

February 1975

## A C K N O W L E D G E M E N T S

The author would like to express his approbation and gratitude to his supervisor, Dr. R.D. Reeves, for the many stimulating discussions he has initiated in the course of this work and is indebted for the personal interest shown and the guidance given. Sincere thanks are also due to Mrs. J.D. Thirkell for the formidable task of transcribing the original script into a more readable form. Appreciation is expressed to Miss. S. Sherriff for typing the references.

"But, my son, be warned: there is no end of opinions ready to be expressed. Studying them can go on forever, and become very exhausting. Here is my final conclusion: fear God and obey His commandments, for this is the entire duty of man." (King Solomon 977 B.C.)

ABSTRACT.

The interference effects caused by a number of matrices including compounds such as NaCl, HCl, KBr, HNO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub> on Cu, Pb, Cd and Al atomic absorption signals when the elements are atomized from three non-flame graphite atomizers (furnace, cup and rod) are studied over several concentration ranges. Investigations show that most of the interferences found occur in the vapour phase. A comprehensive literature survey has been done and from this survey and the experimental work carried out, discussions are presented on the postulated mechanisms of interference. Two main theories are given for the vapour phase interference,

i) entrapment of the atom in the matrix particle forming in the vapour,

ii) rapid molecular condensation in the vapour phase.

Several degrees of interference (both enhancement and depression) were obtained for the different chemical and atomization systems used. Attempts were made at rationalizing the degree and type of interference in terms of the postulated models. Supporting evidence for the atom entrapment theory was gained from an investigation of the nature of the non-atomic absorption peak obtained mainly when alkali halides are present in the sample. Evidence is produced showing that the absorption spectra obtained from alkali halides here and by other workers are charge-transfer spectra.

An investigation into the use of a graphite atomizer for zinc analysis in bovine serum is presented and compared to determinations using flame atomic absorption on the same samples.

TABLE OF CONTENTS.

ACKNOWLEDGEMENTS	....	...	...	...	i
ABSTRACT	...	...	...	...	ii
TABLE OF CONTENTS	...	...	...	...	iv
LIST OF FIGURES	...	...	...	...	vii
I. INTRODUCTION					
1. General Introduction	...	...	...	...	1
a) Historical	...	...	...	...	1
b) Instrumentation	...	...	...	...	2
c) Theoretical	...	...	...	...	2
2. Development of Flameless A.A.S.	...	...	...	...	3
3. Interferences in A.A.S.	...	...	...	...	8
a) Interferences in Flame Absorption Cells.	...	...	...	...	9
b) Interferences in Flameless Atomizers.	...	...	...	...	18
4. Objects of the present work.	...	...	...	...	38
II. EXPERIMENTAL PROCEDURES AND APPARATUS					
1. Instrumentation	...	...	...	...	40
a) Atomic absorption	...	...	...	...	40
b) Flame Photometry	...	...	...	...	42
c) Electrochemistry	...	...	...	...	42
2. Electrode Types	...	...	...	...	43
a) Rod	...	...	...	...	43
b) Tube Furnace	...	...	...	...	43
c) Cup	...	...	...	...	44

TABLE OF CONTENTS.

3. Analytical Reagents.	...	...	...	44
4. Experimental Procedure	...	...	...	45
5. Recording and Treatment of Data.	...	...	...	46
III. RESULTS AND DISCUSSION.				
		1. <u>Synthetic Solutions.</u>	...	48
i) Copper	...	...	...	48
A. Results.	...	...	...	48
a. Effect of some Alkali Halides on Copper	...	...	...	49
b. Effect of Added Anions on Copper .	...	...	...	51
c. Combined effect of NaCl and $H_3PO_4$ on Cu absorption signals using the three electrodes	...	...	...	53
d. Double Cavity Interference Experiments	...	...	...	56
B. Discussion.	...	...	...	58
ii) Lead	...	...	...	66
A. Results.	...	...	...	66
a. Effect of added acids (2m) on Pb signals	...	...	...	67
b. Effect of NaCl and $H_3PO_4$ .	...	...	...	67
c. Double Cavity Interference Experiments.	...	...	...	69
B. Discussion.	...	...	...	71
iii) Cadmium.	...	...	...	73
A. Results	...	...	...	73
Effects of $H_3PO_4$ and NaCl on Cd signals	...	...	...	73
B. Discussion.	...	...	...	75





LIST OF FIGURES.

