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Frank. Talerice
University of Windsor

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NL-339 (3/77)

AN ASSESSMENT OF ANALYTICAL METHODS AND THEIR BIASES IN THE DETERMINATION OF MAJOR ELEMENTS IN ROCK ANALYSIS

by

Frank Talerico

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of Geology
in Partial Fulfillment of the Requirements
for the Degree of Master of Science at
The University of Windsor

Windsor, Ontario, Canada
1978

ABSTRACT

Replicate analyses of a granodiorite sample (NSX) by up to six different methods--atomic absorption, flame emission, gravimetry, titration, spectrophotometry and x-ray fluorescence--for eight elements--silica, aluminum, total iron, calcium, magnesium, sodium, potassium and manganese--were made to examine if there is bias between methods and to assess the precision and accuracy of each method. In addition, several international standard reference materials were run as control samples and to show that precision and accuracy in this study is repeatable to the values recommended for the standards. Sample NSX has also been well analyzed by thirty-five different laboratories; hence the replicate determination on NSX by the different methods gives information on accuracy of the method.

Results show that there are statistically significant differences between the different methods in terms of precision and also the different analytical methods yield different results. It is inferred that these differences are inherent in the methodology and there are biases between methods. Survey of data for three Canadian reference standards, show that while analytical results scatter widely, tabulation by method shows some systematic bias. In particular, MgO determination by titration is always higher.

As a result of the assessment of means and standard deviations of results, it is recommended that atomic absorption should be used for the determination of silicon, x-ray fluorescence for aluminum, flame emission

for sodium and potassium, titration for calcium and magnesium, while manganese is especially well determined by atomic absorption, titration, spectrophotometry and x-ray fluorescence. These method preferences actually relate to the position of the elements in the periodic table.

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I sincerely thank my thesis advisor, Dr. A. Turek, for the suggestion of this topic and for his guidance which proved invaluable to the completion of this study. Also, I thank Dr. T. E. Smith for his assistance and the use of the x-ray equipment. Dr. P. Hudec introduced me to the Wang computer which expedited the processing of data. Numerous discussions with Dr. J. Huang, Mr. D. Mitchell and Mr. D. Quirt on argon plasma and computer programming are gratefully acknowledged.

TABLE OF CONTENTS

ABSTRACT.. pge. (ii)

ACKNOWLEDGEMENTS.. (iv)

LIST OF TABLES.. (x)

LIST OF FIGURES.. (xvi)

LIST OF APPENDICES.. (xviii)

I. INTRODUCTION.. 1

II. LITERATURE REVIEW.. 3

  A. BRIEF HISTORY.. 3

  B. GENERAL EVIDENCE OF BIASES.. 4

  C. STATISTICAL EVIDENCE OF BIASES.. 7

  D. SUGGESTED SOLUTIONS TO STATISTICAL BIASES...... 8

  E. EVIDENCE OF ANALYTICAL METHOD BIASES........... 8

  F. SUGGESTED SOLUTIONS TO ANALYTICAL METHOD BIASES. 9

  G. CONCLUSIONS.. 11

III. EXPERIMENTAL SAMPLE PREPARATION PROCEDURES............. 16

  A. SAMPLE PREPARATION.. 16

  B. PREPARATION OF SOLUTION 'A'.. 16

  C. PREPARATION OF SOLUTION 'B'.. 17

  D. PREPARATION OF SOLUTION 'JA'.. 17

  E. PREPARATION OF STANDARD SOLUTIONS............... 18

  F. PREPARATION OF X-RAY FLUORESCENCE GLASS PELLETS. 19

IV. ANALYTICAL PROCEDURES.. 20

  A. ATOMIC ABSORPTION SPECTROSCOPY.................. 20

    a. Theory.. 20

    b. Analytical Procedure.. 22

      1. Silicon by Atomic Absorption Spectroscopy.. 22

TABLE OF CONTENTS (CONT'D)

2. Aluminum by Atomic Absorption Spectroscopy........................ 28

3. Total Iron by Atomic Absorption Spectroscopy........................ 31

4. Calcium by Atomic Absorption Spectroscopy........................ 34

5. Magnesium by Atomic Absorption Spectroscopy........................ 37

6. Sodium by Atomic Absorption Spectroscopy........................ 43

7. Potassium by Atomic Absorption Spectroscopy........................ 46

8. Manganese by Atomic Absorption Spectroscopy........................ 49

B. FLAME EMISSION SPECTROSCOPY........................ 52

a. Theory.. 52

b. Analytical Procedure........................ 54

1. Sodium by Flame Emission Spectroscopy........................ 54

2. Potassium by Flame Emission Spectroscopy........................ 57

C. GRAVIMETRY.. 60

a. Theory.. 60

b. Analytical Procedure........................ 61

1. Silicon by Gravimetry................ 61

2. Aluminum by Gravimetry.............. 62

D. TITRATION.. 66

a. Theory.. 66

b. Analytical Procedure........................ 68

1. Total Iron by Titration............. 68

TABLE OF CONTENTS (CONT'D)

2. Calcium by Complexiometric Titration 72
3. Magnesium by Titration 77
(i) Theory 77
(ii) Procedure 79
Reagents 79
Method 80
E. SPECTROPHOTOMETRY 87
a. Theory 87
b. Analytical Procedure 89
1. Silicon by Spectrophotometry 89
2. Aluminum by Spectrophotometry 92
3. Total Iron by Spectrophotometry 96
4. Manganese by Spectrophotometry 100
F. X-RAY FLUORESCENCE SPECTROSCOPY 103
a. Theory 103
b. Analytical Procedure 105
V. STATISTICAL TREATMENT OF RESULTS 107
A. INTRODUCTORY STATEMENT 107
B. TERMINOLOGY AND DEFINITIONS 107
a. Accuracy 107
b. Precision 107
c. Arithmetic Mean ($\bar{x}$) 107
d. Slope (m) 108
e. Standard Deviation (S.D.) 108
f. Confidence Limits 108
g. Coefficient of Variation (C.V.) 108

TABLE OF CONTENTS (CONT'D)

h. Variance (Var.)........ 108
i. Correlation Coefficient (r)........ 108
j. Rejection of Values........ 109
  1. Sample Set........ 109
  2. Population Set........ 109
k. Significance by Comparison of Sample Means to a Population........ 110
l. Significance by Comparison of Variances........ 110
m. Significance by Comparison of Means........ 110
VI. EVALUATION OF ANALYTICAL RESULTS........ 113
A. SILICON........ 113
B. ALUMINUM........ 121
C. TOTAL IRON........ 128
D. CALCIUM........ 136
E. MAGNESIUM........ 142
F. SODIUM........ 149
G. POTASSIUM........ 153
H. MANGANESE........ 159
VII. SUMMARY AND CONCLUSIONS........ 165
APPENDIX I........ 172
APPENDIX II........ 173
APPENDIX III........ 174
APPENDIX IV........ 175
APPENDIX V........ 176
APPENDIX VI........ 177

TABLE OF CONTENTS (CONT'D)

APPENDIX VII.................................... 178

APPENDIX VIII.................................... 179

APPENDIX IX.................................... 181

APPENDIX X.................................... 184

APPENDIX XI.................................... 186

APPENDIX XII.................................... 191

APPENDIX XIII.................................... 194

APPENDIX XIV.................................... 196

APPENDIX XV.................................... 198

REFERENCES.................................... 200

LIST OF TABLES

TABLE PAGE

1. RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY ET AL, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976): SY-2 Values by Method Rather than Laboratory 13

2. RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY ET AL, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976): SY-2 Averages for All Reported Values (19[illegible] Study + 1976 Supplement) 13

3. RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY ET AL, 197[illegible] INCLUDING ITS SUPPLEMENT I (ABBEY, 1976): SY-3 Values by Method Rather than Laboratory 14

4. RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY ET AL, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976): SY-3 Averages for All Reported Values (1975 Study + 1976 Supplement) 14

5. RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY ET AL, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976): MRG-1 Values by Method Rather than Laboratory 15

6. RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY ET AL, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976): MRG-1 Averages for All Reported Values (1975 Study + 1976 Supplement) 15

7. IONIC STANDARDS FOR SILICON IN SOLUTION 'A' BY ATOMIC ABSORPTION 24

8. IONIC STANDARDS FOR SILICON IN SOLUTION 'JA' BY ATOMIC ABSORPTION 26

9. SILICON IN SOLUTION 'JA' BY ATOMIC ABSORPTION 27

10. SILICON IN SOLUTION 'A' BY ATOMIC ABSORPTION 27

11. IONIC STANDARDS FOR ALUMINUM IN SOLUTION 'B' BY ATOMIC ABSORPTION 30

12. ALUMINUM IN SOLUTION 'B' BY ATOMIC ABSORPTION 30

13. IONIC STANDARDS FOR TOTAL IRON BY ATOMIC ABSORPTION 33

LIST OF TABLES (CONT'D)

14. TOTAL IRON BY ATOMIC ABSORPTION 33

15. IONIC STANDARDS FOR CALCIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION 36

16. CALCIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION 36

17. IONIC STANDARDS FOR MAGNESIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION 39

18. IONIC STANDARDS FOR MAGNESIUM WITHOUT LANTHANUM OXIDE BY ATOMIC ABSORPTION 41

19. MAGNESIUM WITHOUT LANTHANUM OXIDE BY ATOMIC ABSORPTION 42

20. MAGNESIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION 42

21. IONIC STANDARDS FOR SODIUM BY ATOMIC ABSORPTION 45

22. SODIUM BY ATOMIC ABSORPTION 45

23. IONIC STANDARDS FOR POTASSIUM BY ATOMIC ABSORPTION 48

24. POTASSIUM BY ATOMIC ABSORPTION 48

25. IONIC STANDARDS FOR MANGANESE BY ATOMIC ABSORPTION 51

26. MANGANESE BY ATOMIC ABSORPTION 51

27. IONIC STANDARDS FOR SODIUM BY FLAME EMISSION 56

28. SODIUM BY FLAME EMISSION 56

29. IONIC STANDARDS FOR POTASSIUM BY FLAME EMISSION 59

30. POTASSIUM BY FLAME EMISSION 59

31. GRAVIMETRIC DETERMINATION OF SILICON 65

32. GRAVIMETRIC DETERMINATION OF ALUMINUM 65

33. IONIC STANDARDS FOR SILICON BY SPECTROPHOTOMETRY 91

34. SILICON IN SOLUTION 'A' BY SPECTROPHOTOMETRY 91

35. IONIC STANDARDS FOR ALUMINUM BY SPECTROPHOTOMETRY 95

36. ALUMINUM BY SPECTROPHOTOMETRY 95

37. IONIC STANDARDS FOR TOTAL IRON BY SPECTROPHOTOMETRY 98

LIST OF TABLES (CONT'D)

38. TOTAL IRON BY SPECTROPHOTOMETRY........................ 99

39. IONIC STANDARDS FOR MANGANESE BY SPECTROPHOTOMETRY........ 102

40. MANGANESE BY SPECTROPHOTOMETRY........................ 102

41. PERCENT OXIDE FOR X-RAY FLUORESCENCE DETERMINATION........ 106

42. REJECTION TEST FOR NSX SAMPLES........................ 112

43. SILICON IN 'JA' BY ATOMIC ABSORPTION........................ 115

44. SILICON IN 'A' BY ATOMIC ABSORPTION........................ 115

45. SILICON BY GRAVIMETRY........................ 116

46. SILICON BY SPECTROPHOTOMETRY........................ 116

47. SILICON BY X-RAY FLUORESCENCE........................ 117

48. F-test AND T-test FOR SILICON BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY........................ 118

49. F-test AND T-test FOR SILICON BY ATOMIC ABSORPTION AND GRAVIMETRY........................ 118

50. F-test AND T-test FOR SILICON BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE........................ 119

51. F-test AND T-test FOR SILICON BY GRAVIMETRY AND X-RAY FLUORESCENCE........................ 119

52. F-test AND T-test FOR SILICON BY GRAVIMETRY AND SPECTROPHOTOMETRY........................ 120

53. F-test AND T-test FOR SILICON BY X-RAY FLUORESCENCE AND SPECTROPHOTOMETRY........................ 120

54. RESULTS FOR (SOLUTION 'A') ALUMINUM BY ATOMIC ABSORPTION........................ 123

55. RESULTS FOR (SOLUTION 'A') ALUMINUM BY SPECTROPHOTOMETRY........................ 123

56. ALUMINUM BY X-RAY FLUORESCENCE........................ 124

57. RESULTS FOR (SOLUTION 'B') ALUMINUM BY GRAVIMETRY........ 124

58. F-test AND T-test FOR ALUMINUM BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY........................ 125

59. F-test AND T-test FOR ALUMINUM BY ATOMIC ABSORPTION AND GRAVIMETRY........................ 125

LIST OF TABLES (CONT'D)

60. F-test AND T-test FOR ALUMINUM BY ATOMIC ABSORPTION AND X RAY FLUORESCENCE.......... 126

61. F-test AND T-test FOR ALUMINUM BY GRAVIMETRY AND SPECTROPHOTOMETRY.......... 126

62. F-test AND T-test FOR ALUMINUM BY X-RAY FLUORESCENCE AND SPECTROPHOTOMETRY.......... 127

63. F-test AND T-test FOR ALUMINUM BY GRAVIMETRY AND X-RAY FLUORESCENCE.......... 127

64. RESULTS FOR IRON BY ATOMIC ABSORPTION.......... 130

65. RESULTS FOR IRON BY SPECTROPHOTOMETRY.......... 130

66. IRON BY TITRATION (DICHROMATE).......... 131

67. TOTAL IRON BY X-RAY FLUORESCENCE.......... 132

68. F-test AND T-test FOR TOTAL IRON BY ATOMIC ABSORPTION AND TITRATION.......... 133

69. F-test AND T-test FOR TOTAL IRON BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY.......... 133

70. F-test AND T-test FOR TOTAL IRON BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE.......... 134

71. F-test AND T-test FOR TOTAL IRON BY TITRATION AND SPECTROPHOTOMETRY.......... 134

72. F-test AND T-test FOR TOTAL IRON BY X-RAY FLUORESCENCE AND SPECTROPHOTOMETRY.......... 135

73. F-test AND T-test FOR TOTAL IRON BY TITRATION AND X-RAY FLUORESCENCE.......... 135

74. RESULTS FOR CALCIUM BY ATOMIC ABSORPTION.......... 138

75. CALCIUM BY X-RAY FLUORESCENCE.......... 138

76. RESULTS FOR CALCIUM OXIDE BY EDTA TITRATION.......... 139

77. F-test AND T-test FOR CALCIUM BY ATOMIC ABSORPTION AND TITRATION.......... 140

78. F-test AND T-test FOR CALCIUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE.......... 140

79. F-test AND T-test FOR CALCIUM BY TITRATION AND X-RAY FLUORESCENCE.......... 141

LIST OF TABLES (CONT'D)

80. RESULTS FOR (WITHOUT LANTHANUM OXIDE) MAGNESIUM BY ATOMIC ABSORPTION.......... 144

81. RESULTS FOR (WITH LANTHANUM OXIDE) MAGNESIUM BY ATOMIC ABSORPTION.......... 144

82. MAGNESIUM OXIDE BY EDTA TITRATION.......... 145

83. MAGNESIUM BY X RAY FLUORESCENCE.......... 146

84. F-test AND T-test FOR MAGNESIUM BY ATOMIC ABSORPTION AND TITRATION.......... 147

85. F-test AND T-test FOR MAGNESIUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE.......... 147

86. F-test AND T-test FOR MAGNESIUM BY TITRATION AND X-RAY FLUORESCENCE.......... 148

87. RESULTS FOR SODIUM BY ATOMIC ABSORPTION.......... 151

88. RESULTS FOR SODIUM BY FLAME EMISSION.......... 151

89. F-test AND T-test FOR SODIUM BY ATOMIC ABSORPTION AND FLAME EMISSION.......... 152

90. RESULTS FOR POTASSIUM BY ATOMIC ABSORPTION.......... 155

91. RESULTS FOR POTASSIUM BY FLAME EMISSION.......... 155

92. POTASSIUM BY X-RAY FLUORESCENCE.......... 156

93. F-test AND T-test FOR POTASSIUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE.......... 157

94. F-test AND T-test FOR POTASSIUM BY FLAME EMISSION AND X-RAY FLUORESCENCE.......... 157

95. F-test AND T-test FOR POTASSIUM BY ATOMIC ABSORPTION AND FLAME EMISSION.......... 158

96. RESULTS FOR MANGANESE BY ATOMIC ABSORPTION.......... 161

97. RESULTS FOR MANGANESE BY SPECTROPHOTOMETRY.......... 161

98. MANGANESE BY X-RAY FLUORESCENCE.......... 163

99. F-test AND T-test FOR MANGANESE BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY.......... 163

100. F-test AND T-test FOR MANGANESE BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE.......... 163

LIST OF TABLES (CONT'D)

101. F-test AND T-test FOR MANGANESE BY SPECTROPHOTOMETRY AND X-RAY FLUORESCENCE.................................. 164

102. SUMMARY OF ANALYTICAL RESULTS FOR NSX 'IN-HOUSE' SAMPLE.................................. 165

103. PREFERRED METHOD, ACCORDING TO STATISTICAL PARAMETERS.................................. 170

LIST OF FIGURES

1. Schematic layout of atomic absorption unit (Ewing, 1960) and diagram of energy absorbance............ pge. 22
2. Calibration curve for silicon by atomic absorption (on solution 'A').. 23
3. Calibration curve for silicon by atomic absorption (on solution 'JA').. 25
4. Calibration curve for silicon by atomic absorption (on solution 'B').. 29
5. Calibration curve for total iron by atomic absorption..... 32
6. Calibration curve for calcium by atomic absorption........ 35
7. Calibration curve for magnesium with lanthanum oxide by atomic absorption................................ 38
8. Calibration curve for magnesium without lanthanum oxide by atomic absorption................................ 40
9. Calibration curve for sodium by atomic absorption......... 44
10. Calibration curve for potassium by atomic absorption...... 47
11. Calibration curve for manganese by atomic absorption...... 50
12. Schematic layout of flame emission unit (Ewing, 1960) and diagram of energy emission...................... 52
13. Calibration curve for sodium by flame emission............ 55
14. Calibration curve for potassium by flame emission......... 58
15. Bonding structure of urea (Skoog and West, 1974).......... 62
16. Bonding structure of ammonium acetate to aluminum (Skoog and West, 1974)................................ 63
17. Single cell photoelectric photometer (Adapted from Evans Electroselenium Limited, n.d.)...................... 67
18. Formation of five-membered chelate ring (Adapted from Skoog and West, 1974)................................ 72

LIST OF FIGURES (CONT'D)

19. Calcium titration EDTA calibration graph.................... 74

20. Calcium titration graph for BCR-1 standard sample.......... 74

21. Calcium titration graph for GA standard sample............ 75

22. Calcium titration graph for AC2-2 standard sample.......... 75

23. Calcium titration graph for SYN.G2 standard sample........ 76

24. Calcium titration graph for NSX-1 rock sample............ 76

25. Titration graph for total (Ca + Mg) in BCR-1.............. 82

26. Titration graph (average change per unit for total (Ca + Mg) in BCR-1.................................... 82

27. Titration graph for total (Ca +Mg) in GA................. 83

28. Titration graph (average change per unit) for total (Ca + Mg) in GA...................................... 83

29. Titration graph for total (Ca + Mg) in AC2-2............. 84

30. Titration graph (average change per unit) for total (Ca +Mg) in AC2-2................................... 84

31. Titration graph for total (Ca + Mg) in SYN.G2............ 85

32. Titration graph (average change per unit) total (Ca +Mg) in SYN.G2.................................... 85

33. Titration graph for total (Ca + Mg) in NSX-5.............. 86

34. Titration graph (average change per unit) total (Ca + Mg) in NSX-5................................... 86

35. Optical diagram of the Bausch & Lomb spectronic-70 (Ewing, 1969).. 88

36. Calibration curve for silicon (on solution 'A') by spectrophotometry... 90

37. Calibration curve for aluminum (on solution 'A') by spectrophotometry... 94

38. Calibration curve for total iron (on solution 'B') by spectrophotometry... 97

39. Calibration curve for manganese by spectrophotometry...... 101

40. Schematic layout of x-ray fluorescence spectrometer....... 103

LIST OF APPENDICES

pge.

I. INSTRUMENTAL CONDITIONS FOR ATOMIC ABSORPTION, FLAME EMISSION AND SPECTROPHOTOMETRY.............. 172

II. X-RAY FLUORESCENCE ANALYTICAL CONDITIONS........... 173

III. SUMMARY OF RESULTS OF ALL SAMPLES................. 174

IV. OXIDE CONVERSION FACTORS............................ 175

V. SPECTROPHOTOMETER CALCULATIONS USING WANG 2200..... 176

VI. TITRATION CALCULATIONS USING WANG 2200............. 177

VII. GRAVIMETRIC CALCULATIONS USING WANG 2200.......... 178

VIII. PROGRAM #1 FOR MONROE 344: Si, Al, Fe, Ca and K DETERMINATIONS................................... 179

IX. PROGRAM #947 FOR WANG 700 SERIES: MAGNESIUM AND MANGANESE DETERMINATIONS........................ 181

X. PROGRAM #665 FOR WANG 700 SERIES: (f) FACTOR USING DEAD TIME CPS FROM QUARTZ..................... 184

XI. X-RAY MATRIX CORRELATION OF MAJOR ELEMENTS......... 186

XII. COMPUTER GRAPHS USING WANG 2200................... 191

XIII. 2*SD REJECTION TEST USING WANG 2200............... 194

XIV. TOTAL POPULATION REJECTION TEST USING WANG 2200.... 196

XV. STATISTICAL COMPARISON BY F-test AND T-test USING WANG 2200 COMPUTER.......................... 198

I. INTRODUCTION

Numerous geochemical studies, both collaborative and individual, have reported results which varied from laboratory to laboratory, from analyst to analyst, from sample to sample and even from time to time. The major cause of variability in analytical results in geochemical collaborative studies has been attributed to inter-laboratory and analyst biases; however, there is a general lack of conformity in the statistical evaluation of analytical data, and no co-operative studies have been made to assess the biases between methods. Thus, perhaps the methods themselves, in their unique characteristics, requirements and interferences have been the cause of much of the scatter of results.

In this thesis several methods of analysis are examined, to determine the possibility ~~of the~~ existence of inter-method bias. Every source of bias is limited as far as possible by limiting the number of analysts involved to one only.

The review of literature is limited by the fact that little has been done on this subject and only recently some of the more alert researchers have alluded to this problem.

In this study, eight elements (silicon, aluminum, total iron, calcium, magnesium, sodium, potassium and manganese) have been determined by up to seven different methods to try to isolate possible bias between methods, using analyses of variance and other statistical procedures. The following tabulation summarizes the elements and methods used in this study:

OXIDES	METHODS*					
	AA	FE	G	T	SP	XRF
SiO_2	X		X		X	X
Al_2O_3	X		X		X	X
Fe_2O_3(t)	X			X		X
CaO	X			X		X
MgO	X			X		X
Na_2O	X	X				
K_2O	X	X				X
MnO	X				X	X

*Where AA is atomic absorption spectroscopy, FE is flame emission spectroscopy, G is gravimetry, T is titration SP is spectrophotometry and XRF is x-ray fluorescence spectroscopy.

II. LITERATURE REVIEW

There has been little written specifically--on methods and their biases in rock analysis. Nevertheless, one can detect, woven into numerous reports, suspicion of biases between methods. With the advent of new instrumental methods, problems have been noted but not necessarily anchored to any one origin. The statistical analyses of these methods lie prone to subjective translation and arbitrary decision. Values often vary, not only laboratory to laboratory, but also method to method. While certain standardization would begin to rectify this situation, several authors have gone further by suggesting other positive action.

A. BRIEF HISTORY

Originally, 'classical' chemical methods were sequential and slow because they involved time-consuming precipitations. However, with the inception of 'analytical chemistry' and its use of new reagents and techniques, methods became more rapid either with greater accuracy, without greater accuracy or at the expense of greater accuracy. Their speed was due to their 'directness', in being more metal specific. Flame photometry added speed plus accuracy to the determination of sodium and potassium. These rapid methods were generally based on colorimetry and their accuracy usually diminished, relative to gravimetric methods. Instrumental methods are mechanically-orientated and as such have better answered the need for accurate standard procedure than did 'classical' methods which required great skill to achieve consistent results (Bennett, 1977).

Today, the types of instrumental methods are multiplying rapidly. This situation was expressed by la Roche and Govindaraju (1976) as a table which showed that from 1964 to 1974, results obtained for MgO in granite by both chemical and physical methods increased in number from 18 to 80 and from 6 to 23, respectively. This tendency towards physical methods also occurred for other elements--Al_2O_3, Fe_2O_3 (total), MnO, CaO, TiO, but not SiO_2.

While this increase in instrumental methods has its benefits, it also has its drawbacks. On the one hand, an analyst may better suit the method to the element because of the variety from which to choose. On the other hand, the achievement of consistent results must now consider another factor--according to Abbey (1977), variations in new methods are infinite and greatly influence the results of techniques used and the final assessment of data. These variations and their influences on biases must be acknowledged and understood so that they can contribute to a more accurate geochemical analysis.

B. GENERAL EVIDENCE OF BIASES

This infinite variation in method and results (Abbey, 1977) has been evidenced in several reports. Abbey <u>et al.</u> (1975) noted, in their collaborative study, that even among laboratories which they felt to be the better laboratories, there existed a number of "conspicuous outliers" in the results. It is interesting to note that, while Abbey considered this to be interlaboratory variation, Roubault <u>et al.</u> (1970) offered a different explanation of variation in results.

Roubault <u>et al.</u> (1970) stated that each determination concerns the difference between a 'true' and a mean/median value. This small or very small 'residual value' is usually hidden among glaring similar values which agree but add no information. This report added further that any analytical method which cannot measure such small values is of little consequence. The variations of results which both Abbey et al. (1977) and Roubault et al. (1970) mentioned could well be studied for evidence of inter-method bias. Tables 1 to 6 of this report break down Abbey's values (listed according to laboratory) into values according to elements and the methods employed.

According to Abbey (1977) and Roubault et al. (1970), the amount of valid information which collaboration offers diminishes as its number of results increases. After reaching peak information, statistical analytical (quantity) data must be replaced with first-rate (quality) analysis (Roubault et al., 1970) Thus, once a close harmony of the more obvious data is established, a closer study of the results could be made (la Roche and Govindaraju, 1976). Of special importance would be concurrent data compiled by one laboratory using a limited number of methods of determination, and special requests could be issued for qualified, specialist laboratories to use several methods on several elements (Roubault et al., 1970). This trend lies close to the aim of this thesis. The number of possible sources of bias is reduced to one 'laboratory' and one analyst, thereby isolating probable source of bias to one factor only--that of method.

Some specific information on such inconsistencies of results is available. La Roche and Govindaraju (1976) note that whereas atomic absorption is poor in precision, x-ray fluorescence shows very good precision. In another case, Abbey et al. (1975) noted that in the determination of carbon dioxide by two variations on a method (acid and combustion), at least two laboratories using both methods reported appreciable differences. Abbey suggests this difference may be caused by non-carbonate carbons or contamination. Yet he states that in several G. S. C. laboratories reporting CO_2 values on rocks which did not contain non-carbonate carbon, there were differences in results; Abbey (1977) did not attribute them to method bias but rather to inter-laboratory bias. Abbey reports the combustion values were persistently but not consistently higher. Then he stated that while bias may be the cause of the high values, not enough information was available to confirm this. In his later supplement (Abbey, 1976), he noted that there is a definite difference between methods but makes no statement on the existence of 'bias'. Turek _et al._ (1978) used four separate methods to determine carbon dioxide and also found combustion methods to give high results.

Others have noted such disagreeing results. Bennett (1977) noted that for calcium determination, results were lower by instrumental than by chemical methods. Varian Techtron (1972) noted that different methods have their own interferences--even atomic absorption and flame emission. Abbey (1977) noted that in Fairbairn's 1951 pioneering report on the first U. S. Geological Survey standards G-1 and W-1, there appeared, to the amazement of analysts and petrographers, a great divergence in (what Abbey considered to be) inter-laboratory results on the same constituent of the same sample. Yet it sould be noted that the methods employed in that 1951 study included chemical and spectrographic analysis.

Interferences can vary even between analyses, be they chemical or physical. Abbey _et al._ (1975) noted that direct interference is more likely to occur in chemical methods than in instrumental methods. This disagrees with Varian Techtron (1972). Interferences can vary between elements within instrumental analysis (Quirt 1978; Appendix I) (Mitchell, 1978). Such a variety of interferences and the resulting variety of values, could be investigated as a factor contributing to inter-method bias.

C. STATISTICAL EVIDENCE OF BIASES

It is well known that collaborative analyses on goechemical standards reveal widespread values (Turek et al., 1978). Analysts tend to assess analytical data by intuitive judgement which often is not in line with statistical judgement (Ellis, 1976; Steele, 1977). These subjective decisions pervade statistical reports on analyses.

Abbey (1977) cites the different parameters which various countries use for rejecting 'outliers'--from France's one and more standard deviations to South Africa's three and more standard deviations. When la Roche and Govindaraju (1976) were faced with a high median and a low mean, they chose as a preferred value the higher of the two because several 'select' laboratories had reported even higher preferred values than their own. It was further noted that the chosen value was almost identical to the preferred median of chemical methods and the preferred mean of physical method. In the case of Na_2O in the same report, only physical methods were used--mainly atomic absorption and flame spectrophotometry. Their decision in this case was to recommend an average of the two results as a preferred value. Such arbitrary actions are, at the moment, necessary because the many variations in the results have no immediate solution. Instances of such subjective decisions are indeed widespread (Abbey, 1975; Abbey, 1976; Abbey, 1977; la Roche and Govindaraju, 1976; Roubault et al., 1970; Ellis, 1976; Steele, 1977).

D. SUGGESTED SOLUTIONS TO STATISTICAL BIASES

Suggested solutions to the problems of divergent results are as numerous as the problems themselves. Abbey et al. (1975) noted that it has been suggested that in the extremely difficult problem of 'choosing' values, one can use 'semi-empirical' methods. Flanagan (in Steele, 1977) suggested the need for 'statistical experimental design' to derive maximum information from submitted collaborative analytical data. La Roche and Govindaraju (1976) devised a letter code to designate sample preparation, analytical method, laboratory, even analyst. Abbey (1977) claims, however, that while letter codes for methods and biases are effective for commercial products, they are impractical for rocks because the variations in methods are infinite and important. In the same report, however, he did suggest several steps which would facilitate more accurate statistical analysis--including a more meaningful, standardized terminology of analytical method and assigned values (Is this not the direction in which la Roche and Govindaraju were headed with the letter code?) and a more consistent procedure for deducing compositional values from raw data. However, he himself failed to take advantage of this breakdown of methods in arriving at the so-called recommended value. This would, indeed, remove much of the subjective element in statistical analysis. The resulting improvement of statistical treatment would in turn improve the understanding of analytical methods, which would in turn improve the statistical analysis, until a complementary cycle is established.

E. EVIDENCE OF ANALYTICAL METHOD BIASES

While biases have several origins--laboratories, elements, analysts--one type is evidenced in several reports yet rarely considered in its own right. Turek et al.(1976) found in his H_2O determinations that the Karl Fischer method showed a higher mean than the Penfield method which also showed a lower precision. Turek et al.(1978) found that in determining carbon dioxide, the different methods (gravimetric, titrimetric and volumetric) showed obvious, distinct biases between means and corresponding standard deviations. Another little-discussed possible source of bias may be in sample heterogeneity--a problem that has been studied by Ridley et al (1976) and Turek et al.(1978).

La Roche and Govindaraju (1976) found many instances of bias between methods. For K_2O, atomic absorption and x-ray fluorescence gave different results. For iron, the preferred mean of physical methods was lower than that of chemical methods. For MnO the mean for chemical methods was higher than that of other methods; the minor constituents by physical methods showed a lower standard deviation than by chemical methods. For the feldspar sample (FK-N) for K_2O only physical methods were used yet results still indicated a bias. Atomic absorption gave a higher mean than x-ray fluorescence but it yielded a lower standard deviation. For aluminum, the mean for chemical methods alone was slightly lower than the mean for either both chemical and physical together or physical methods alone (la Roche and Govindaraju, 1976).

La Roche and Govindaraju (1976) did state that agreement between mean and median is not always the only criteria valuable in determining recommended or proposed values. They feel it is equally necessary to consider agreement between results of different analytical methods.

F. SUGGESTED SOLUTIONS TO ANALYTICAL METHOD BIASES

Chemical and physical analysis work hand in hand with statistical analysis. Christie and Alfsen (1977) stated that reliable reference materials form a basis of control for analytical and chemical methods and would allow for better understanding of method conditions and parameters. The resulting 'true' concentrations would allow any analytical method to be tested statistically. While statistical analysis of collaborative studies would give important information on populations which determine characteristcs, estimation of 'inter-laboratory standard deviation' would allow the analyst to evaluate a given method.

In considering the relationship between analytical method and statistical analysis, Roubault _et al._ (1970) recommended an improvement in quality of method rather than in quantity of data. Here Roubault seems to agree with Abbey (1977) who found that in the collaborative study, precision seemed to deteriorate with an increase in available results. One of Abbey's suggestions, like that of Roubault _et al._ (1970), was an improvement in quality--but by careful selection of a reliable, limited group of analysts to determine a limited, select group of elements.

De Laeter and Rosman (1977) stated that accuracy of analysis depends on many uncertainties. They cite Ridley _et al._ (1976) where homogeneity was shown to be a major contributor to incongruent results. Control must indeed start as early in a study as possible and homogeneity tests are one of the early controls which can be exercised. But it must be noted that while Ridley _et al._ (1976) proved inhomogeneity does cause bias, it does not follow that all bias is caused by inhomogeneity. Strong proof of this point lies in the 1978 report by Turek _et al._ where homogeneity tests were run and showed a good level, yet bias still occurred. This indicates that bias was caused by additional factors.

Other controls have been suggested, such as sending specific instructions with the samples to be analyzed. Turek _et al._ (1978) sent dissolution instructions and specified that atomic absorption alone was to be used. La Roche and Govindaraju (1976) suggested that the method of x-ray fluorescence for geochemical rock standards gives a more systematic control of results. Abbey (1975) stated that some collaborating laboratories used several methods where possible, providing (in some cases) independant checks on results, while others placed all confidence on one method. Abbey declined stating which approach he felt was more effective..

Flanagan (1969) suggested a standard method of rock analysis. Abbey (1977) claimed this would be impractical because (a) there is little difference between methods and (b) silica's varying composition would make the structuring of one method very difficult. One must remember, however, that many differences of results do occur, and that la Roche and Govindaraju (1976) said that these small 'residual' values are what really matter, not useless agreements en masse, which has been termed, somewhat feciciously, the democratic method of arriving at a 'recommended' value.

Abbey (1977) did propose several controls relating to method which included (a) greater communication between institutions regarding samples, (b) more uniformity of sample preparation and homogeneity tests and (c) more careful selection of collaborating laboratories and tasks to be performed.

G. CONCLUSIONS

All in all, based on a review of literature containing aspects of method bias, there seems to exist a paradox. At one end of the spectrum lie the ideal, theoretical conditions of geochemical analysis--systematic controls, complete comprehension, universal standardization, speed and accuracy--while at the other end of this spectrum lie the existant conditions--inconsistent terminology, confusion of method and of results and arbitrary statistical decisions. Nevertheless, all are becoming aware of the situation and eventually, from the many valid suggestions for improvement, the 'existant' conditions may become compatable with the 'ideal' conditions. It is hoped that this study of method biases may contribute to this end.

RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY <u>ET AL</u>., 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976)

Table 1 SY-2 Values by Method Rather than Laboratory

Element	Method*	N	$\bar{x}$	σ^2	σ
SiO_2	A	11	60.25	0.0082	0.09
	S	6	60.24	0.4281	0.65
	G	43	59.87	0.0534	0.23
	X	12	60.21	0.2535	0.50
Al_2O_3	A	18	12.12	0.0215	0.15
	S	10	11.96	0.1018	0.32
	G	10	11.85	0.0176	0.13
	X	12	12.20	0.0797	0.28
CaO	A	25	8.00	0.0137	0.12
	T	17	7.91	0.0088	0.09
	X	14	7.98	0.0275	0.17
MgO	A	32	2.65	0.0092	0.10
	T	21	2.81	0.0090	0.09
	X	8	2.63	0.0037	0.06
Na_2O	A	30	4.27	0.0117	0.11
	E	46	4.36	0.0381	0.20
K_2O	A	31	4.30	0.0934	0.31
	E	44	4.46	0.0258	0.16
	X	14	4.47	0.0068	0.08
MnO	A	37	0.32	0.0001	0.01
	S	20	0.32	0.0001	0.01
Fe_2O_3	A	16	6.34	0.0117	0.11
	S	17	6.25	0.0130	0.11
	T	29	6.32	0.0274	0.17
	X	23	6.31	0.0113	0.12

*Where A is atomic absorption, E is flame emission, T is titration, S is spectrophotometry, G is gravimetry, and X is x-ray.

Table 2 SY-2
Averages for All Reported Values
(1975 Study + 1976 Supplement)*

Element	N	$\bar{x}$	σ^2	σ
SiO_2	4	60.14	0.0250	0.16
Al_2O_3	4	12.03	0.0186	0.14
CaO	3	7.96	0.0015	0.04
MgO	3	2.70	0.0065	0.08
Na_2O	2	4.32	0.0020	0.05
K_2O	3	4.41	0.0061	0.08
MnO	2	0.32	0.0000	0.00
Fe_2O_3	4	6.31	0.0011	0.03

*Values differ from those of Abbey because Abbey selected recommended values whereas these values are based on all reported values, rejecting those values two standard deviations away from the mean.

RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY *ET AL.*, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976)

Table 3 SY-3 Values by Method Rather than Laboratory

Element	& Method*	N	$\bar{x}$	σ^2	σ
SiO_2	A	1	59.77	0.0231	0.15
	S	11	59.35	0.4073	0.74
	G	45	59.49	0.0480	0.22
	X	11	59.92	0.1236	0.35
Al_2O_3	A	30	11.74	0.0580	0.24
	S	8	11.80	0.2491	0.50
	G	20	11.78	0.0762	0.28
	X	11	11.97	0.1148	0.34
CaO	A	35	8.32	0.0322	0.18
	T	23	8.15	0.0157	0.13
	X	14	8.14	0.0704	0.27
MgO	A	40	2.64	0.0048	0.07
	T	20	2.80	0.0082	0.09
	X	7	2.62	0.0002	0.01
Na_2O	A	30	4.08	0.0149	0.12
	E	46	4.16	0.0355	0.19
K_2O	A	21	4.21	0.0085	0.92
	E	43	4.24	0.0109	0.10
	X	13	4.22	0.0219	0.15
MnO	A	38	0.33	0.0001	0.01
	S	26	0.32	0.0001	0.01
Fe_2O_3	A	23	6.51	0.0127	0.11
	S	17	6.44	0.0260	0.16
	T	30	6.55	0.0248	0.16
	X	13	6.42	0.0202	0.14

*Where A is atomic absorption, E is flame emission, T is titration, S is spectrophotometry, G is gravimetry, and X is x-ray.

Table 4 SY-3
Averages for All Reported Values
(1975 Study + 1976 Supplement)*

Element	N	$\bar{x}$	σ 2	σ
SiO_2	4	59.68	0.0504	0.23
Al_2O_3	4	11.82	0.0077	0.09
CaO	3	8.20	0.0068	0.08
MgO	3	2.69	0.0065	0.08
Na_2O	2	4.12	0.0016	0.04
K_2O	3	4.22	0.0002	0.01
MnO	2	0.33	0.0000	0.01
Fe_2O_3	4	6.48	0.0028	0.52

*Values differ from those of Abbey because Abbey selected recommended values whereas these values are based on all reported values, rejecting those values two standard deviations away from the mean.

RESULTS RECEIVED IN COLLABORATIVE STUDY (ABBEY *ET AL.*, 1975) INCLUDING ITS SUPPLEMENT I (ABBEY, 1976)

Table 5 MRG-1 Values by Method Rather than Laboratory

Element	Method*	N	$\bar{x}$	σ^2	σ
SiO_2	A	17	39.33	0.0462	0.21
	S	8	39.38	0.0181	0.13
	G	39	39.15	0.0573	0.24
	X	7	39.42	0.6991	0.84
Al_2O_3	A	30	8.48	0.0307	0.18
	S	6	8.69	0.4852	0.70
	G	17	8.43	0.0377	0.19
	X	7	8.63	0.0184	0.14
CaO	A	39	14.80	0.0243	0.16
	T	20	14.34	0.0305	0.17
	X	9	15.01	0.1508	0.39
MgO	A	37	13.55	0.0423	0.21
	T	15	13.57	0.0732	0.27
	X	4	13.42	0.2604	0.51
Na_2O	A	26	0.71	0.0011	0.03
	E	39	0.74	0.0042	0.07
K_2O	A	29	0.18	0.0001	0.01
	E	37	0.19	0.0006	0.03
	X	2	0.14	0.0025	0.05
MnO	A	43	0.17	0.0000	0.00
	S	21	0.16	0.0002	0.02
Fe_2O_3	A	31	17.92	0.0400	0.20
	S	10	17.82	0.0538	0.23
	T	30	18.00	0.0782	0.28
	X	9	17.64	0.4641	0.68

*Where A is atomic absorption, E is flame emission, T is titration, S is spectrophotometry, G is gravimetry, and X is x-ray.

Table 6 MRG-1
Averages for All Reported Values
(1975 Study + 1976 Supplement)*

Element	N	$\bar{x}$	σ^2	σ
SiO_2	4	39.32	0.0107	0.10
Al_2O_3	4	8.56	0.0113	0.11
CaO	3	14.72	0.0783	0.28
MgO	3	13.51	0.0044	0.07
Na_2O	2	0.73	0.0002	0.02
K_2O	3	0.17	0.0005	0.02
MnO	2	0.17	0.0000	0.01
Fe_2O_3	4	17.85	0.0181	0.13

*Values differ from those of Abbey because Abbey selected recommended values whereas these values are based on all reported values, rejecting those values two standard deviations away from the mean.

III. EXPERIMENTAL SAMPLE PREPARATION PROCEDURES

A. SAMPLE PREPARATION

A typical rapid rock analysis scheme involves the determination of thirteen constituents (Turek and Riddle, 1977). Most elements are determined on solution 'B' (Al_2O_3, Fe_2O_3, CaO, MgO, NaO, K_2O, TiO_2, P_2O_5, MnO). Solution 'A' is prepared for the determination of SiO_2. Separate aliquots of powder are required for the determination of H_2O, CO_2 and FeO.

Silicon cannot be determined on solution 'B' because it escapes during the dissolution. An alternate method called here 'JA' is given by Ward (1977) and is useful in the determination of Al_2O_3 and SiO_2 by atomic absorption. This solution 'JA' is not appropriate for colorimetric (spectrophotometer) methods, because boric acid interferes with color production. Therefore, solution 'A' had to be made for spectrophotometric determination of SiO_2 and as a check on solution 'B' for Al_2O_3.

B. PREPARATION OF SOLUTION 'A'

A rock powder fusion was made and dissolved to produce solution 'A' (Turek and Riddle, 1977). Six separate dissolutions of sample NSX, one of feldspar #70, one blank, and one GA reference sample were prepared.

Accurately, about 0.1 g of the sample was weighed into a graphite crucible which contained 1.5 g of flux (1 part lithium metaborate to 2 parts lithium tetraborate). The flux was weighed in first, so as to wrap around the rock sample during fusion. The mixture was placed in a muffle furnace for thirty minutes at a setting of 1125°C and then was removed and allowed to cool. The bead was dissolved in a 400-ml plastic beaker which was half full of water with 40 ml of 25% v/v nitric acid. When dissolution was complete, the solution was quantitatively transferred into a 500-ml volumetric nalgene flask, made up to volume, and mixed thoroughly.

C. PREPARATION OF SOLUTION 'B'

Solution 'B' was a dissolution of the rock powder by hydrochloric, perchloric and hydrofluoric acids (Turek and Riddle, 1977). Nine dissolutions of sample NSX were made and also one of: BCR-1, GA, 'in-house' AC-2 and a blank. A reference sample synthetically prepared from ionic standards to simulate G-2 (SYN.G2) was prepared by G. Marzetti and used in this study.

Accurately, about 1 g (9 times) of the NSX sample, 0.5 g of BCR-1, GA and AC2-2 were placed in separate 30-ml platinum crucibles. The dried rock powder was wetted down and baked to dryness, using 10 ml of hydrofluoric acid (48% HF). Another 10 ml of hydrofluoric were added to the crucibles (no heat) and allowed to go to dryness. At dryness, 5 ml of hydrofluoric and 5 ml of perchloric acid (72% $HClO_4$) were added and reheated to dryness. The samples were heated on maximum heat setting until all fumes were given off and for one-half hour at the highest setting. After cooling, 20 ml of 6N HCl were added to dissolve the encrusted residue. Contents of the platinum dishes were then transferred to 500-ml volumetric flasks, rinsing frequently with 2½N HCl, and made up to volume with triple-distilled water.

D. PREPARATION OF SOLUTION 'JA'

The method given by Ward (1977), was modified for use with a Parr acid digestion bomb and prevents the volatilization of silicon as SiF_4.

Accurately, about 0.5 g of dried rock powder samples were placed into the teflon liners of the Parr digestion bombs. Prior to sealing each bomb, 4 ml of 2½N hydrochloric acid, 2 ml of 2½N nitric acid, and 10 ml of concentrated hydrofluoric acid (48%) were poured into the teflon liners. The sealed bombs were then heated in a warming oven at 90° for three hours. They were cooled for one hour in a refrigerator: then, the contents of the teflon liners were quantitatively transferred to 500-ml plastic volumetric flasks. In order to complex the remaining hydrofluoric acid, 9.33 g of boric acid crystals were added to each flask and made up to volume with triple-distilled water.

The preparation of solution 'JA' has two advantages over solution 'B':

(i) Solution 'B' requires 24 hours for dissolution, whereas solution 'JA' requires approximately 4 hours.

(ii) During digestion of solution 'B', silicon is baked off and therefore cannot be analyzed, whereas in solution 'JA', the system is closed, silicon does not escape and hydrofluoric acid is complexed by the boric acid.

E. PREPARATION OF STANDARD SOLUTIONS

For each element to be analyzed, standard solutions were prepared for the purpose of construction of calibration curves. These standard solutions were made from Fisher Chemical Company certified ionic stock solutions of 1000 µg/ml concentration. A range of standards which would bracket the amount of the constituents being analyzed was prepared for each element.

Iron standards were acidified with 6N hydrochloric acid; a separate set of standards for calcium and one for magnesium were prepared and diluted with a releasing agent--lanthanum oxide.

The range of concentration of the standard solutions and the working conditions are listed in each element's respective table. Working conditions were obtained from Varian Techtron (1976), for use with model AA-175.

F. PREPARATION OF X-RAY FLUORESCENCE GLASS PELLETS

For x-ray analysis, glass pellets were prepared because of their superiority over rock pellets with regard to homogeneity and to reduce the matrix effect. It should be noted, however, that sodium escapes during high temperature fusion in glass pellets, whereas sodium can be analyzed in rock pellets.

Accurately, about 1.0 g of rock sample were weighed into a graphite crucible which already contained 2.0 g of lithium tetraborate flux. The flux was weighed in first, so as to wrap around the rock powder during fusion. The ratio of rock powder to flux must be exactly one part sample to two parts flux.

The mixture was placed in a muffle furnace (preheated to 1150°C) for twenty minutes. Immediately, the melt was poured out onto a freshly cleaned aluminum plate. The resulting glass bead, when cool, was crushed for three minutes in a shatterbox. The resulting glass powder was transferred into an air-tight plastic vial and kept in a dessicator.

The total amount of glass powder was mixed with four drops of 2% w/v polyvinyl alcohol (which acts as a binder). Borax was added to provide a backing for the pellets and the whole mixture was pelletized in a 32-mm die for fifteen seconds at 5.98 KPa (9-ton) pressure. The resulting glass pellets were labelled and dried for 24 hours.

IV. ANALYTICAL PROCEDURES

A. ATOMIC ABSORPTION SPECTROSCOPY

a. Theory

The method of atomic absorption spectroscopy consists of creating a plasma to contain the free atoms of the elements to be measured. The free atoms are present in both excited and ground states; a beam of light of exactly the same wavelength as that emitted by the excited atoms is passed through the plasma or flame. The intensity of the light beam is measured before and after passing through the absorbing ground-state atoms. The amount of absorbed energy is directly proportional to the number of atoms present.