FIG. II. 1.	View of the workhead of the Varian Techtron Carbon Rod Atomizer Model CRA 63	...	p.p. 41/42
FIG. II. 2a.	Sketch of the rod atomizer.	...	p.p. 43/44
FIG. II. 2b.	Sketch of the furnace atomizer.	...	p.p. 43/44
FIG. II. 2c.	Sketch of the cup atomizer.	...	p.p. 43/44
<u>Copper.</u>			
FIG. III. 1-1.	Ashing voltage determination curve	...	p.p. 49/50
FIG. III. 1-2	Series of analytical curves of Cu at various atomize voltages	...	p.p. 49/50
FIG. III. 1-3.	The effect of various anions and corresponding cations 1,000 ppm concentration on copper analytical curves on the CRA.	...	p.p. 50/51
Fig. III. 1-4.	Effect of NaCl and KBr on Cu (2.5 ppm) on the rod, furnace and cup.	...	P.P. 50/51
Fig. III. 1-5.	Peak profiles of copper	...	p.p. 51/52
Fig. III. 1-6a.	The effect of $H_3PO_4$ on Cu on the rod and furnace.	...	p.p. 54/55
Fig. III. 1-6b.	The combined effect of $H_3PO_4$ and NaCl on Cu signals on the furnace, cup and rod.		p.p. 54/55
Fig. III. 1-7a.	The effect of interferences on Cu signals using separate cavities in the rod.	...	p.p. 57/58
Fig. III. 1-7b.	The effect of interferences on Cu signals when mixing of the two species is for a limited time.	...	P.P. 57/58
Fig. III. 1-7c.	The effect of interferences on Cu signals using separate cavities in the furnace ..		p.p. 57/58

LIST OF FIGURES.Lead.

- FIG. III. 1-8a. Analytical curves of Pb in  $H_2O$  at several atomization voltages on the rod. ... p.p. 66/67
- FIG. III. 1-8b. Analytical curves of Pb in 2M  $HNO_3$  at several atomization voltages on the rod. ... p.p. 66/67
- FIG. III. 1-9. Analytical curves of Pb at low concentrations in 2M HCl and  $HNO_3$  obtained with the furnace ... p.p. 67/68
- Fig. III. 1-10. Double cavity experiments with Pb in the furnace and on the rod. ... p.p. 69/70
- Fig. III. 1-11. Peak profiles for Pb. ... p.p. 71/72

Cadmium.

- Fig. III. 1-12a. Ashing voltage curve for Cd. ... p.p. 74/75
- Fig. III. 1-12b. Effect of NaCl and  $H_2PO_4$  on Cd. absorption signals with the furnace, rod and cup. ... p.p. 74/75
- Fig. III. 1-13. Peak profiles for Cd. ... p.p. 75/76

Residual Analyses.

- Fig. III. 1-14a. Standard curve for  $Cl^-$  analysis. ... p.p. 82/83
- Fig. III. 1-14b. Cation graphs for the Na, Cu, Pb and Al. ... p.p. 82/83
- Fig. III. 1-14c.  $Cl^-$  residues from  $CuCl_2$ ,  $PbCl_2$ ,  $AlCl_3$ , NaCl. ... p.p. 82/83

Non-atomic Absorption Peak.

- Fig. III. 1-15. NaCl ashing voltage and time determination curves. ... p.p. 87/88
- Fig. III. 1-16. The molecular absorption peaks of KBr and NaCl as a function of concentration. ... p.p. 88/89
- Fig. III. 1-17a. NaCl molecular absorption wavelength dependence curve using the furnace, cup and rod atomizers. ... p.p. 89/90
- Fig. III. 1-17b. KBr molecular absorption wavelength dependence curve using the furnace, cup and rod atomizers. ... p.p. 89/90

LIST OF FIGURES.

- Fig. III. 1-18. Comparison of NaCl molecular absorption wavelength dependence curve obtained in this work with that obtained by Koirttyohann and Pickett and Müller. ... p.p. 91/92
- Fig. III. 1-19. Comparison of KBr molecular absorption wavelength dependence curve obtained in this work with that obtained by Koirttyohann and Pickett and Müller. ... p.p. 91/92
- Fig. III. 1-20. Wavelength dependence curve of the 'scattered' radiation caused by the atomization of a 10,000 ppm NaCl solution.. p.p. 93/94
- Zinc Analysis.
- Fig. III. 2-1a. Analytical curve of zinc on carbon rod atomizer. ... p.p. 97/98
- Fig. III 2-1b. Analytical curve of zinc by flame atomic absorption. ... p.p. 97/98