Compounds, upon vaporizing in the flame, partially or totally dissociate into their atomic constituents. The number of excited atoms, N_j, is related to the number of ground-state atoms, N_o, at any given temperature, T, as noted by the Boltzmann Principle (Price, 1969).

$$N_j = N_o \times \frac{P_j}{P_o} \exp \frac{-E_j}{kT}$$

where P_j and P_o are statistical weights of the two energy states E_j and E_o, respectively.

The ratio $N_j:N_o$, the proportion of excited-state atoms to ground-state atoms is therefore a function of temperature.

The value E_j (wavelength of the spectral line corresponding to the transition between ground and excited states) is inversely proportional to the number of atoms in the excited state.

Atoms in the ground state only absorb energy at wavelengths corresponding to their own resonance lines. When an electron is raised from a lower excitation state (E_1) to a higher excitation state (E_2), a line spectrum is produced. The first energy line produced by excitation of the atoms is usually the most sensitive and therefore the most frequently used in atomic absorption. The absorption at the peak of energy line is proportional to the concentration of atoms held in the plasma vapour.

A narrow band of radiation at a specified wavelength is emitted by a light source, a hollow cathode lamp. The radiation is directed through the plasma vapour containing the atoms and onto the opening slit of the monochromator which separates the desired energy lines from others being emitted. The intensity of transmitted radiation is governed by Beer's Law (Price, 1969):

$$I_t = I_o \exp(-abc)$$

where I_o is the intensity of incident radiation; I_t is the intensity of transmitted radiation; 'a' is the absorption coefficient at the wavelength used; 'b' is the concentration of absorbing atoms and 'c' is the length of the absorption path.

Absorbance is proportional to the concentration for any given absorption path length at any given wavelength (Varian Techtron, 1971).

The model used for this thesis was Atomic Absorption Spectrophotometer AA-175 Series by Varian Techtron Pty., Ltd.

The calculations for percent oxide in the sample solutions are:

$$\%\ \text{Oxide} = \frac{\text{Conc.} \times \text{Vt} \times \text{D} \times \text{CF} \times 10^{-4}}{\text{Wt. of Sample}}$$

where Conc. is the concentration of the analyte in ug/ml; Vt is the total volume of the sample solution in ml; D is the dilution factor and CF is the conversion factor (see Appendix IV).

The concentration of the analyte (Conc.) is obtained by deducing a calibration factor; CF = 1/slope from the calibration curves.

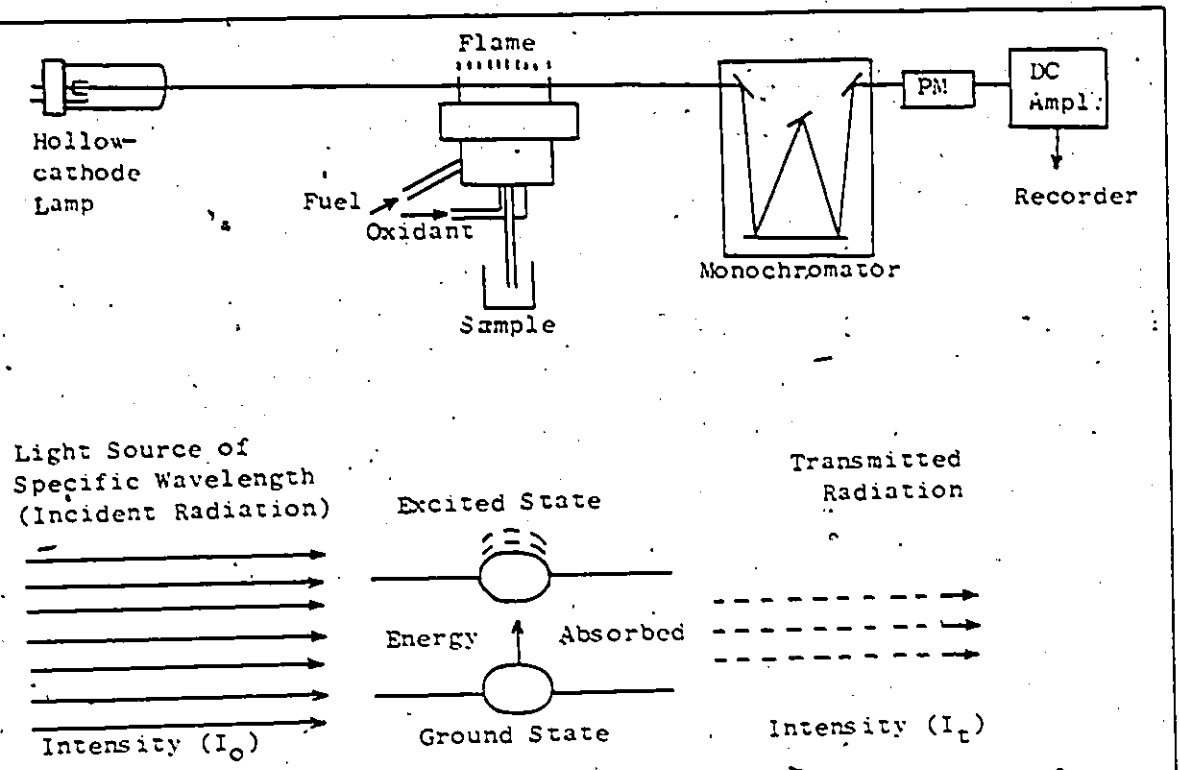


Fig. 1. Schematic layout of atomic absorption unit (Ewing, 1969) and diagram of energy absorbance.

b. Analytical Procedure

1. Silicon by Atomic Absorption Spectroscopy

Silicon was determined on two dissolutions, sample 'JA' and sample 'A'. Solution 'B' was not used because the silicon evaporated during dissolution.

Ionic standards of 50 µg/ml Si to 400 µg/ml Si were used for both dissolutions. Working conditions for the ionic standards and the sample solutions were identical (Appendix I and Table 7). The calibration curves are produced in Figs. 2 and 3. Absorbance readings for the samples are in Tables 9 and 10. The concentration of silicon in solution as percent oxide is reported in Tables 43 and 44.

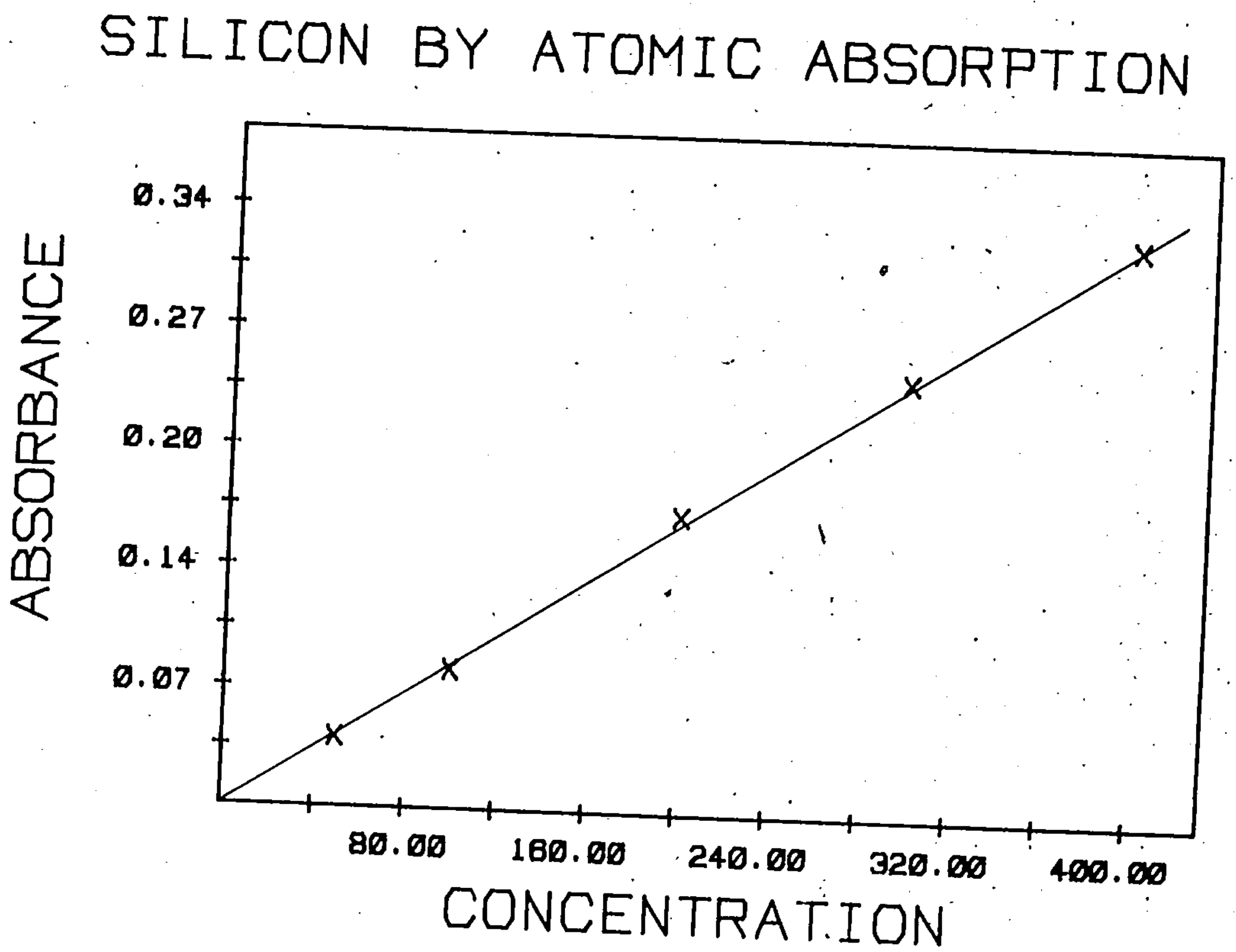


Fig. 2
Calibration curve for silicon by atomic absorption (on solution 'A')
(μg/ml)

TABLE 7. IONIC STANDARDS FOR

SILICON IN SOLUTION 'A' BY ATOMIC ABSORPTION

WORKING CONDITIONS

WAVELENGTH	250.7 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	15.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	reducing; yellow outer edge
SUPPORT GAS	nitrous oxide
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
50	0.046	6	0.045	0.040
100	0.089	6	0.090	0.080
200	0.170	6	0.174	0.170
300	0.255	6	0.254	0.250
400	0.334	6	0.337	0.330

THE SLOPE IS 0.0008
THE INTERCEPT IS -0.0086
THE CORRELATION COEFFICIENT IS 0.99986

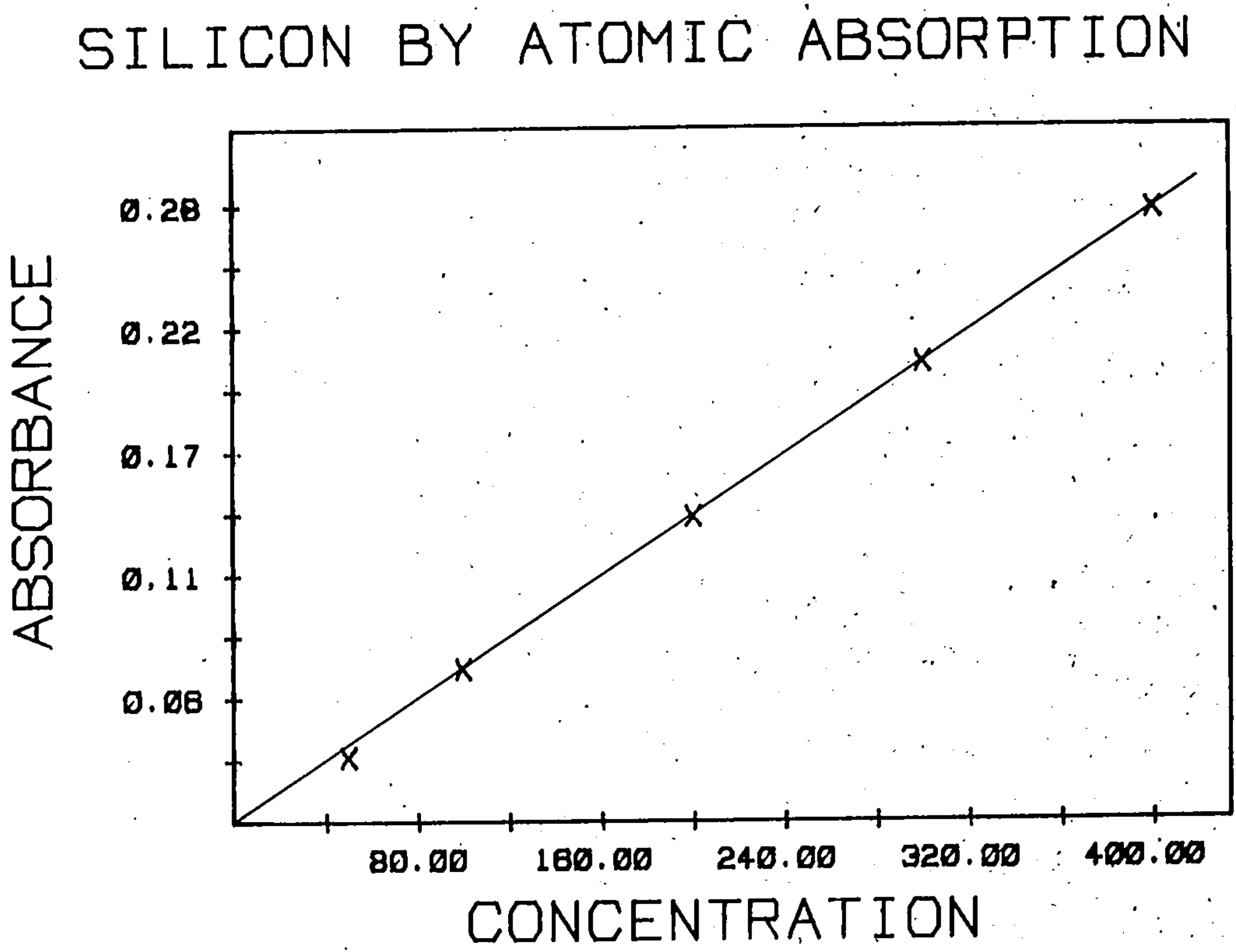


Fig. 3
Calibration curve for silicon by atomic absorption (on solution 'JA')
(μg/ml)

TABLE 8 . IONIC STANDARDS FOR SILICON IN SOLUTION 'JA' BY ATOMIC ABSORPTION

WORKING CONDITIONS

WAVELENGTH	250.7 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	15.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	reducing; yellow outer edge
SUPPORT GAS	nitrous oxide
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
50	0.040	6	0.041	0.030
100	0.079	6	0.079	0.070
200	0.152	6	0.153	0.140
300	0.225	6	0.226	0.210
400	0.295	6	0.296	0.280

THE SLOPE IS 0.0007
THE INTERCEPT IS -0.0098
THE CORRELATION COEFFICIENT IS 0.99995

TABLE 9

SILICON IN SOLUTION 'JA' BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.180	6	0.180	0.180
GA	0.225	6	0.225	0.225
SYN.G2	0.229	6	0.229	0.228
NSX-1	0.221	6	0.221	0.221
NSX-2	0.241	6	0.246	0.241
NSX-3	0.225	6	0.225	0.225
NSX-4	0.224	6	0.224	0.224
NSX-5	0.220	6	0.220	0.220
NSX-6	0.222	6	0.222	0.222
NSX-7	0.222	6	0.222	0.222
NSX-8	0.224	6	0.224	0.224
NSX-9	0.222	6	0.222	0.222

TABLE 10

SILICON IN SOLUTION 'A' BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
GA	0.053	6	0.052	0.052
SiO_2-Pure	0.076	6	0.074	0.074
NSX-1	0.052	6	0.052	0.051
NSX-2	0.056	6	0.056	0.056
NSX-3	0.053	6	0.052	0.053
NSX-4	0.051	6	0.050	0.050
NSX-5	0.052	6	0.051	0.051
NSX-6	0.064	6	0.064	0.063
NSX-7	0.052	6	0.051	0.051

2. Aluminum by Atomic Absorption Spectroscopy

Aluminum was determined on both solution 'B' and solution 'A'. Solution 'A' was the dissolution used in the calculations of biases. Solution 'B' was not used, due to lower values obtained (Tetley, 1973).

Ionic standards prepared ranged from 20 μg/ml Al to 100 μg/ml Al for both solutions. The working conditions are the same for the ionic standards and the sample solutions (Table 11). Typical calibration curve for aluminum standards is shown in Fig. 4. Readings are recorded in Tables 11 and 12. The percent oxides for both solution 'A' and 'B' were calculated and noted in Table 54.

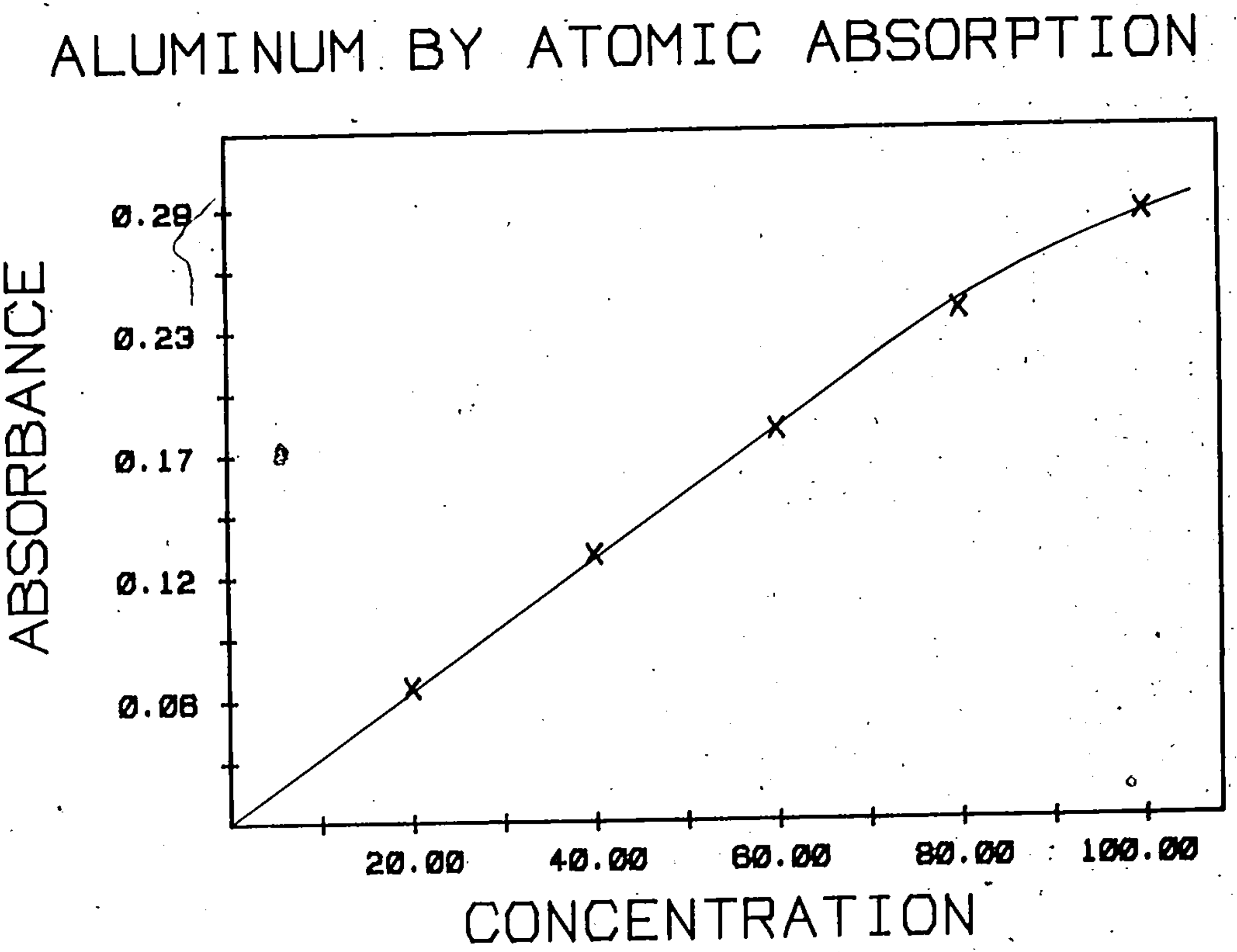


Fig. 4
Calibration curve for aluminum by atomic absorption (on solution 'B')
(μg/ml)

TABLE 11. IONIC STANDARDS

ALUMINUM IN SOLUTION 'A' BY ATOMIC ABSORPTION

WORKING CONDITIONS

WAVELENGTH	309.3 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	10.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	reducing; red cone 1-2 cm high
SUPPORT GAS	nitrous oxide
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
20	0.069	6	0.069	0.065
40	0.133	6	0.135	0.127
60	0.198	6	0.199	0.186
80	0.255	6	0.258	0.242
100	0.299	6	0.300	0.288

THE SLOPE IS 0.0030
THE INTERCEPT IS 0.0002
THE CORRELATION COEFFICIENT IS 0.99920

SLOPE DERIVED FROM STRAIGHT
PORTION OF CURVE

TABLE 12.

ALUMINUM IN SOLUTION 'A' BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
GA	0.048	6	0.052	0.051
SYN.G2	0.256	6	0.260	0.260
NSX-1	0.051	6	0.052	0.052
NSX-2	0.056	6	0.056	0.057
NSX-3	0.053	6	0.053	0.053
NSX-4	0.052	6	0.054	0.051
NSX-5	0.052	6	0.052	0.050
NSX-6	0.062	6	0.062	0.060
NSX-7	0.052	6	0.052	0.050
BLANK	0.000	6	0.000	0.000

3. Total Iron by Atomic Absorption Spectroscopy

Total iron was determined directly on solution 'B'. The ionic standards ranging from 15 to 6 µg/ml were acidified with 6N HCl.

The working conditions are listed in Appendix I. Fig. 5 is the calibration graph. Tables 13 and 14 are the absorbance readings. Concentrations as percent oxide are listed in Table 64.

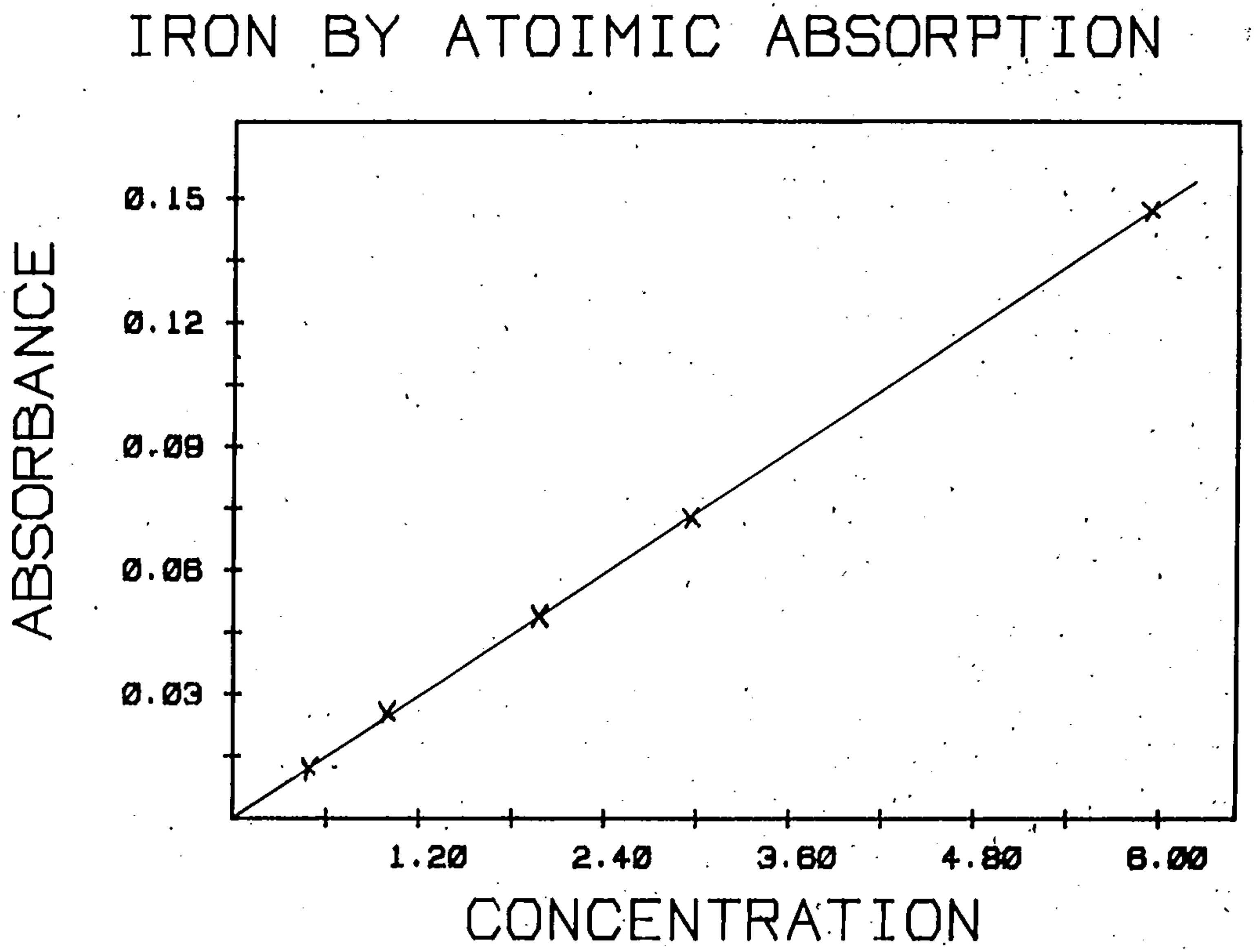


Fig. 5
Calibration curve for total iron by atomic absorption
(μg/ml)

TABLE 13. IONIC STANDARDS FOR IRON BY ATOMIC ABSORPTION

WORKING CONDITIONS	
WAVELENGTH	248.3 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	5.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	absorbance

CONC. OF STANDARD μg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.5	0.010	6	0.013	0.010
1	0.024	6	0.026	0.020
2	0.047	6	0.050	0.050
3	0.071	6	0.073	0.070
6	0.146	6	0.146	0.140

THE SLOPE IS 0.0244
THE INTERCEPT IS 0.0005
THE CORRELATION COEFFICIENT IS 0.99990

TABLE 14.

IRON BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.108	12	0.108	0.110
GA	0.058	12	0.050	0.050
AC2-2	0.071	12	0.071	0.073
SYN.G2	0.048	12	0.047	0.047
NSX-1	0.068	12	0.066	0.069
NSX-2	0.069	12	0.068	0.072
NSX-3	0.064	12	0.066	0.069
NSX-4	0.064	12	0.064	0.067
NSX-5	0.068	12	0.068	0.071
NSX-6	0.065	12	0.066	0.069
NSX-7	0.067	12	0.067	0.070
NSX-8	0.068	12	0.067	0.070
NSX-9	0.069	12	0.069	0.072
BLANK	0.002	12	0.000	0.000

4. Calcium by Atomic Absorption Spectroscopy

Calcium was determined directly on solution 'B'. A releasing agent, lanthanum oxide (4633.2 ppm) was used to dilute all samples and standards. The use of a releasing agent is recommended by Varian Techtron (1971).

The ionic standards were not prepared using lanthanum oxide because they only contained calcium but the blank solution was diluted with the releasing agent.

Standards were prepared ranging from 0.5 µg/ml to 7 µg/ml. The calibration curve is shown in Fig. 6. Tables 15 and 16 are the absorbance readings. Percent oxides are listed in Table 74.

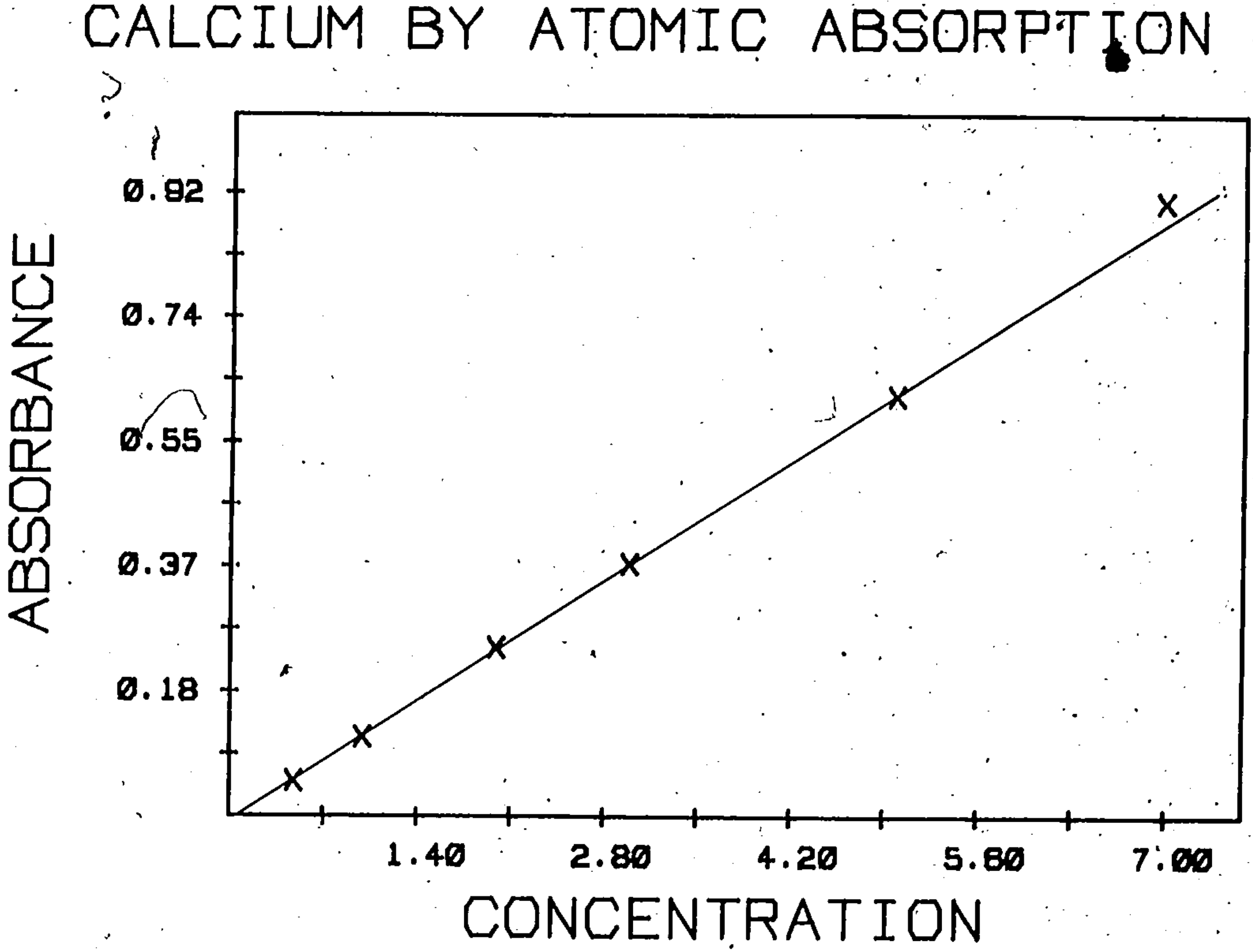


Fig. 6
Calibration curve for calcium by atomic absorption
(μg/ml)

TABLE 15. IONIC STANDARDS FOR

CALCIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION

WORKING CONDITIONS

WAVELENGTH	422.7 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	3.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	reducing; red cone 1-1.5 cm high
SUPPORT GAS	nitrous oxide
MODE	absorbance @ 10 sec. intergrade

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.5	0.052	6	0.054	0.054
1	0.116	6	0.115	0.118
2	0.248	6	0.251	0.250
3	0.374	6	0.374	0.375
5	0.616	6	0.629	0.625
7	0.890	6	0.931	0.913

THE SLOPE IS 0.1283
THE INTERCEPT IS -0.0066
THE CORRELATION COEFFICIENT IS 0.99967

TABLE 16

CALCIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.640	6	0.676	0.598
GA	0.471	6	0.469	0.391
AC2-2	0.399	6	0.394	0.316
SYN.G2	0.228	6	0.225	0.147
NSX-1	0.383	6	0.383	0.305
NSX-2	0.393	6	0.393	0.315
NSX-3	0.378	6	0.379	0.301
NSX-4	0.382	6	0.380	0.302
NSX-5	0.364	6	0.359	0.281
NSX-6	0.359	6	0.360	0.282
NSX-7	0.360	6	0.364	0.286
NSX-8	0.379	6	0.382	0.305
NSX-9	0.343	6	0.343	0.265
BLANK	0.078	6	0.000	0.000

5. Magnesium by Atomic Absorption Spectroscopy

Magnesium was determined directly on solution 'B'. The sample solutions and blank were the same as those used for calcium determinations. Magnesium also needed a releasing agent, lanthanum oxide (Varian Techtron, 1972) Operating conditions are listed in Appendix I. The standards ranged from 0.1 µg/ml to 2 µg/ml. The calibration graph (Fig. 7) was prepared using only 0.1 µg/ml to 0.8 µg/ml which bracketed the concentration of the sample solutions.

Two sets of samples were analyzed, one set without a releasing agent and the other with a releasing agent. Concentration as percent oxides for the two sets are tabulated in Tables 80 and 81; the results using the releasing agent are more correct and illustrate the need for the use of a releasing agent. Absorbance readings are in Tables 19 and 20.

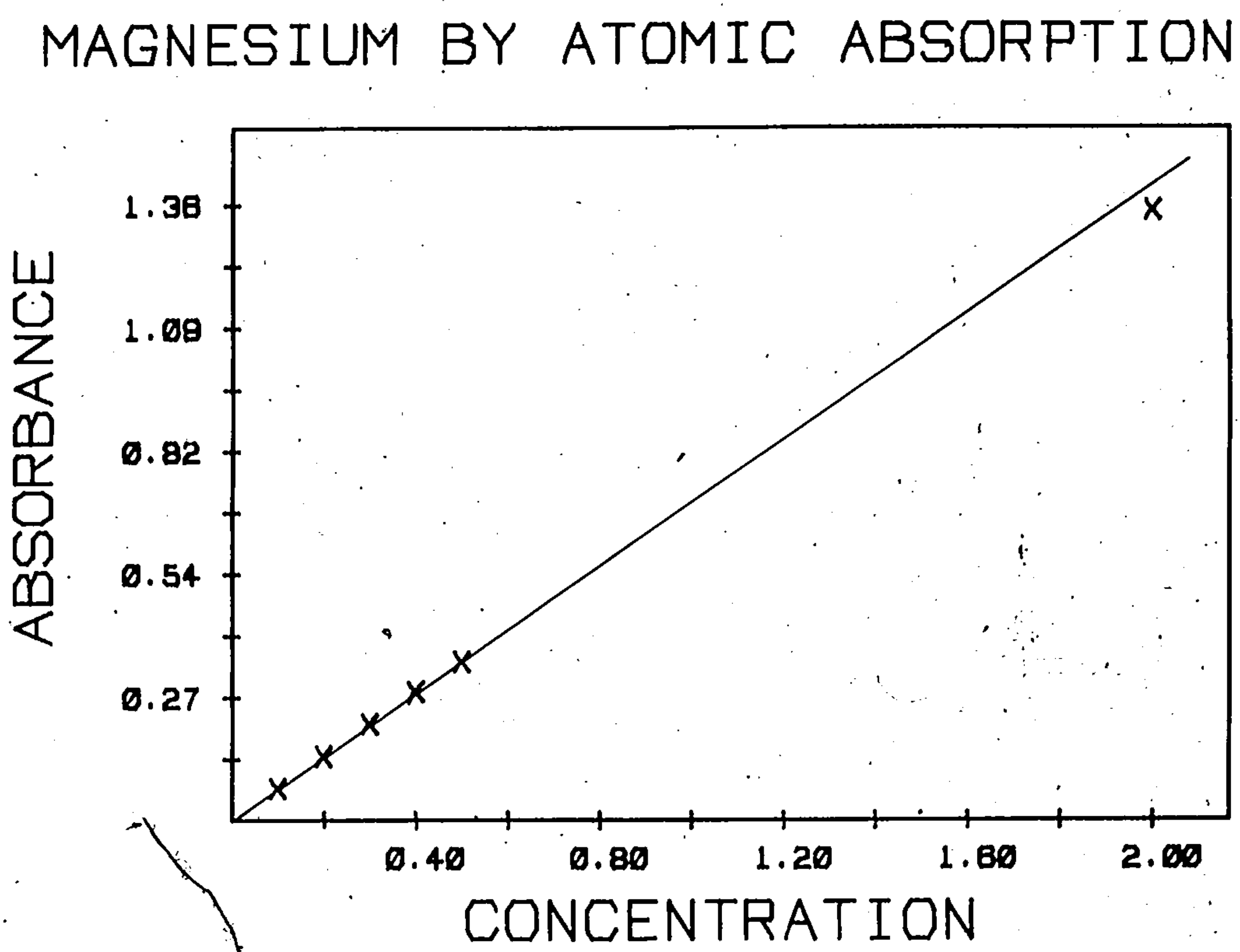


Fig. 7
Calibration curve for magnesium with lanthanum oxide by atomic absorption
(µg/ml)

TABLE 17. IONIC STANDARDS FOR MAGNESIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION

WORKING CONDITIONS

WAVELENGTH	285.2 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	3.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.1	0.071	6	0.071	0.076
.2	0.157	6	0.146	0.150
.3	0.227	6	0.223	0.225
.4	0.302	6	0.291	0.298
.5	0.372	6	0.360	0.367
2	1.364	6	1.363	1.363

THE SLOPE IS 0.7496
THE INTERCEPT IS -0.0006
THE CORRELATION COEFFICIENT IS 0.99991

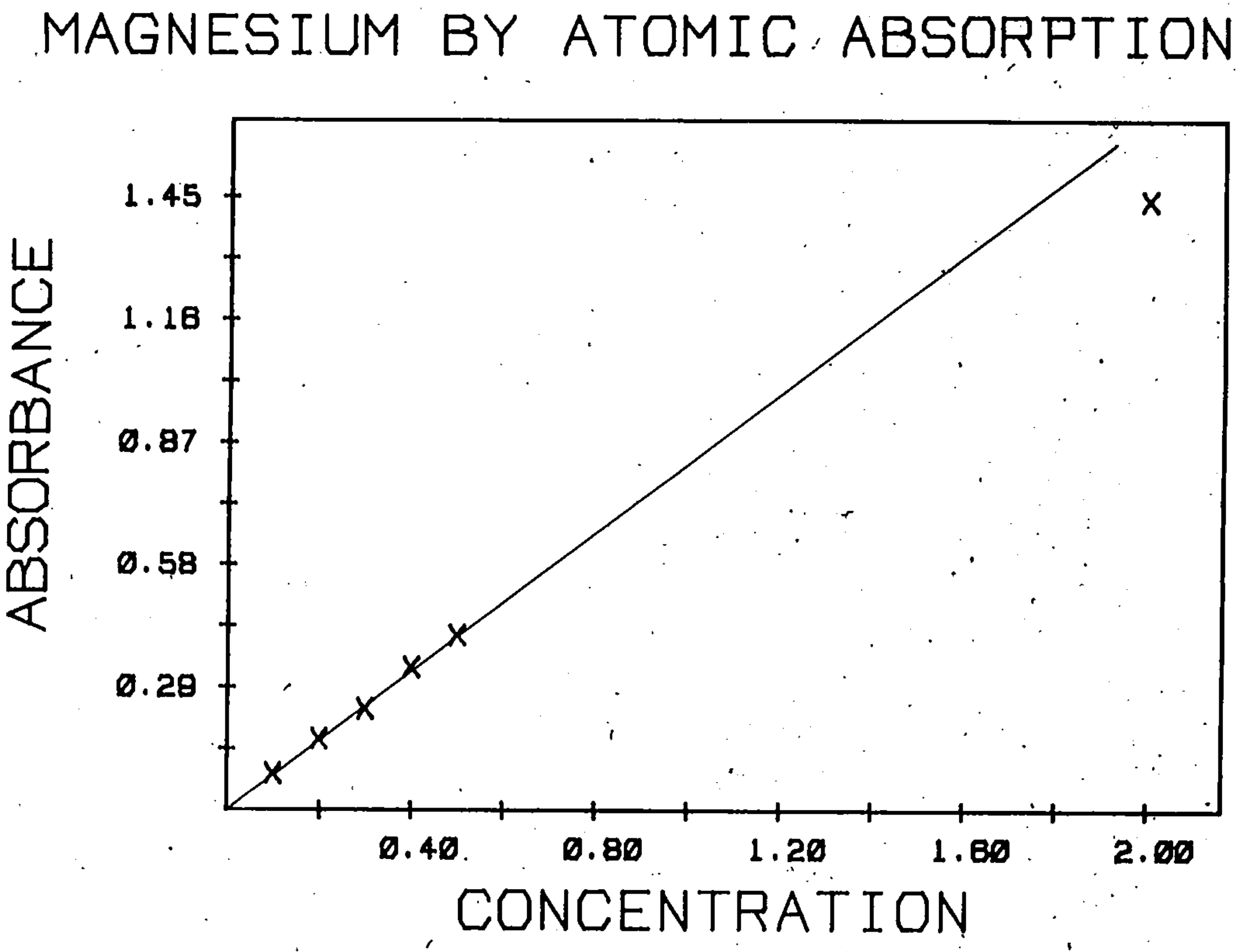


Fig. 8
Calibration curve for magnesium without lanthanum oxide by atomic absorption
(μg/ml)

TABLE 18. IONIC STANDARDS FOR

MAGNESIUM WITHOUT LANTHANUM OXIDE BY ATOMIC ABSORPTION

WORKING CONDITIONS

WAVELENGTH	285.2 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	3.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.1	0.086	6	0.088	0.088
.2	0.170	6	0.171	0.171
.3	0.242	6	0.249	0.245
.4	0.339	6	0.340	0.345
.5	0.429	6	0.429	0.423
2	1.444	6	1.444	1.456

THE SLOPE IS 0.8580
THE INTERCEPT IS -0.0003
THE CORRELATION COEFFICIENT IS 0.99995

TABLE 19

MAGNESIUM WITHOUT LANTHANUM OXIDE BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.400	6	0.400	0.378
GA	0.480	6	0.483	0.461
AC2-2	0.612	6	0.614	0.592
SYN.G2	0.366	6	0.367	0.345
NSX-1	0.611	6	0.614	0.592
NSX-2	0.626	6	0.624	0.602
NSX-3	0.607	6	0.607	0.585
NSX-4	0.615	6	0.615	0.593
NSX-5	0.603	6	0.602	0.580
NSX-6	0.574	6	0.574	0.552
NSX-7	0.593	6	0.591	0.569
NSX-8	0.596	6	0.597	0.575
NSX-9	0.498	6	0.498	0.476
BLANK	0.022	6	0.000	0.000

TABLE 20

MAGNESIUM WITH LANTHANUM OXIDE BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.884	6	0.881	0.832
GA	0.485	6	0.487	0.438
AC2-2	0.605	6	0.603	0.554
SYN.G2	0.371	6	0.368	0.319
NSX-1	0.595	6	0.597	0.548
NSX-2	0.603	6	0.603	0.554
NSX-3	0.604	6	0.602	0.553
NSX-4	0.603	6	0.601	0.552
NSX-5	0.597	6	0.589	0.540
NSX-6	0.558	6	0.556	0.507
NSX-7	0.576	6	0.582	0.533
NSX-8	0.561	6	0.568	0.519
NSX-9	0.475	6	0.489	0.440
BLANK	0.049	6	0.000	0.000

6. Sodium by Atomic Absorption Spectroscopy

Sodium was determined directly on solution 'B'. The ionic standards ranged from 0.5 µg/ml to 4 µg/ml.The calibration curve is Fig. 9. The absorbance readings are in Tables 21 and 22. The concentration as percent oxides are in Table 87.

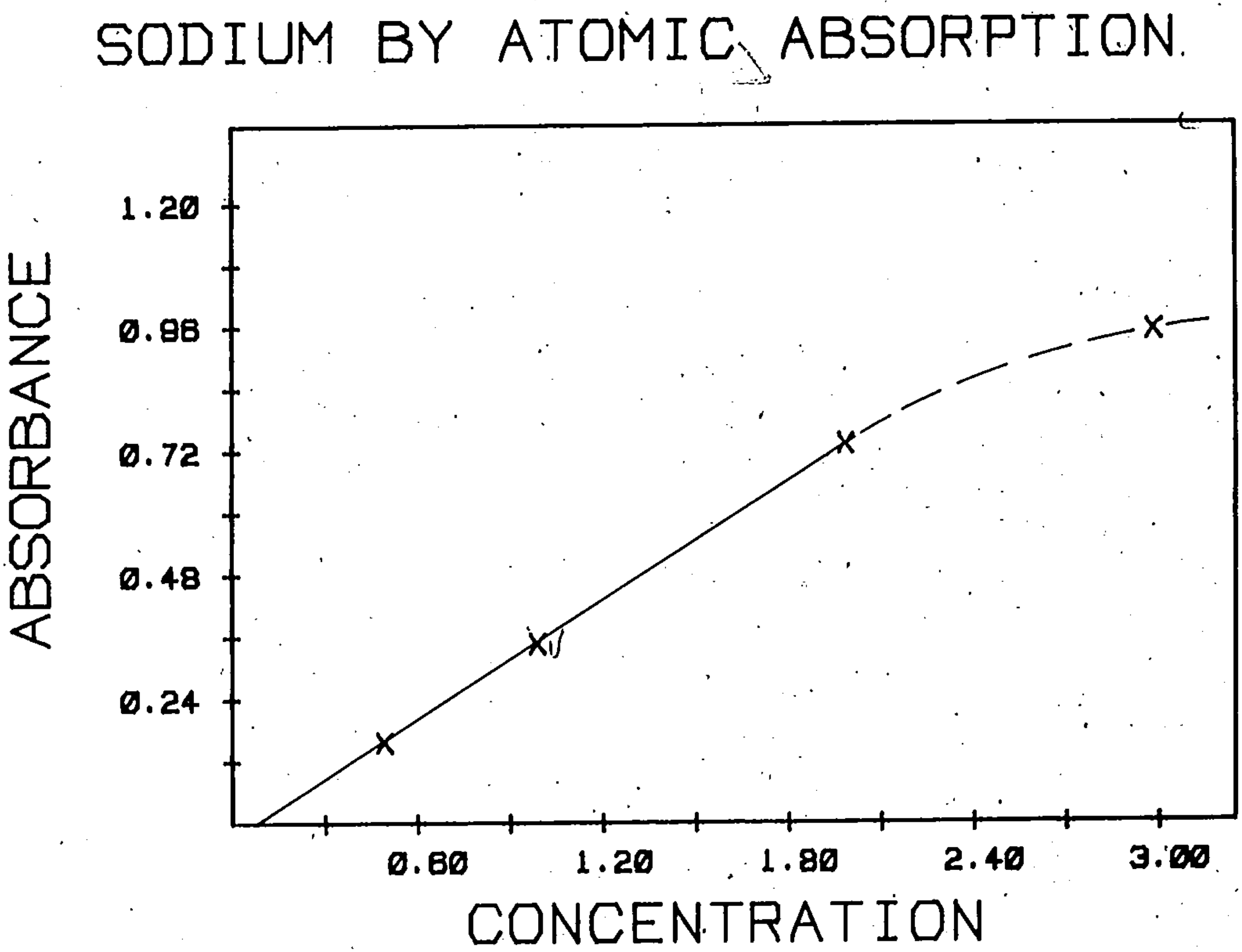


Fig. 9
Calibration curve for sodium by atomic absorption
(μg/ml)

TABLE 21 . IONIC STANDARDS FOR SODIUM BY ATOMIC ABSORPTION

WORKING CONDITIONS	
WAVELENGTH	589.6 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	5.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.5	0.154	6	0.154	0.160
1	0.385	6	0.377	0.350
2	0.754	6	0.748	0.740
3	1.174	6	1.165	1.170
4	1.334	6	1.328	1.330

THE SLOPE IS 0.3829
THE INTERCEPT IS -0.0119
THE CORRELATION COEFFICIENT IS 0.99938

SLOPE DERIVED FROM STRAIGHT
PORTION OF CURVE

TABLE 22

SODIUM BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	1.086	6	1.042	1.012
GA	1.099	6	1.100	1.070
AC2-2	1.055	6	1.051	1.021
SYN.G2	1.232	6	1.249*	1.219
NSX-1	1.055	6	1.049	1.019
NSX-2	1.080	6	1.044	1.101
NSX-3	1.059	6	1.061	1.031
NSX-4	1.090	6	1.070	1.040
NSX-5	1.121	6	1.000	1.043
NSX-6	1.048	6	1.073	1.034
NSX-7	1.079	6	1.066	1.036
NSX-8	1.118	6	1.080	1.050
NSX-9	0.928	6	0.939	0.909

7. Potassium by Atomic Absorption Spectroscopy

Potassium was analyzed directly on solution 'B'. Working conditions are listed in Appendix I. The ionic standards spanned 0.5 μg/ml to 4 μg/ml. The calibration graph is in Fig. 10. Absorbance readings are given in Tables 23 and 24. Concentration as percent oxides is reported in Table 90.

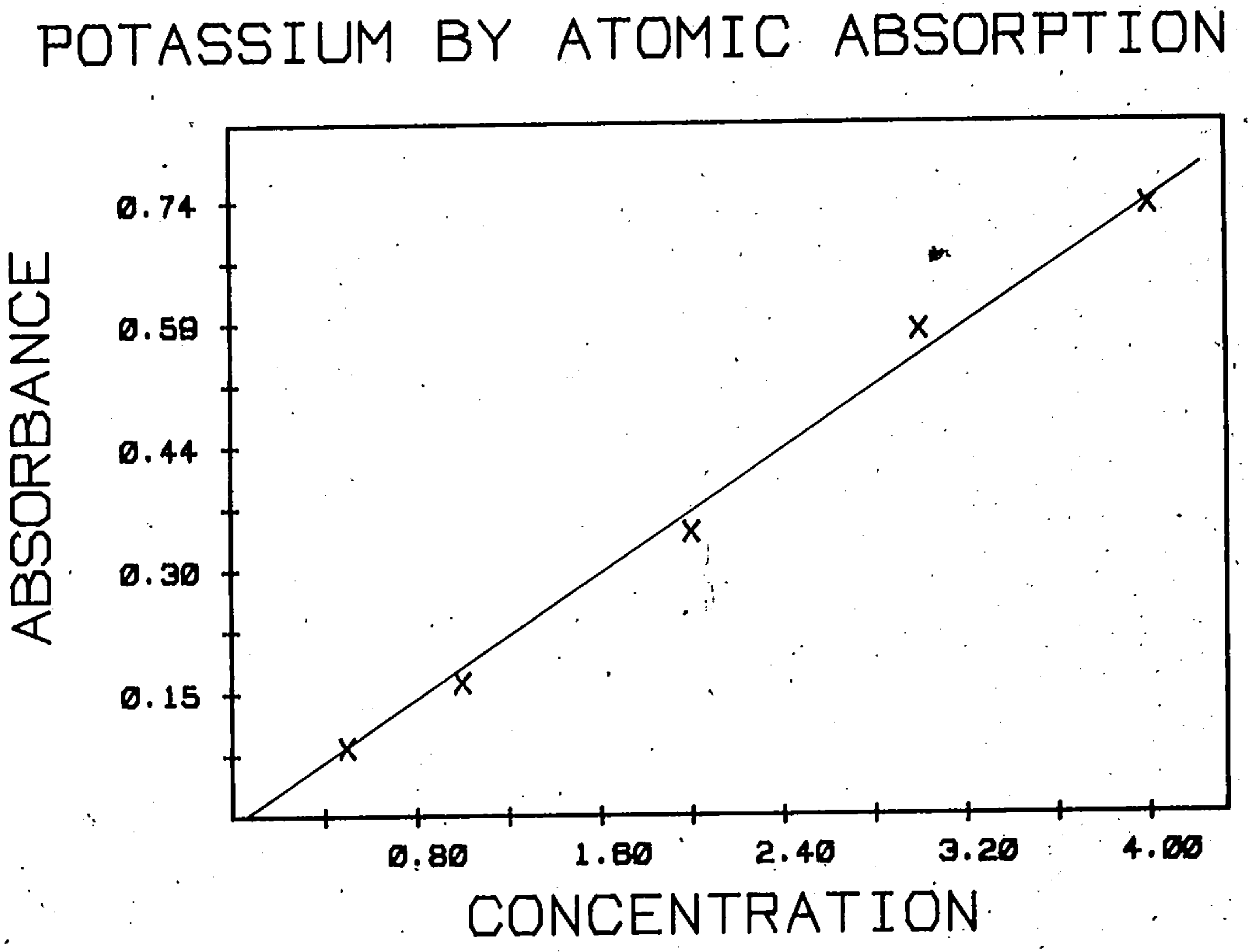


Fig. 10
Calibration curve for potassium by atomic absorption
(μg/ml)

TABLE 23. IONIC STANDARDS FOR POTASSIUM BY ATOMIC ABSORPTION

WORKING CONDITIONS	
WAVELENGTH	766.5 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	5.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	absorbance

CONC. OF STANDARD μg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.5	0.078	6	0.076	0.085
1	0.170	6	0.170	0.163
2	0.349	6	0.347	0.345
3	0.586	6	0.587	0.587
4	0.764	6	0.746	0.738

THE SLOPE IS 0.1860
THE INTERCEPT IS -0.0065
THE CORRELATION COEFFICIENT IS 0.99884

TABLE 24

POTASSIUM BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.334	6	0.319	0.319
GA [illegible]	0.699	6	0.693	0.693
AC2-2	0.682	6	0.676	0.676
SYN.G2	0.838	6	0.849	0.849
NSX-1	0.669	6	0.673	0.673
NSX-2	0.684	6	0.697	0.696
NSX-3	0.678	6	0.678	0.678
NSXy4	0.689	6	0.679	0.678
NSX-5	0.701	6	0.687	0.687
NSX-6	0.681	6	0.679	0.679
NSX-7	0.589	6	0.591	0.591
NSX-8	0.632	6	0.629	0.628
NSX-9	0.547	6	0.556	0.556
BLANK	0.000	6	0.000	0.000

8. Manganese by Atomic Absorption Spectroscopy

Manganese was determined directly on solution 'B'. The working conditions are listed in Appendix I. Ionic standards were prepared from 0.5 µg/ml to 3 µg/ml. The plot of the calibration curve is given in Fig. 11. Absorbance readings are given in Tables 25 and 26. Percent oxide is noted in Table 96.

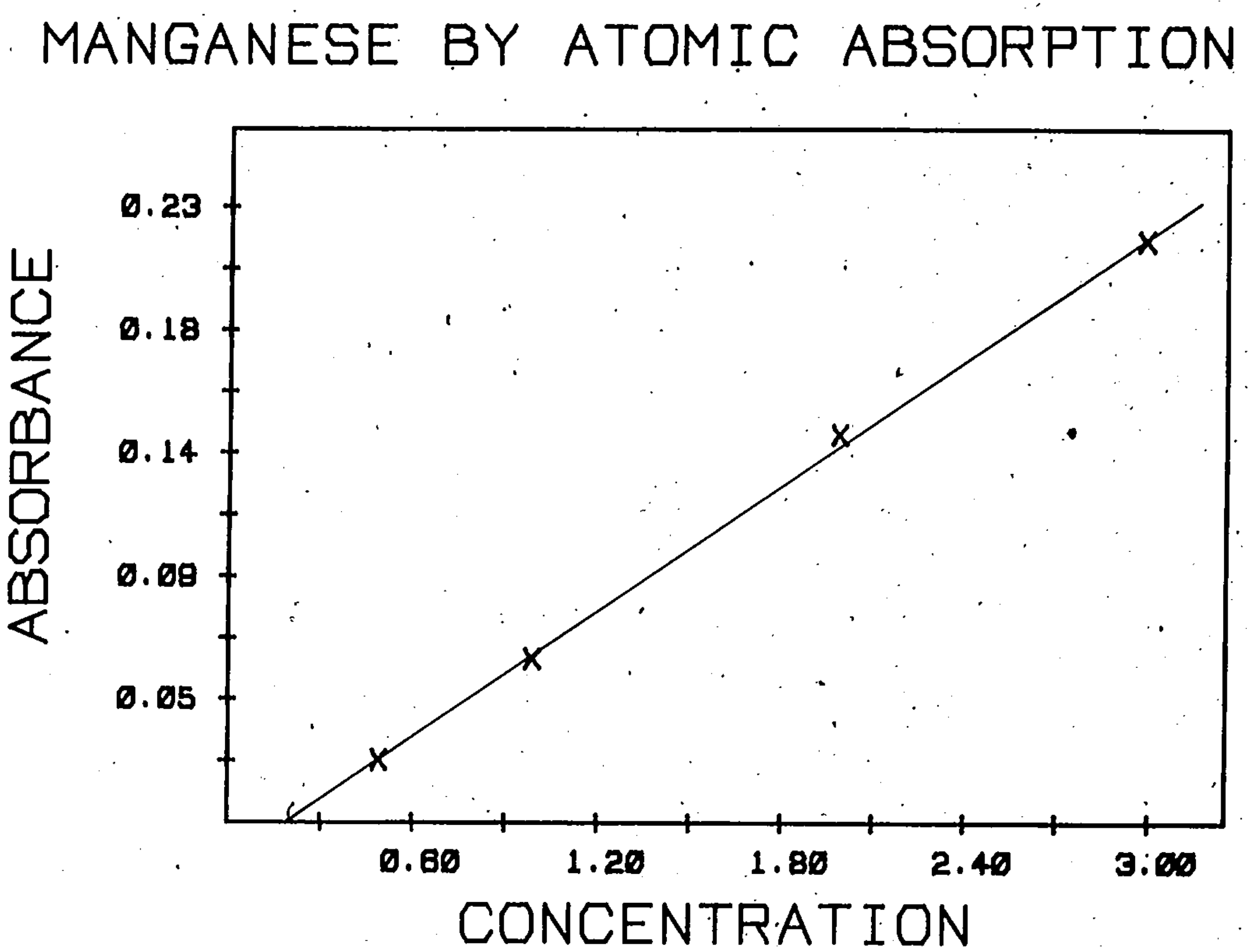


Fig. 11
Calibration curve for manganese by atomic absorption
(µg/ml)

TABLE 25 . IONIC STANDARDS FOR

MANGANESE BY ATOMIC ABSORPTION

WORKING CONDITIONS	
WAVELENGTH	279.5 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	5.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	absorbance

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.5	0.023	6	0.026	0.024
1	0.060	6	0.064	0.062
2	0.144	6	0.148	0.146
3	0.218	6	0.219	0.219

THE SLOPE IS 0.0786
THE INTERCEPT IS -.0151
THE CORRELATION COEFFICIENT IS 0.99955

SLOPE DERIVED FROM STRAIGHT
PORTION OF CURVE (FIRST 3 POINTS)

TABLE 26.

MANGANESE BY ATOMIC ABSORPTION

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.115	6	0.114	0.114
GA	0.051	6	0.052	0.052
AC2-2	0.051	6	0.050	0.050
SYN.G2	0.053	6	0.053	0.053
NSX-1	0.048	6	0.048	0.048
NSX-2	0.047	6	0.047	0.047
NSX-3	0.049	6	0.048	0.048
NSX-4	0.049	6	0.048	0.048
NSX-5	0.049	6	0.049	0.049
NSX-6	0.046	6	0.046	0.046
NSX-7	0.047	6	0.046	0.046
NSX-8	0.047	6	0.046	0.046
NSX-9	0.040	6	0.040	0.040

B. FLAME EMISSION SPECTROSCOPY

a. Theory

Atoms present or injected into a thermally produced plasma emit and absorb radiation of discrete and characteristic wavelengths. In emission spectroscopy, lines are used which are produced in almost any transition and sometimes those which are produced by ionized atoms.

An emission spectral line is produced when energy of the characteristic length is emitted by an atom when an electron drops from higher excitation state (E_2) to a lower state (E_1). This change in energy level gives a quantum of energy ($h\nu$)--a photon; where h is Planck's constant and ν is frequency (Ewing, 1969).

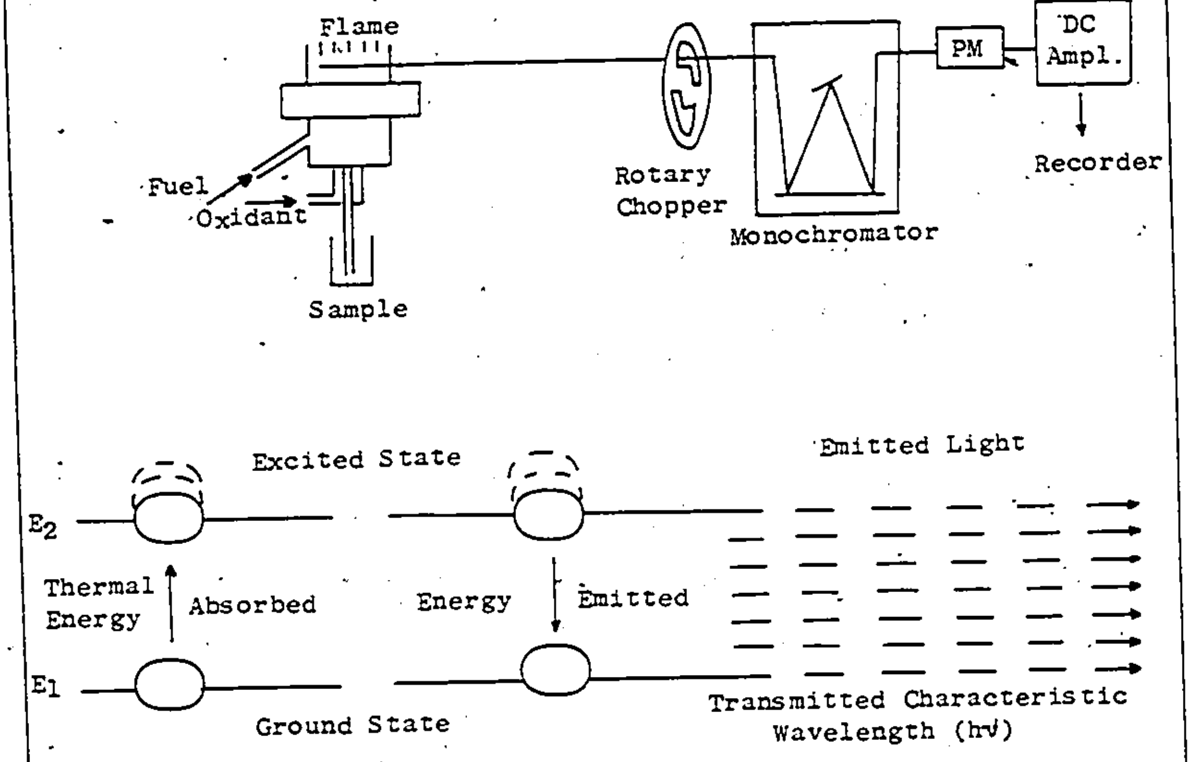


Fig. 12. Schematic layout of flame emission unit (Ewing, 1969) and diagram of energy emission.

The excited atoms emit light of the characteristic wavelength. The intensity of this transmittance is related to the concentration of the element in the sample. Detailed description of flame chemistry is given by Ewing (1969), Price (1969), Ernest and Billings (1972) and Skoog and West (1971).

The instrument used for flame emission is the same one used for atomic absorption analysis, the hollow cathode lamp is of course not used and the readings are in percent transmittance (%T).

The equation for the calculations of percent oxide in the sample solutions is:

$$\%\ \text{Oxide} = \frac{\text{Conc.} \times \text{Vt} \times \text{D} \times \text{CF} \times 10^{-4}}{\text{Wt. of Sample}}$$

where Conc. is the concentration of the analyte in µg/ml; Vt is the total volume of the sample solution in ml; D is the dilution factor and CF is the conversion factor (Appendix IV).

The concentration of the analyte (Conc.) is obtained by deducing a calibration factor; CF = 1/slope from the calibration curves.

b. Analytical Procedure

1. Sodium by Flame Emission Spectroscopy

Sodium was determined on solution 'B' by flame emission. The working conditions are listed in Appendix I.

Varian Techtron (1972) reported that partial ionization occurs in the air-acetylene flame; however, this is not considered a serious problem. Calibration curve is Fig. 13. Transmittance readings are given in Tables 27 and 28. Percent oxides are listed in Table 88.

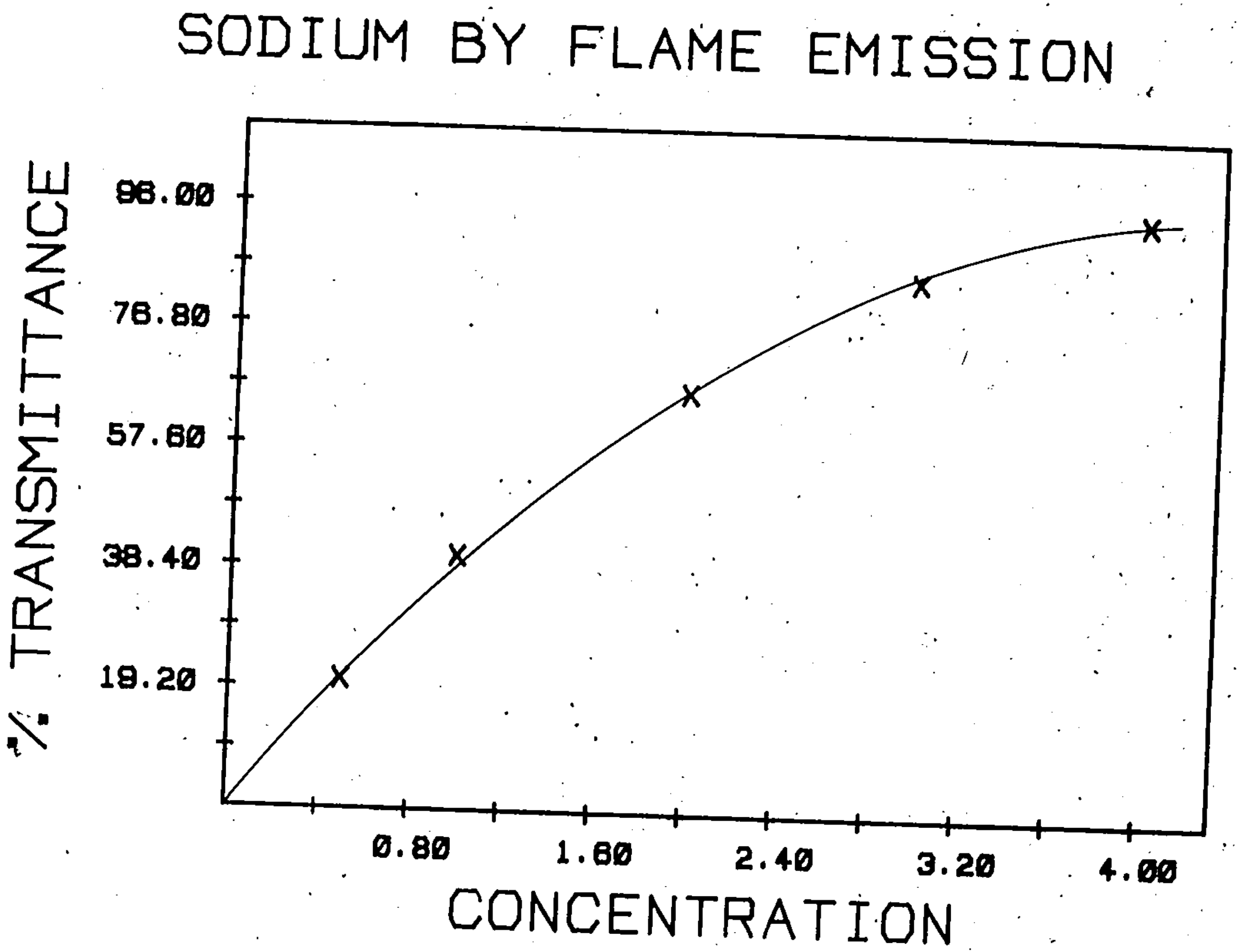


Fig. 13
Calibration curve for sodium by flame emission (µg/ml)

TABLE 27. IONIC STANDARDS FOR
SODIUM BY FLAME EMISSION

WORKING CONDITIONS

WAVELENGTH	589.0 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	0.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	transmittance

CONC. OF STANDARD µg/ml	ACTUAL READING %T	ANALYSIS REPEATS	ZERO CORRECTED %T	AVERAGE READING %T
.5	24.500	6	21.500	20.650
1	44.300	6	45.730	40.550
2	66.000	6	68.070	67.100
3	88.200	6	88.690	85.610

CONCENTRATION DERIVED DIRECTLY
FROM CURVE

TABLE 28
SODIUM BY FLAME EMISSION

ROCK SAMPLE	ACTUAL READING %T	ANALYSIS REPEATS	BLANK & ZERO CORRECTED %T	AVERAGE READING %T
BCR-1	81.400	6	81.280	78.510
GA	85.500	6	83.500	80.730
AC2-2	84.300	6	82.700	79.930
SYN.G2	92.800	6	90.880	88.110
NSX-1	83.300	6	81.800	79.030
NSX-2	81.200	6	80.030	77.260
NSX-3	83.000	6	80.750	77.980
NSX-4	82.000	6	80.580	77.810
NSX-5	83.300	6	81.830	79.060
NSX-6	81.400	6	80.200	77.430
NSX-7	80.200	6	79.280	76.510
NSX-8	80.700	6	79.100	76.330
NSX-9	74.600	6	73.800	71.030

2. Potassium by Flame Emission Spectroscopy

Potassium was determined on solution 'B' by flame emission. Working conditions are listed in Appendix I.

Potassium is partially ionized in the air-acetylene flame (Varian Techtron, 1972). Again, this is not a serious analytical problem at low concentrations. The calibration curve is Fig. 14. Percent transmittance is given in Tables 29 and 30. Percent oxides are listed in Table 91.

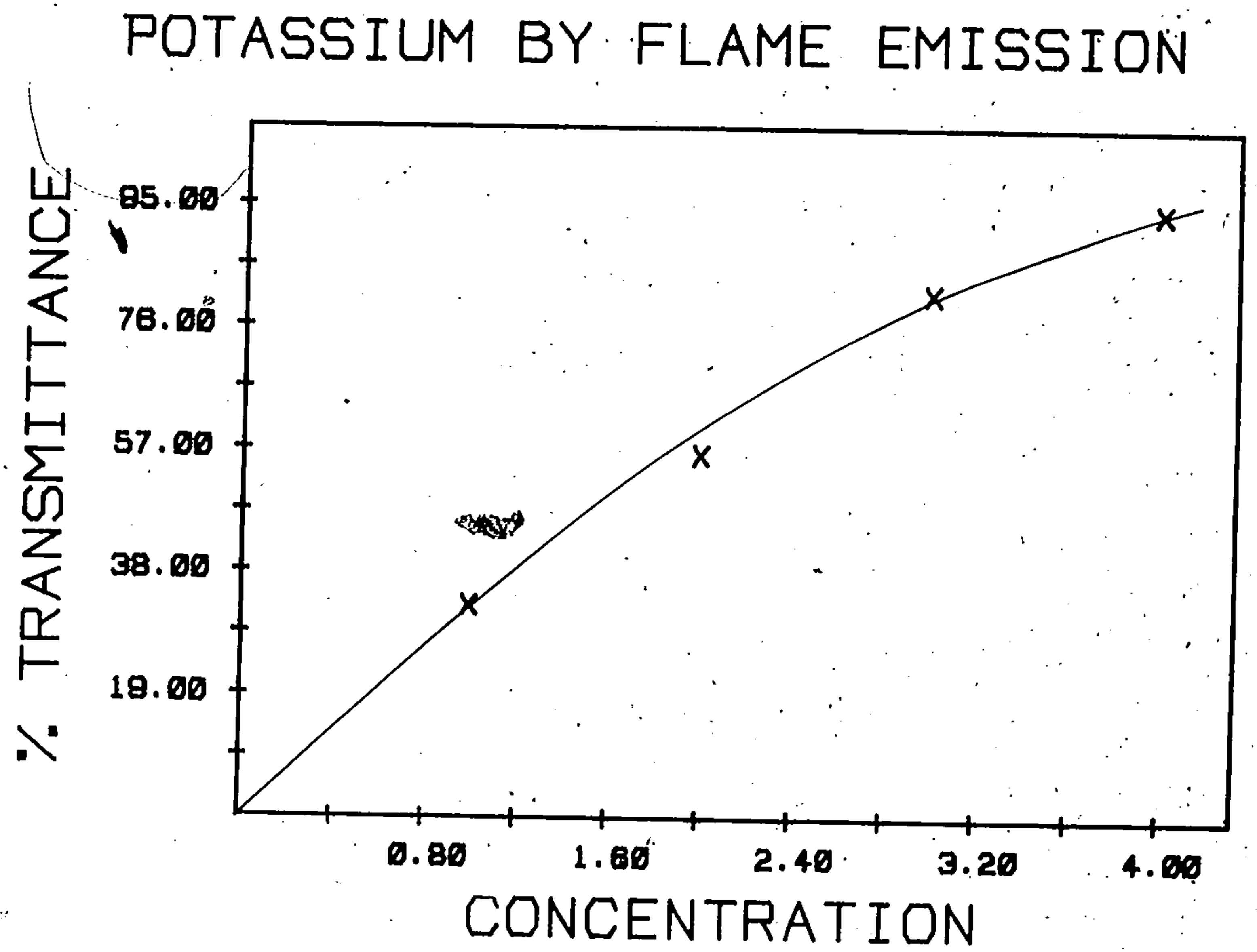


Fig. 14
Calibration curve for potassium by flame emission
(μg/ml)

TABLE 29 . IONIC STANDARDS FOR

POTASSIUM BY FLAME EMISSION

WORKING CONDITIONS

WAVELENGTH	766.5 nm
SLIT WIDTH	.2 nm
LAMP CURRENT	0.0 mA
FUEL	acetylene
FLAME STOICHIOMETRY	oxidizing
SUPPORT GAS	air
MODE	transmittance

CONC. OF STANDARD µg/ml	ACTUAL READING %T	ANALYSIS REPEATS	ZERO CORRECTED %T	AVERAGE READING %T
.5	12.200	6	12.100	12.800
1	34.100	6	34.170	33.090
2	59.000	6	58.900	56.770
3	85.400	6	85.900	81.850
4	97.500	6	98.670	94.840

CONCENTRATION DERIVED DIRECTLY
FROM CURVE

TABLE 30.

POTASSIUM BY FLAME EMISSION

ROCK SAMPLE	ACTUAL READING %T	ANALYSIS REPEATS	BLANK & ZERO CORRECTED %T	AVERAGE READING %T
BCR-1	51.000	6	49.880	49.650
GA	92.900	6	92.100	91.870
AC2-2	92.400	6	91.620	91.390
SYN.G2	106.200	6	104.950	104.720
NSX-1	92.800	6	93.820	93.590
NSX-2	90.600	6	89.730	89.500
NSX-3	90.200	6	89.500	89.270
NSX-4	90.400	6	89.070	88.840
NSX-5	90.500	6	89.270	89.040
NSX-6	89.600	6	88.600	88.370
NSX-7	82.000	6	80.250	80.020
NSX-8	84.300	6	83.670	83.440
NSX-9	77.300	6	75.970	75.740
BLANK	0.300	6	0.000	0.000

C. GRAVIMETRY

a. Theory

Gravimetric analysis, or quantitative analysis by weight, is based on the procedure of isolating and weighing an element or a definite compound of the element in as pure a form as possible (Vogel, 1961). The element to be determined is most commonly precipitated chemically from a solution of the sample; after filtration and/or other suitable treatment, the solid residue is weighed. In gravimetric analysis, a large portion of the determinations involve the transformation of the constituent or compound into a suitable form for weighing. The constituent then can easily be calculated from a knowledge of the formula of the compound and the atomic weights of the constituent elements. The general formula for percent oxide is:

$$\%\ \text{Oxide} = \frac{\text{Gravimetric Factor} \times \text{Wt. of Precipitate} \times 100}{\text{Wt. of Sample in the Aliquot}}$$

where the weight of sample in the aliquot, calculated from the total sample volume is:

$$\text{Wt. of Sample in Aliquot} = \frac{\text{Volume of Aliquot} \times \text{Wt. of Sample}}{\text{Total Volume of Sample}}$$

The gravimetric factor is given by the formula:

$$\text{G. F.} = \frac{\text{Formula Wt. of Oxide to be Determined}}{\text{Formula Wt. of Precipitate}}$$

Calculations were completed on a Wang-System 2200 mini-computer. The program plot for these calculations is listed in Appendix VII.

b. Analytical Procedure

1. Silicon by Gravimetry

Silicon was determined as an 'insoluble' silicate--quinoline silicomolybdate (Vogel, 1961). Solution 'A' was used for this determination.

Sodium hydroxide pellets were added to deter silicon from slowly precipitating out before the formation of the complex. Thymol Blue (0.04%) indicator was added as a visual indicator for pH control. Hydrochloric acid was added slowly, noting the colour change from blue through yellow just to red; excess dilute hydrochloric acid was added to ensure the acidity of the solution. Ammonium molybdate solution was added to produce heteropoly acids. Concentrated hydrochloric acid (50 ml) was added to form a precipitate. Quinoline (50 ml) was added to destroy molybdophosphoric acid produced by the presence of phosphorous.

The suspension was warmed to allow full formation of the coagulate. The solution was quickly cooled before filtering in a sintered glass filtering crucible.

This experiment was performed quickly to minimize the contamination of the solution by the silicon from the glassware. The precipitate was weighed as: $(C_9H_7)_4 \quad H_4(SiO_4 \cdot 12MoO_3)$.

The following formula was used to calculate % SiO_2:

$$\%SiO_2 = \frac{(\text{wt. precipitate} - \text{wt. blank})(\text{vol. aliquot})(\text{gravimetric factor})(100)}{(\text{total volume})(\text{total sample wt.})}$$

where gravimetric factor is:

$$GF = \frac{\text{Mwt }(SiO_2)}{\text{Mwt}\left[(C_9H_7)_4 \quad (H_4\ SiO_4 \cdot 12MoO_3)\right]}$$

$$= 0.0260753$$

2. Aluminum by Gravimetry

Aluminum was determined gravimetrically on solution 'A'. The method is essentially that given by Vogel (1961) with modification. Aluminum reacts with the organic precipitant 8-hydroxyquinoline to form an insoluble chelate, aluminum oxinate, in the pH range 4.5 to 9.5.

$$Al^{3+} + 3C_9H_6(OH)N: \rightleftharpoons Al\left[C_9H_6(O^-)N:\right]_3(s) + 3H^+$$

Eight-hydroxyquinoline (C_9H_7ON) oxinate, forms sparingly soluble derivatives with metallic ions such as aluminum:

$M(C_9H_6ON)_3$ (M being the metallic ion eg., Aluminum).

Urea was used for the homogeneous generation of hydroxide ions:

$$CO(NH_2)_2 + 3H_2O = CO_2 + 2NH_4^+ + 2OH^-$$

Urea was added to produce a dense readily filterable and highly pure precipitate. The solution becomes a colourless, crystalline form, insoluble in water with a melting point of 75°C - 76°C.

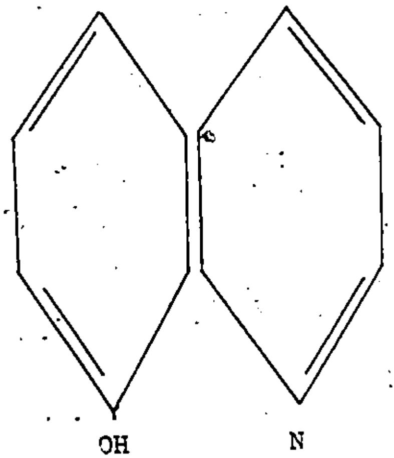


Fig. 15. Bonding structure of 8-hydroxyquinoline (Skoog and West, 1974).

Precipitation is complete when the solution changes from a green-yellow to a pale orange-yellow colour. The precipitate formed was coagulated by warming to 70°C, forming an insoluble complex with aluminum. The 8-hydroxyquinoline decomposes at approximately 80°C. At 70°C, the reaction is quick and below 70°C the 8-hydroxyquinoline precipitates out.

The aluminum co-ordinates with a pair of electrons on nitrogen and on the phenoxide oxygen of each 8-hydroxyquinoline anion. In doing this, three protons are displaced and it assumes a co-ordination number of 6. Precipitation is complete as long as pH does not fall below 4.5. This is an organic precipitant and therefore a low temperature has to be used to dry it.

Hydrochloric acid was added during decomposition so that hydrogen ions would become available and no hydroxide compounds precipitate. The acid is also added so that $Al + 3OH$ will not complex as $Al(OH)_3$ and lose some Al in the precipitate. The reaction occurs within a pH range of 4 to 5.

The addition of acetic acid prevents precipitation when 8-hydroxyquinoline is added to the aluminum. The acetic acid gradually evaporated and aluminum oxinate precipitated slowly from a homogeneous solution. Enough acetic acid remained in solution to prevent excess 8-hydroxyquinoline from co-precipitating.

The ammonium acetate is added to act as buffer, to raise the pH to 4.5 to allow a reaction to occur whereby the oxygen and nitrogen bonds to aluminum.

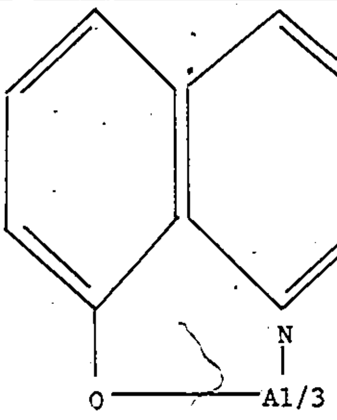


Fig. 16. Bonding a structure of 8-hydroxyquinoline to aluminum (Skoog and West, 1974).

The solution was left standing at room temperature to stabilize before filtering. The precipitate may adhere to the beaker walls, so it had to be loosened with a rubber policeman. The beakers were covered with watch-glasses to maintain some of the acetic acid in solution from totally evaporating, since some had to remain to keep the 8-hydroxyquinoline from precipitating.

The dry glass crucibles were brought to constant weight before filtering and at the final weighing. Constant weight was obtained by cooling the crucibles in a dessicator so that the precipitate would not absorb water.

The crucibles with the precipitate had to be handled with tissue or gloves to minimize transfer of heat and moisture to the crucibles before weighing.

The precipitate was weighed as $Al(C_9H_6ON)_3$: the gravimetric factor can be calculated using the formula:

$$GF = \frac{\text{Molecular Wt. of } (Al_2O_3)}{2 \times \text{Molecular Wt. of } Al(C_9H_6ON)_3}$$

$$= 0.1109614$$

Concentrations as percent oxide are in Table 57.

TABLE 31.

GRAVIMETRIC DETERMINATION OF SILICON

ROCK SAMPLE	WEIGHT OF SAMPLE g	TOTAL VOLUME ml	ALIQUOT VOLUME ml	WEIGHT IN ALIQUOT g
SiO_2-Pure	0.1000	500	20	0.0040
SiO_2-Pure	0.1000	500	20	0.0040
GA (1)	0.1000	500	20	0.0040
GA (2)	0.1000	500	20	0.0040
NSX-1	0.1012	500	20	0.0040
NSX-2	0.1110	500	20	0.0044
NSX-3	0.1044	500	20	0.0041
NSX-4	0.1001	500	20	0.0040
NSX-5	0.1017	500	20	0.0040
NSX-6	0.1260	500	20	0.0050
NSX-7	0.1014	500	20	0.0040

TABLE 32.

GRAVIMETRIC DETERMINATION OF ALUMINUM

ROCK SAMPLE	WEIGHT OF SAMPLE g	TOTAL VOLUME ml	ALIQUOT VOLUME ml	WEIGHT IN ALIQUOT g
AL 80 ppm	0.5000	500	20	0.0200
SYN.G2	0.5000	500	20	0.0200
GA	0.1000	500	20	0.0040
NSX-1	0.1012	500	20	0.0040
NSX-2	0.1110	500	20	0.0044
NSX-3	0.1044	500	20	0.0041
NSX-4	0.1001	500	20	0.0040
NSX-5	0.1017	500	20	0.0040
NSX-6	0.1260	500	20	0.0050
NSX-7	0.1014	500	20	0.0040

D. TITRATION

a. Theory

Titration is a technique for determining the amount of a substance by measuring the quantity of a reagent required to react completely with a sample containing that substance (Skoog and West, 1974). The concentration of the unknown sample is obtained by comparing the unknown to a standard solution which is a reagent of exactly known composition.

The equivalence point (stoichiometric completion of the reaction) is the point wherein the standard solution becomes chemically equivalent to the substance with which it must react. It is the theoretical point when the chemical reaction becomes complete. When a distinct visible change occurs, it is the end point. The difference between the end point and the theoretical equivalence point is called the titration error.

Photometric titration is the photoelectric registration of the distinct colour change at end point. The constituent to be analyzed is a wavelength absorbing medium. The change in absorbance/transmittance of a solution is related to the change in concentration of the light-absorbing constituent. The colour change is related to the amount of light able to pass through the solution. A photocell registers the intensity of light as electric pulses. The electrical pulses are presented on the photo-extinction scale of the external galvanometer (Evans Electroselenium Limited, n.d.). Best performance of most photometers is when readings on samples fall in the range between approximately 10% to 80% transmittance.

The analytical wavelength is produced by a filter. The best filter is one which produces the best spread of readings between a blank and a standard. The choice of filter also corresponds to a visual colour for the light beam which is complementary to that of the solution. The readings are plotted as percent reading against volume of titrant. The intersection of two straight lines on the titration curve establishes the end-point value.

Various texts extensively describe the principles of titration (eg. Vogel, 1961; Kenner and O'Brian, 1971; Skoog and West, 1971 and 1974; Willard et al., 1965).

Calculations were done on the Wang-System 2200 mini-computer. The program is listed in Appendix VI.

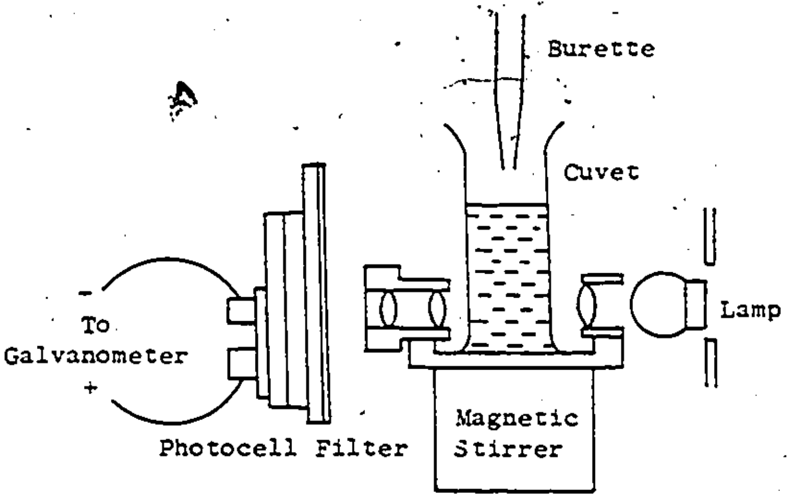


Fig. 17
Single cell photoelectric photometer
(Adapted from Evans Electroselenium Limited, n.d.)

b. Analytical Procedure

1. Total Iron by Titration

Total iron was determined by an oxidation-reduction titration on solution 'B' with potassium dichromate ($K_2Cr_2O_7$), 0.01392 normal, as the oxydizing agent. It does not oxidize the chloride ion made available by the addition of hydrochloric acid. The product stays as Cr^{3+} ions since no other stable oxidation state exists between $Cr_2O_7^{2-}$ and Cr^{3+}. Half-cell reaction in acid solution is

$$Cr_2O_7^{2-} + 14H^{+} + 6e \longrightarrow 2Cr^{3+} + 7H_2O$$

Before titration, 10 ml of HCl was added to the 20 ml aliquot, to ensure reduction of iron to iron II.

$$Fe_2O_3 + 6H^{+}_{(HCl)} \longrightarrow 2Fe^{3+} + 3H_2O$$

The iron is present as a chloro-complex (dark brown), and consequently used as a reduction indicator. A stannous chloride solution (10% w/v) was added drop-wise until the yellow solution turned clear.

$$Sn\,Cl_2.2H_2O + HCl \longrightarrow Sn^{2+} + ----.$$

The iron was reduced to the ferrous state by the reaction with tin II (stannous) chloride. After the reduction, speed was necessary in order to prevent a negative error by oxidation of ferrous iron in the acid solution by oxygen in the air.

To prevent pre-precipitation, the solution was kept warm so that the iron remained in solution (reduction).

$$\underset{(excess)}{Sn^{2+}} + \underset{(yellow)}{2Fe^{3+}} \longrightarrow Sn^{4+} + 2Fe^{2+}$$
$$(colourless \longrightarrow light\ green)$$

Iron and tin are present as chloro-complexes with the following reaction:

$$SnCl_4^{2-} + 2FeCl_4^{-} \longrightarrow SnCl_6^{2-} + 2Fe^{2+} + 6Cl^{-}$$

The $FeCl_4^-$ has a yellow colour (dark brown concentrate) while Fe^{2+} is a pale green colour and colourless in the reduced solution.

Completion was marked by the disappearance of the yellow colour. Near the end point, the reaction was slow and the stannous chloride had to be added drop-wise. To guarantee that all iron was reduced to the ferrous state, two drops of stannous chloride were added in excess. But excess stannous chloride causes errors in later steps, so the solution must be diluted before titration.

The potassium chloride formed during titration reacts with stannous tin, therefore the excess stannous chloride was removed before titration by the addition of mercury(II)chloride. On addition of mercury (II), mercury (I) chloride forms an insoluble substance which will separate from the solution as a silky, finely-divided precipitate.

$$Sn^{2+} + Hg^{2+} \rightleftharpoons Hg_2Cl_2\downarrow + Sn^{4+}$$

The mercuric chloride was added quickly to prevent the reaction: $Sn^{+2} + Hg_2^{2+} \longrightarrow 2Hg^o + Sn^{4+}$, and the H^o from oxidizing, producing high results.

If too much stannous ions are added in the reduction step, mercuric chloride reacts to form elemental mercury which in turn reacts with potassium dichromate, causing an error. Within three minutes, a finely divided, shiny white precipitate should form after the addition of mercuric chloride.

Absence of a precipitate indicates that the amount of stannous chloride was low and that all the ferric iron was not reduced. A heavy, white to grey precipitate is an indication that too much stannous chloride was added; therefore, solution should be discarded.

Immediately after the formation of the mercuric chloride precipitate, sulfuric acid, phosphoric acid and the diphenylamine indicator were added quickly to prevent air oxidation of the ferrous ion.

Sulfuric acid (5 ml of conc.) was added to ensure correct acidity and provide hydrogen ions since the indicator works better in the presence of sulfate ions.

Phosphoric acid (5 ml of conc.) was added to prevent a premature colour change before the equivalence point, to act as a colour clarifier and reduce interference. Phosphoric acid forms a colourless complex $Fe(H_2PO_4)_6^{-3}$ with ferric ions as they are produced during the reaction. The formation of the colourless complex prevents the tan colour of the $FeCl_4^-$ from obscuring the end point.

The complex also served to depress the potential of the ferric-ferrous half-cell and keep the potential at a lower value before the end point. This caused a sharper potential break at the end point.

$$E = E_o + .059 \log \frac{Fe^{3+}}{Fe^{2+}}$$ (concentration lowered by complexing)

Diphenylamine sulfanate (8 ml) was the redox indicator used. The indicator itself oxidized from colourless to a lavender shade. The presence of the complexed ferric ions and the green colour of the chromic ions combined with the indicator colour to form a grey to black colour just before the end point. The end point was a light purple colour which lasted for thirty seconds. Blank runs were impossible since the colour change was not sharp in the absence of iron.

$$K_2Cr_2O_7 + 6Fe^{2+} + 7H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 6Fe^{3+} + 3SO_4^{2+} + 7H_2O$$

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$

The above method is that of Maxwell (1968) with modification. The percent total iron (as Fe_2O_3) was calculated using the formula:

$$\% \, Fe_2O_3(T) = \frac{\text{Vol titrant } (K_2Cr_2O_7)}{1000} \times \text{Normality} \times \frac{159.08}{2} \times \frac{100}{\text{Sample Wt. (g)}}$$

where Normality was 0.01392.

Concentration of Fe_2O_3 as percent oxide is given in Table 66.

2. Calcium by Complexiometric Titration.

Calcium was determined on solution 'B' by an EDTA titration using an EEL photometric titrator.

EDTA is ethylenediamine tetra acetic acid disodium salt.

$$(Na^{+}OOCCH_2^{-})\ (HOOCCH_2)\ N-CH_2-CH_2-N(CH_2COOH)(CH_2COO^{-}Na^{+})$$

It forms a soluble, stable chelate and complexes with metal ions to form a 1:1 metal complex. The acid (H_4Y) is insoluble in water and is prepared as the disodium salt (Na_2H_2Y). EDTA has donor nitrogen and oxygen atoms which form as many as six five-membered chelate rings.

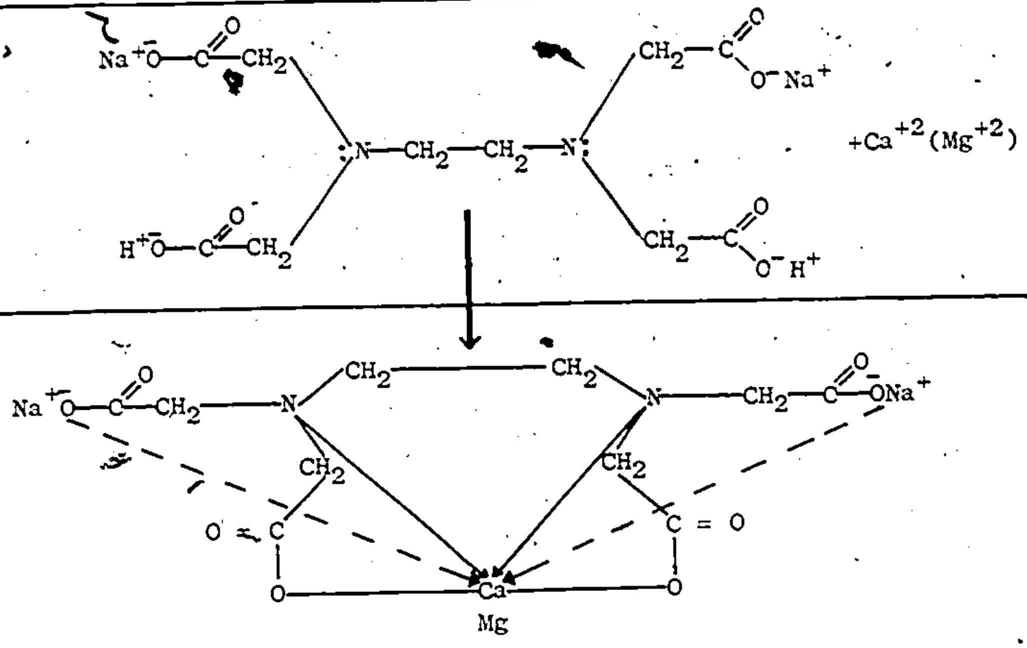


Fig. 18 Formation of five-membered chelate ring (Adapted from Skoog and West, 1974).

EDTA was standardized against the primary standard $CaCO_3$, treated with HCl:

$$CaCO_3 + 2HCl \longrightarrow Ca^{+2} + CO_2(g) + H_2O + 2Cl^{-}$$

The solution was buffered with KOH to 12.5 for quantitative reaction. The buffered solution consumed liberated H^{+} ions and prevented a reaction with other ions.

A calcium selective indicator was used; Patton-Reader's reagent--HHSNN (Perlman, 1966), in preference to other metallic ions, and thus indicated a colour change when the calcium was depleted by the EDTA complex.

Interferences were overcome by adding hydroxylamine hydrochloride (10%w/v) which reduced some of the metals (particularly Fe) to a lower valence state (Maxwell, 1968). Triethanolamine (20%w/v) complexed with iron and titanium. Aluminum interferences were eliminated by buffering the solution at a pH of 12.5 with potassium hydroxide which precipitated aluminum as the hydroxide. Other interferences were eliminated by the selective indicator.

The titrations were done using an EEL photoelectric titrator with a blue-green filter (No. 603) giving the end point. Sample solution (15 ml) was titrated against 0.0018 M EDTA. The graphical solution to the end point is shown in Figs. 19 to 24.

The calculations were completed on Wang-System 2200 mini-computer. The program for this plot is listed in Appendix VI. Percent oxides and the formula for the calculations are in Table. 76. Percent oxide was calculated by using the formula:

$$\% \text{ CaO} = \frac{\text{Vol. of Titrant} \times (F)/\text{Volume of Solution}/\text{Vol. Aliquot} \times 100}{\text{Weight of Sample}}$$

where (F) = 0.0001020 g of CaO/ml of EDTA

Fig. 19. Calcium titration,

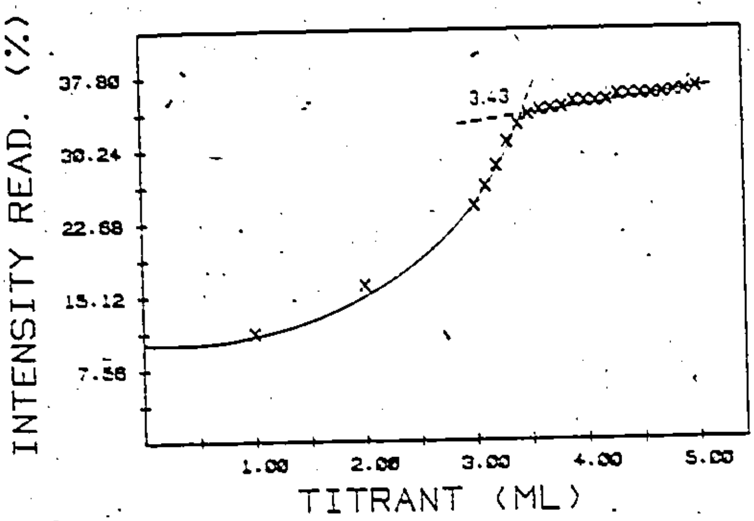


Fig. 20. Calcium titration graph for

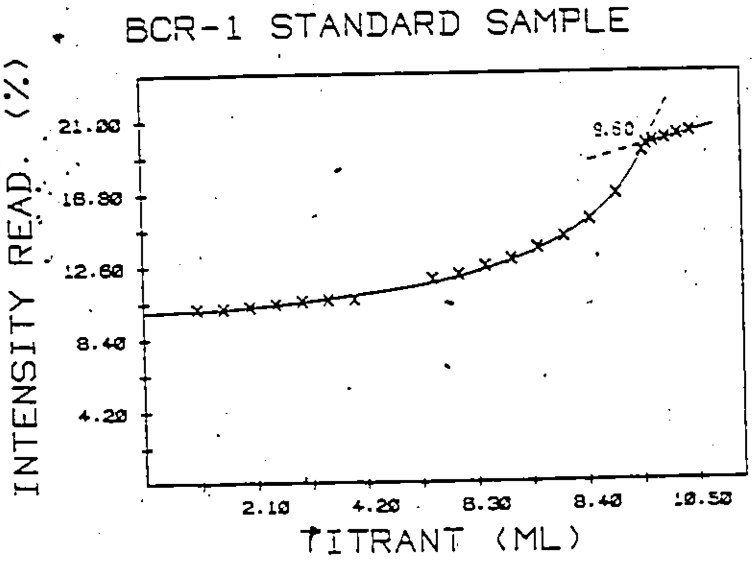


Fig. 21. Calcium titration graph for

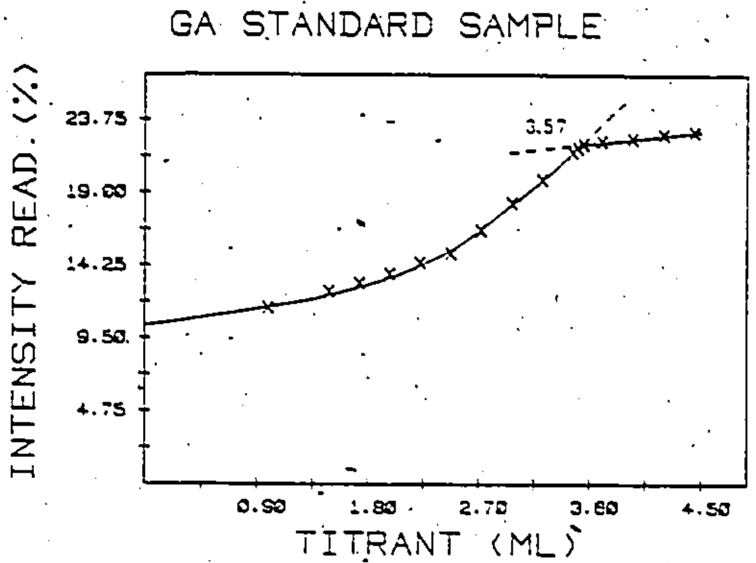


Fig. 22. Calcium titration graph for

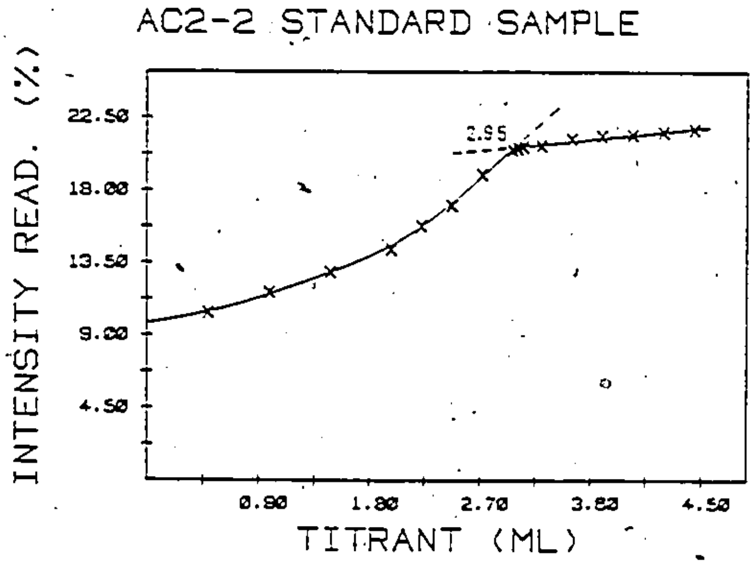


Fig. 23. Calcium titration graph for

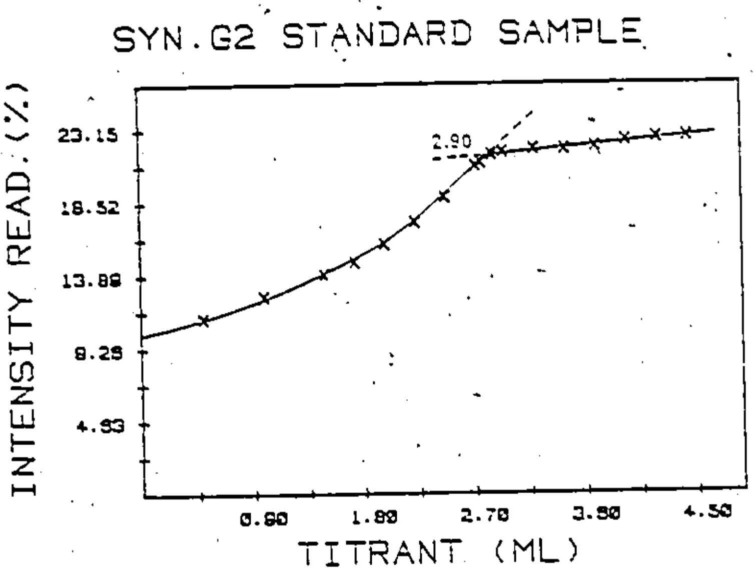
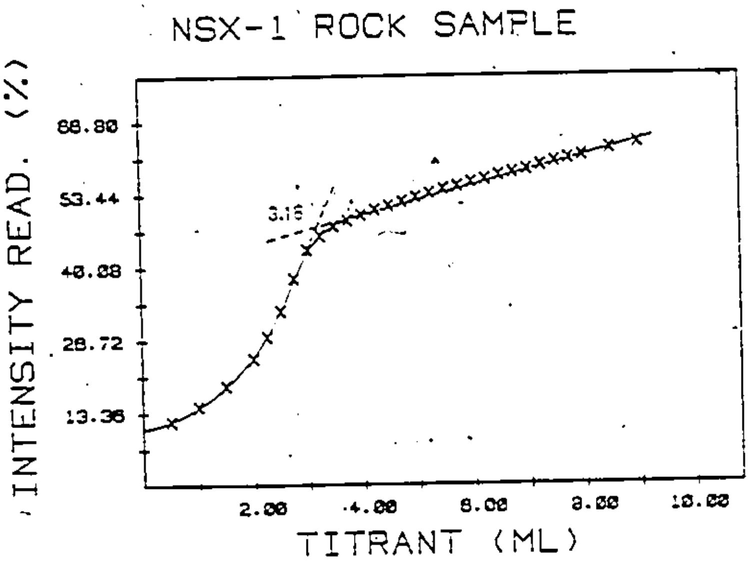


Fig. 24 Calcium titration graph for



3. Magnesium by Complexiometric Titration

(i) Theory

The theory of magnesium complexiometric titration is similar to that of calcium titration, except that during the titration with EDTA, a weak calcium complex forms first. Then any free magnesium present forms a strong magnesium EDTA chelate.

$$M^{++} + H_2Y^{=} \rightleftharpoons MY^{=} + 2H^{+}$$

When these reactions are complete, a drop of EDTA solution in 'excess' extracts the magnesium from the magnesium-dye complex, liberating the free dye (green colour). The colour change at the end point is from a light red to a bright green.

The EEL titrator was used for photo-electric assessment of the end point of chemical titrations. The solution sample was titrated against EDTA using a complementary optical filter and a suitable indicator. The type of filter selected had to be compatable with the end colour of the used indicator.

Readings were shown on the photo-extinction scale of the external galvanometer. The change in the galvanometer readings were recorded for each equal addition of titrant. The galvanometer response was plotted as volume of EDTA against percent transmittance.

The end point for calcium titration is the second inflection point on the curve and in cases where the end point was vaguely defined, the average change per unit of titrant against volume of titrant added was plotted (Figs. 25 to 34).

The end point is the first positive change of the curve after the second inflection. This point should coincide with the point where the second deflection ends and a constant slope or almost constant results begin. This point indicates a constant change in colour which may be regarded as the 'stoichiometric point'.

The tungsten lamp emits its major portion of energy near the infrared region. Only 15% falls within the visible region.

The selenium photocell increases the relative response sensitivity, being greatest for the green through yellow wavelength. The strongest wavelength of the Fraunhofer Lines for magnesium are 5183.621Å and for calcium, 4307.74Å, according to the sun's spectrum (Weast, 1975). The wavelength for the colour green is 5200Å with upper and lower limits being 5750Å and 4912Å, respectively.

The indicator was a mixture of Phthalein Purple and Methyl Red. The maximum wavelength of the indicator is 5300Å with absorbance of 3000 above pH of 7, and with the addition of Methyl Red the sensitivity and colour span was extended to a higher wavelength. The filter chosen was specially made for this titration and was complimentary to Phthalein Purple. The filter is composed of a thin orange film sandwiched between two layers of green polarized plastic sheets.

Eriochrome Black T was tested on a calcium and magnesium (50 µg/ml) standard and a calcium and magnesium (1000 µg/ml). Values obtained were calculated values. Shapiro (1959) found that EDTA titrations of small amounts of magnesium (0.01-2%) with high calcium, were unobtainable and proposed a rapid photometric determination with Thiazone Yellow for low magnesium rocks.

Metals such as iron, titanium, aluminum, copper, nickel, manganese and cesium mask the end point by oxidation or blockage. Interference by these metals may be lowered by adding potassium cyanide for copper and nickel, triethanolamine for iron and aluminum, and hydorxylamine for reducing oxidants.

Iron and aluminum (1000 μg/ml) were added to the calcium and magnesium (1000 μg/ml) and titrated with EDTA. Masking solution and Erio-T indicator were also added. The end point was vaguely definable. The procedure was repeated using the calcium and magnesium (50 μg/ml) and the end point did not appear.

The same procedure was followed using Phthalein Purple mixed with Methyl Red. The results were excellent, the colour change was from a light red to a distinct bright green, at the end point. This is an innovation, developed in this study. The results from BCR-1, AC2-2, GA, Synthetic G2, and NSX 1-9 were examined and they are in close proximity to literature values and values obtained by other methods.

The above method was a modification based on Maxwell, 1968; Skoog and West, 1974; Vogel, 1961; Shapiro, 1959; Kenner and O'Brian, 1971. I believe this is a significant inovation in the determination of magnesium by complexiometric titration and it is planned to report this in an appropriate scientific journal.

Concentrations as percent oxide are in Table 82. The following is the detailed procedure:

(ii) Procedure

Magnesium oxide is determined by difference as $\left[(MgO + CaO) - (CaO) \right]$.

Reagents

1. EDTA solution (0.002 M). Dissolve 1.4925 g disodium salt with triple-distilled water (2 litres).

2. Hydroxylamine hydrochloride solution (10%). Dissolve 10 g to 100 ml with triple-distilled water.

3. Triethanolamine and potassium cyanide. Dissolve 64 g of KCN in 600 ml of triple-distilled water. Add 400 ml of triethanolamine.

4. Ammonia ammonium chloride buffer. Dissolve 68 g of NH_4Cl in 200

ml of triple-distilled water, add 570 ml of NH_4OH. Dilute to 1 litre with triple-distilled water.

5. Phthalein Purple indicator (Phthalein complexore). Mix thoroughly by grinding in porcelain mortar: 0.1 g of Phthalein Purple, 0.075 g of Napthol Green-B, 0.005 g of Methyl Red and 10 g of KCl.

Method

1. Pipet a suitable aliquot of solution 'B' (15 ml) into a 60-ml EEL reaction vessel. Drop in a miniature bar magnet.
2. Add 2 ml of hydroxylamine hydrochloride solution and stir.
3. Add 10 ml of ammonia ammonium chloride buffer to obtain a pH >10.5.
4. Add 5 ml of metal masking reagent (triethanolamine and potassium cyanide) and stir.
5. Add approximately 0.5 mg of Phthalein Purple, i.e. until the galvanometer reading drops to ten percent transmittance with polarized green filter, as described above.
6. Titrate against 0.002 M EDTA, using the EEL colourimetric titrator with the green filter.
7. Record titer and galvanometer reading every .25 ml, until colour change is imminent. Continue recording every .05 ml until the colour change is complete and the galvanometer indicates an almost constant response.

8(a) End point is deduced from a graph of the volume of EDTA titrant against percent transmittance.

(b) The end point is the second inflection of the curve but for vague end points or more precise work, end point may also be deduced by plotting average change per unit of titrant added (galvanometer reading) against volume of titrant added. The first upward deflection, after the largest per unit average change, indicates the equivalence point (eg. Fig. 25). This should coincide with the inflection point deduced from interpretation method 8(a).

9. Standardization of EDTA: 5 ml of a standard solution (50 ppm each of calcium and magnesium). A titer of approx 4 ml should result. Calculate a factor, x, for 1 ml of EDTA $\equiv$ x grams of magnesium.

Calculations:

$$1 \text{ ml of } 0.01 \text{ M EDTA} \equiv 0.0002432 \text{ g Mg (Vogel, 1961)}$$

$$1 \text{ ml of } 0.0018453 \text{ M EDTA} \equiv \frac{0.0002432 \times 0.0018453 \times 1.6579 \text{ g MgO}}{0.01}$$

$$= 0.0000742 \text{ g MgO}$$

$$\% \text{ MgO} = \frac{\left[\text{Vol. (CaO + MgO)} - \text{Vol. (CaO)}\right] \times 0.0000742 \times \frac{\text{Samp. Vol.}}{\text{Aliquot}} \times 100}{\text{Sample Weight}}$$

Fig. 25. Titration graph for

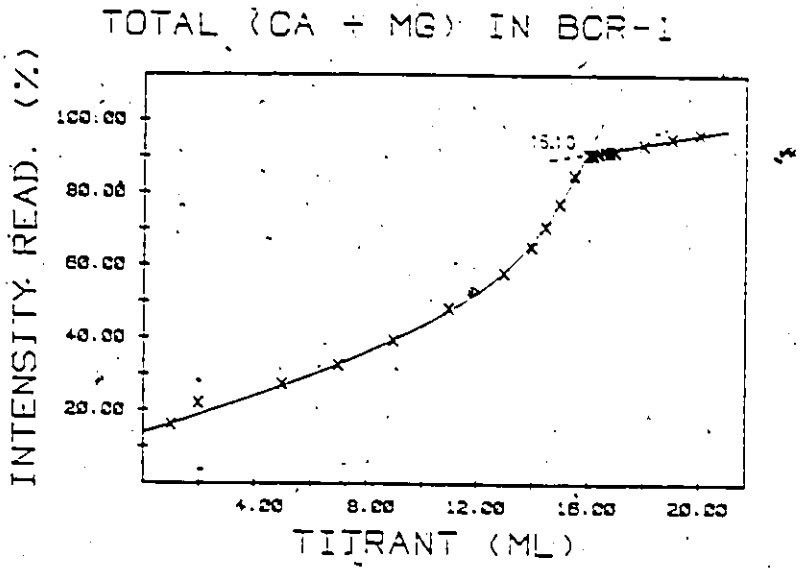


Fig. 26. Titration graph (average change per unit) for

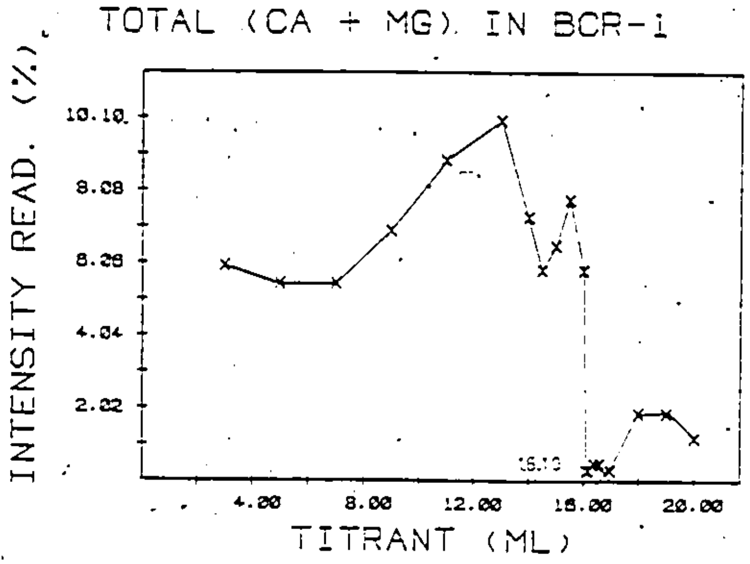


Fig. 27 . Titration graph for

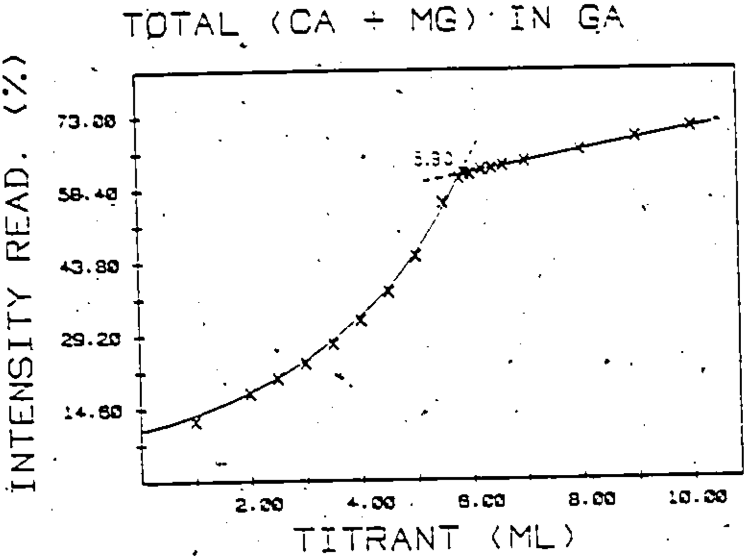


Fig. 28 Titration graph (average change per unit) for

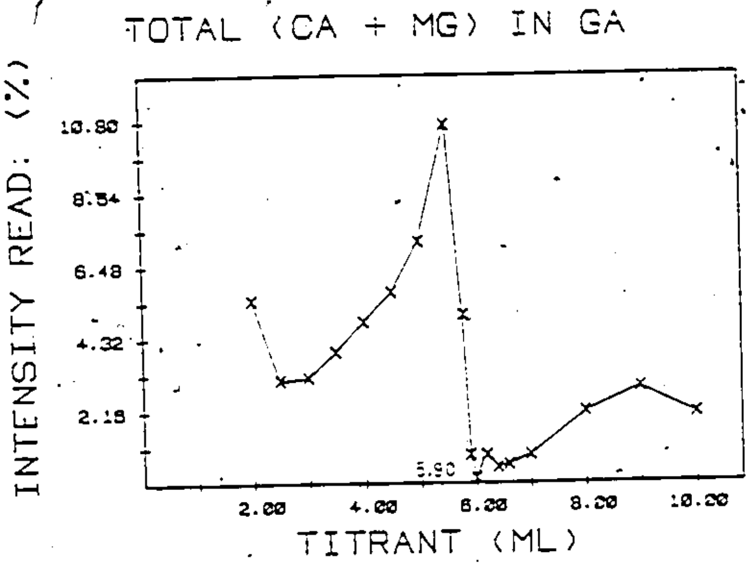


Fig. 29 . Titration graph for

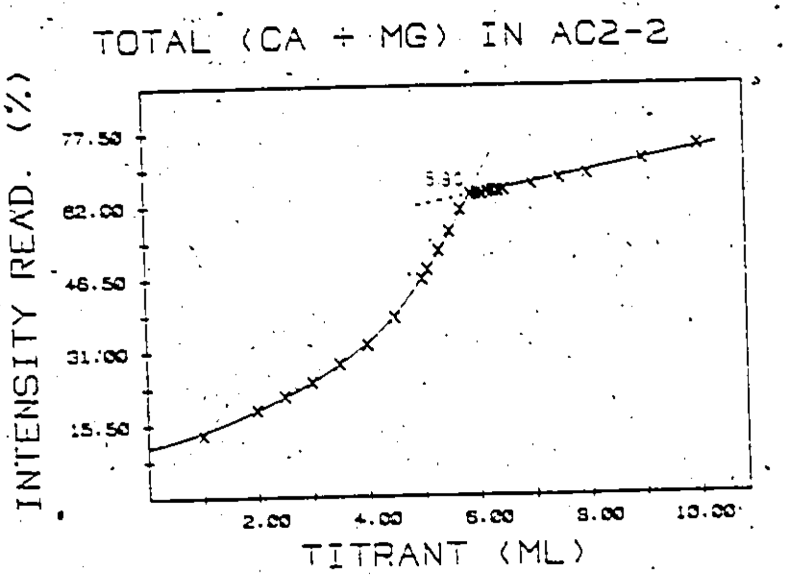


Fig. 30. Titration graph (average change per unit) for

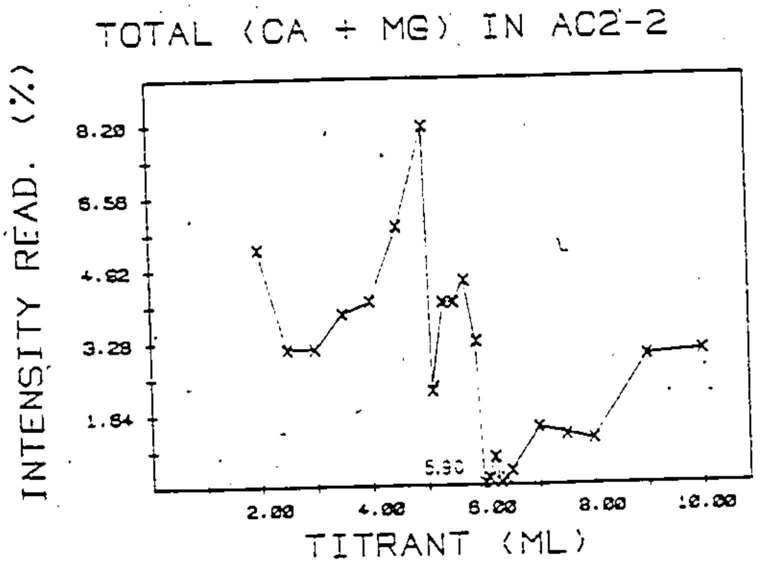


Fig. 31 Titration graph for

TOTAL (CA ÷ MG) IN SYN.G2

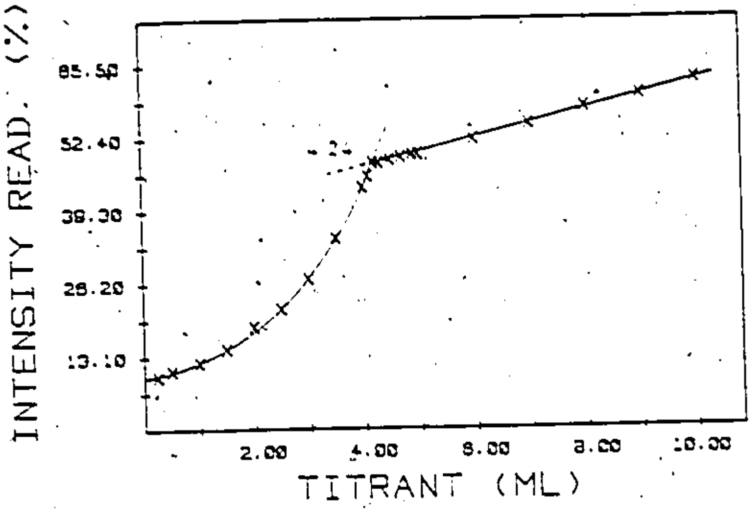


Fig. 32 .Titration graph (average change per unit) for

TOTAL (CA ÷ MG) IN SYN.G2

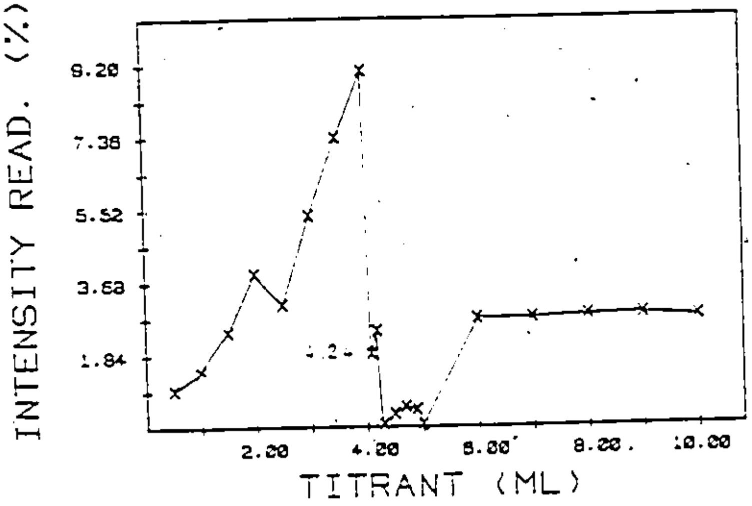


Fig. 33. Titration graph for

TOTAL (CA ÷ MG) IN NSX-5

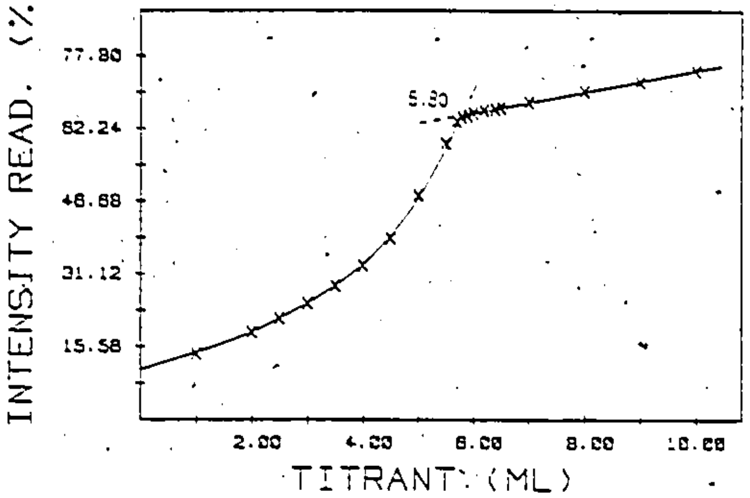
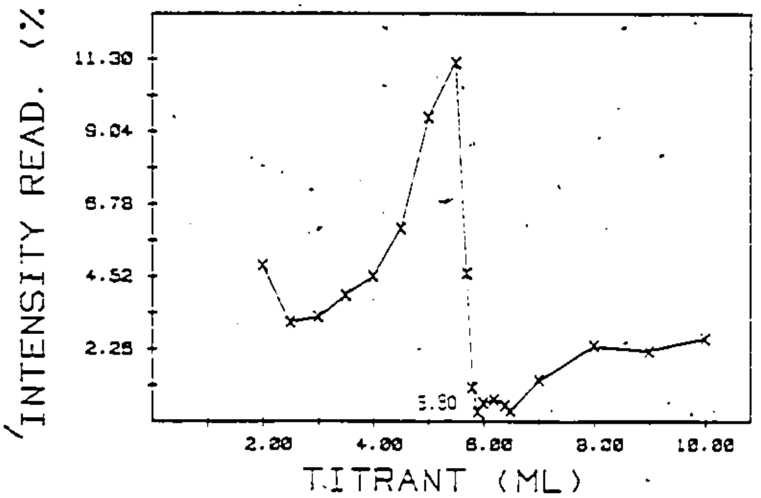


Fig. 34. Titration graph (average change per unit) for

TOTAL (CA ÷ MG) IN NSX-5



E. SPECTROPHOTOMETRY

a. Theory

Spectrophotometric methods are based on the absorption of electromagnetic radiation. Electromagnetic energy is transferred to the constituents of the sample solution, resulting in the atoms being promoted from their ground state to a higher, excited state. As is the case with atomic absorption, there is a relationship between excited- and ground-state atoms. Atoms in the ground state absorb energy which corresponds to their own spectral lines.

When a beam of monochromatic radiation passes through a sample solution of an absorbing species, the radiant power of the beam is progressively reduced, as part of the energy is absorbed by the particles of that species. Decrease of intensity is dependant upon the concentration of the substance responsible for the absorption and upon the length of the path travelled by the beam (Skoog and West, 1974). The above relationships are expressed by Beer's Law, which has been discussed in the section on Atomic Absorption Spectroscopy.

There are two difficulties involved: (a) true absorption curves cannot be determined and (b) Beer's Law is not always followed, therefore the apparent absorptivity will vary with both concentration and instruments. The above difficulties are overcome by using a monochromator capable of isolating a distinct narrow band of wavelengths.

The instrument 'Spectronic 20' is extensively used for the visible region, 340nm to 625nm (it is capable of extension to 950mm by changing the phototube). This is a single-beam instrument using a vacuum phototube as detector.

The Spectronic-70 instrument was used in this thesis (Fig. 35). It is similar to the Spectronic-20 without the reference phototube and mask.

All calculations were performed on the Wang-System 2200 mini-computer. The program is listed in Appendix V. The percent oxides were derived from the general formula:

$$\% \text{ Oxide} = \frac{\text{Conc. x Vt x Vd x CF x } 10^{-4}}{\text{Wt. of Sample x Va}}$$

where Conc. is the concentration of the analyte in µg/ml; Vt is the total volume of the sample solution in ml; Vd is the diluted volume in ml; Va is the aliquot volume in ml and CF is the conversion factor (Appendix IV).

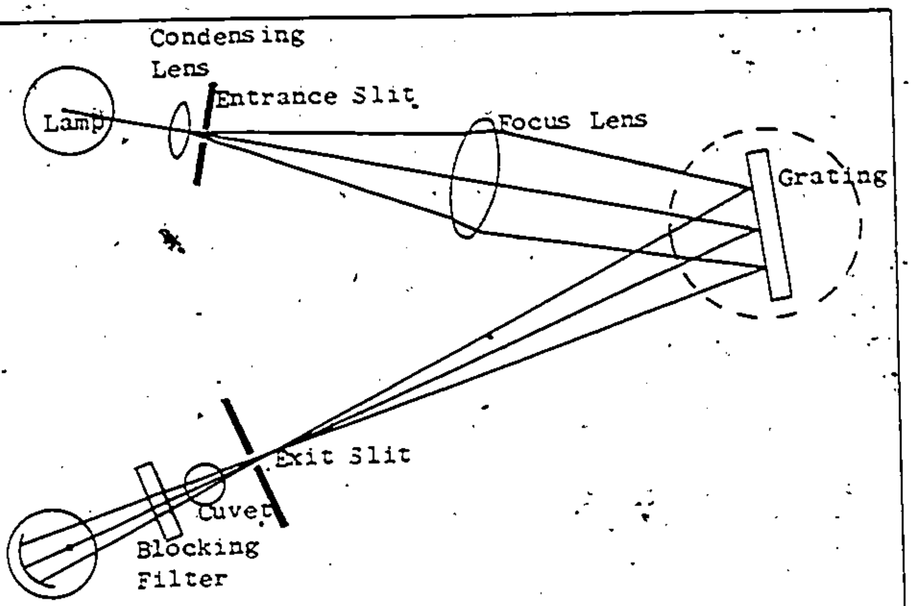


Fig. 35
Optical Diagram of the Bausch & Lomb Spectronic-70 (Ewing, 1969)

b. Analytical Procedure

1. Silicon by Spectrophotometry

Silicon was determined on solution 'A'. Solution 'B' could not be used because silicon escaped during the dissolution; solution 'JA' also could not be used because the boric acid interfered with colour development.

Dissolved silicic acid reacted with a molybdate solution in an acid medium, resulting in a yellow silicomolybdic complex: $Si(Mo_{12}O_{40})^{-4}$ (Tetley, 1974). Measurements were made on the reduced complex, molybdenum blue. Reduction was accomplished by the addition of sodium sulfite in 1-ammino-2-naphthol-4-sulfonic acid (Vogel, 1961). A wavelength of 650 nm was used for maximum absorbance. The molybdenum blue complex required time and stability to form; therefore, the solutions were allowed to stand overnight.

Phosphorous interfered by developing a phosphomolybdate complex. The addition of (10%) tartaric acid reduced that interference. The tartaric acid had to be added after the silicomolybdate complex formed and before the reduction to the molybdenum blue complex.

An aliquot of the concentrated solution 'A' (10 ml) was transferred to a 200-ml volumetric flask. To this was added 25 ml of sodium fluoride, 4 ml of ammonium molybdate and 50 ml of triple-distilled water. The mixture was swirled and allowed to stand for 10 min. To obtain the proper pH, 10 ml of tartaric acid was added. Finally, 3 ml of reducing solution were added and the flask was made up to volume with triple-distilled water.

The calibration graph is Fig. 36. Absorbance readings are in Tables 33 and 34. Concentrations as percent oxide are listed in Table 46. Since Beer's Law gives a straight line, only two points were required for calibration of ionic standards.

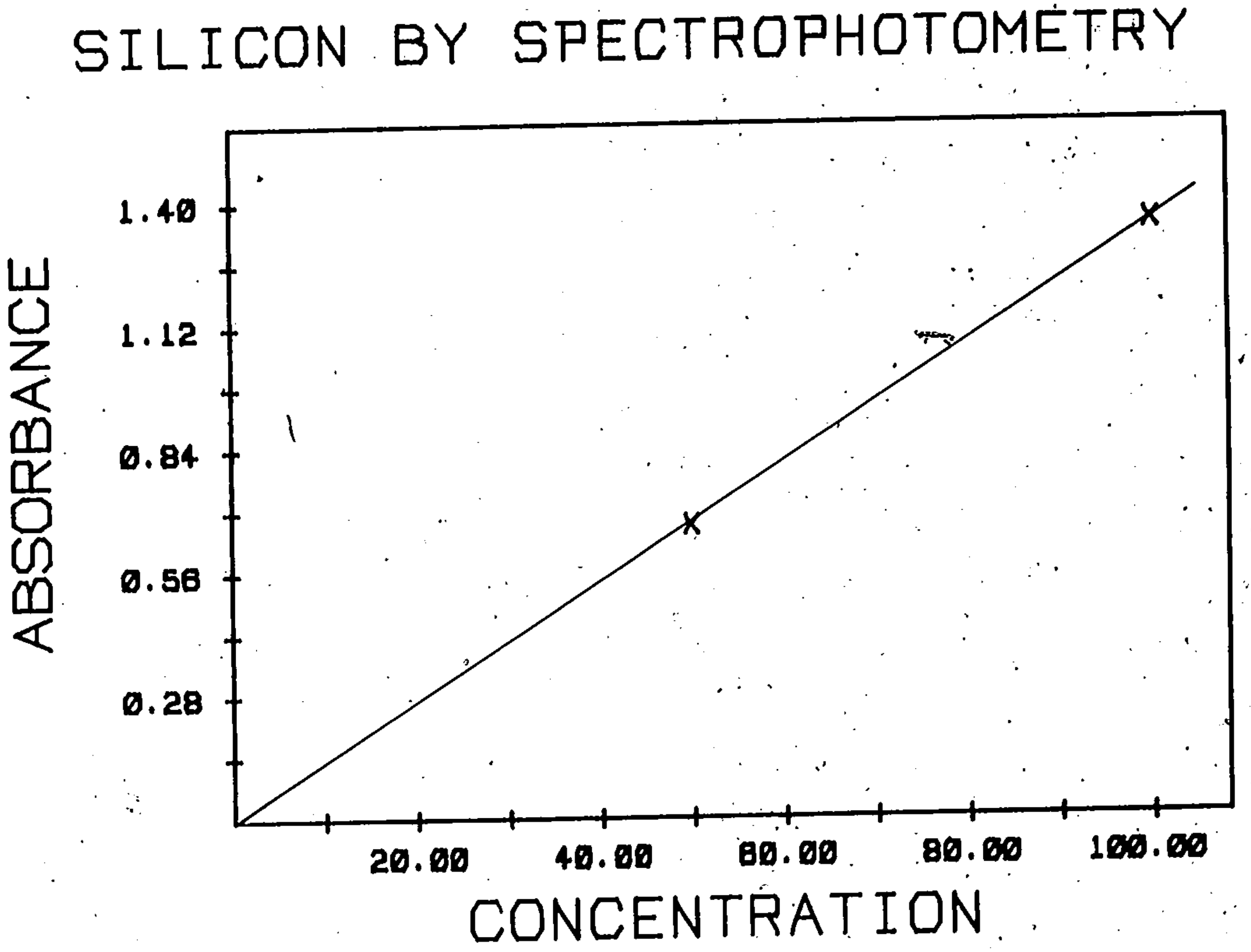


Fig. 36
Calibration curve for silicon (on solution 'A') by spectrophotometry
(μg/ml)

TABLE 33. IONIC STANDARDS FOR SILICON BY SPECTROPHOTOMETRY

WORKING CONDITIONS	
INSTRUMENT	SPECTRONIC 70
MAKE	BAUSCH & LOMB
WAVELENGTH	650.0 nm
MODE	ABSORBANCE

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
50	0.705	3	0.703	0.670
100	1.390	3	1.390	1.357

THE SLOPE IS 0.0135
THE INTERCEPT IS -0.0040
THE CORRELATION COEFFICIENT IS 1.00000

TABLE 34.

SILICON IN SOLUTION 'A' BY SPECTROPHOTOMETRY

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
GA	0.933	3	0.900	0.900
SiO -Pure	1.233	3	1.230	1.230
NSX-1	0.927	3	0.894	0.894
NSX-2	1.020	3	0.987	0.987
NSX-3	0.950	3	0.917	0.917
NSX-4	0.923	3	0.890	0.890
NSX-5	0.937	3	0.904	0.904
NSX-6	1.150	3	1.117	1.117
NSX-7	0.923	3	0.890	0.890
BLANK	0.033	3	0.000	0.000

2. Aluminum by Spectrophotometry

Aluminum was determined spectrophotometrically on solution 'A', as the alizarin red-S complex (sodium alizarin-3-sulfonate)(Turek, 1973; Turek and Riddle, 1977). Solution 'A' had to be used for the determination of aluminum due to the extinction of the slope of the graph (Log I./I. vs Conc.) above the concentration of 3 ppm. This was due to the precipitation of the complex (Tetley, 1974). Above this concentration, a further proportionally increased intensity would not occur, as Beer-Lambert's Law was not followed (Ewing, 1969). The concentration of the solution had to lie on the straight line portion of the graph (before the inflection occurs). It was impossible to achieve this, and hence dilutions were required.

The alizarin-coloured complex $Al^{+3} + nAzH \longrightarrow AlAz_n^{(3-n)+} + nH^+$ was a red colour with maximum absorbence at 475 nm. The procedure used was a modification by Turek and Riddle (1977) of the method originally described by Shapiro and Brannock (1962).

Iron (III) strongly interfered by forming a green-coloured complex with alizarin sulfonate. The absorption peak overlapped the aluminum-calcium-alizarin complex peak, but this interference was eliminated by reducing Fe (III) to Fe (II). Ferrous iron then reacted with thioglycolic acid to form a blue complex, thereby eliminating the interference.

Calcium interfered by producing a calcium-alizarin complex which enhanced the absorption of the complex formed (Tetley, 1974). Between pH 3.9 and pH 4.6, the complex has a ratio of 2:1 for aluminum to alizarin sulfonate and a ratio of 1:1 for calcium-alizarin sulfonate. The calcium interference was thus used to enhance the intensity of the complex. The solution was buffered to pH 4.2 with sodium acetate-acetic acid to ensure that all the aluminum present would form a complex, whereas calcium could not form a complex under these pH conditions.

Lithium borate and silicon interfered by enhancing the colour but this interference was negligible (Tetley, 1974).

Seven ml of solution 'A' were pipetted into a 100-ml volumetric flask along with 2 ml of $CaCl_2$ (14%), 1 ml hydroxylamine hydrochloride (10%), 1 ml of potassium ferricyanide solution and allowed to stand for 5 minutes, 10 ml of buffer solution was added and allowed to stand for 10 minutes. Finally, 10 ml of alizarin red-S solution (0.05%) was pitetted in; the flask was made up to volume with triple-distilled water, mixed and allowed to form a stable colour (3 hours).

A set of standards and a blank were perpared at the same time as the sample solutions. Absorbance readings were obtained at 475 nm (Tables 35 and 36).

A calibration grapn of the standards was plotted (Fig. 37). The concentrations were deduced from the straight line portion of the curve before the flattening of the curve. Concentrations as percent oxides are listed in Table 55.

6

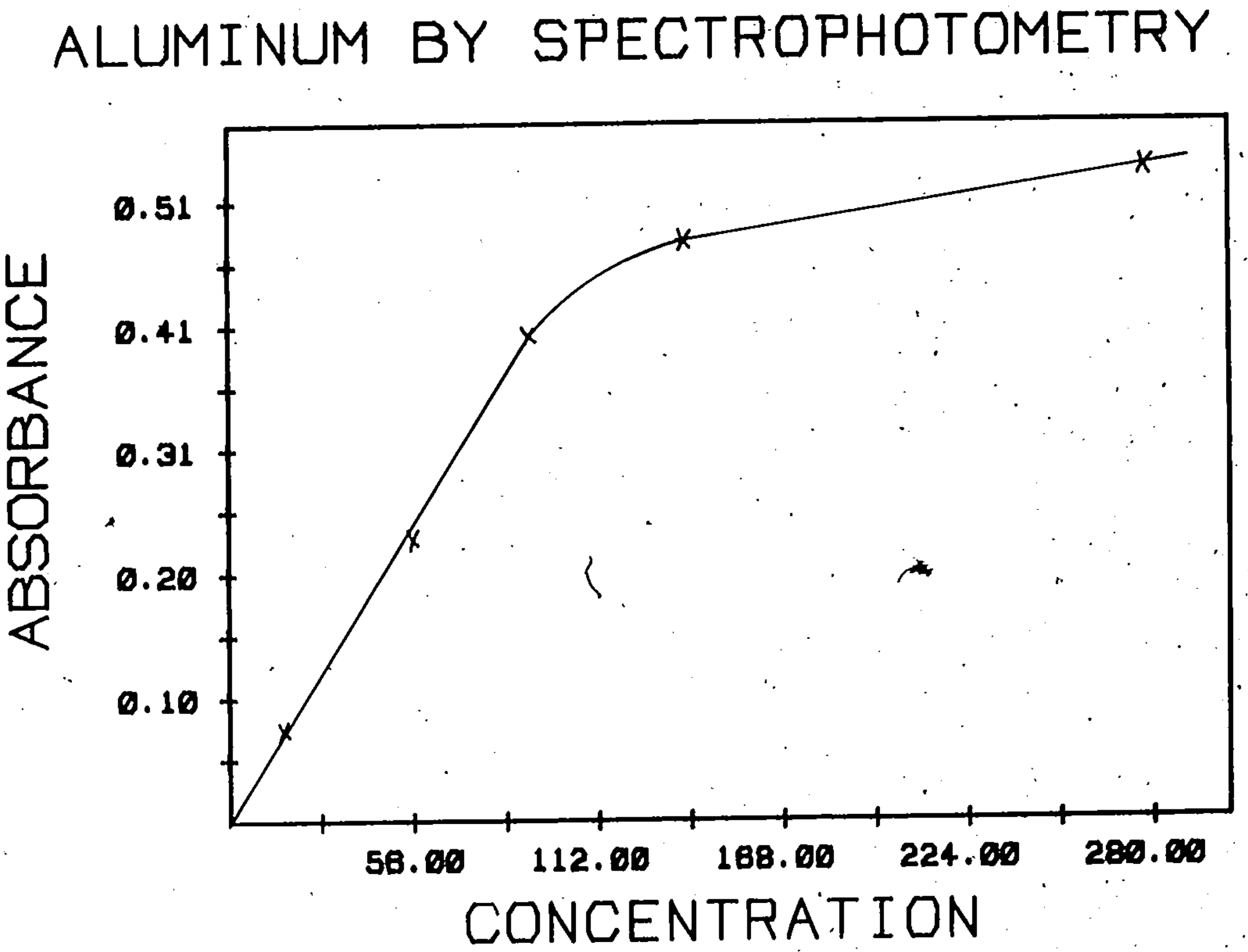


Fig. 37
Calibration curve for aluminum (on solution 'A') by spectrophotometry
(µg/ml) / 100 ml

TABLE 35. IONIC STANDARDS FOR ALUMINUM BY SPECTROPHOTOMETRY

WORKING CONDITIONS	
INSTRUMENT	SPECTRONIC 70
MAKE	BAUSCH & LOMB
WAVELENGTH	475.0 nm
MODE	ABSORBANCE

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
5	0.439	3	0.075	0.075
10	0.600	3	0.230	0.230
15	0.768	3	0.397	0.397

THE SLOPE IS 0.0244
THE INTERCEPT IS -0.0102
THE CORRELATION COEFFICIENT IS 0.99358

SLOPE DERIVED FROM STRAIGHT PORTION
OF CURVE USING FIRST 3 POINTS

TABLE 36.

ALUMINUM BY SPECTROPHOTOMETRY

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
GA	0.628	3	0.258	0.258
SYN.G2	0.639	3	0.266	0.266
NSX-1	0.688	3	0.318	0.317
NSX-2	0.721	3	0.353	0.352
NSX-3	0.660	3	0.290	0.290
NSX-4	0.650	3	0.285	0.281
NSX-5	0.640	3	0.272	0.270
NSX-6	0.783	3	0.412	0.413
NSX-7	0.660	3	0.288	0.288
BLANK	0.370	3	0.000	0.000

3. Total Iron by Spectrophotometry

Total iron was determined spectrophotometrically as the red ferrous bipyridine complex--2,2'-bipyridine (Riley, 1958).

The complex ion contained three molecules of bipyridyl in which the six co-ordination positions of iron were occupied by nitrogen atoms. The colour system obeyed Beer's Law, independant of the pH (range 1.5 to 12). Reduction to iron II valence state from iron III in the sample was done by the addition of hydroxylamine hydrochloride. The solution was buffered with sodium acetate to a pH range of 4.8 to 5.0.

Copper, molybdenum and silver interfere at levels greater than 5, 7 and 5 ppm, respectively, but these elements were not in sufficient concentrations in the samples in this thesis to cause any appreciable interference. All solutions were prepared at the same time. Concentrations were deduced from the graph (Fig. 38). Absorbance readings are given in Table 37. Concentration as percent oxides are listed on Table 65. Percent transmittance is given in Table 38.

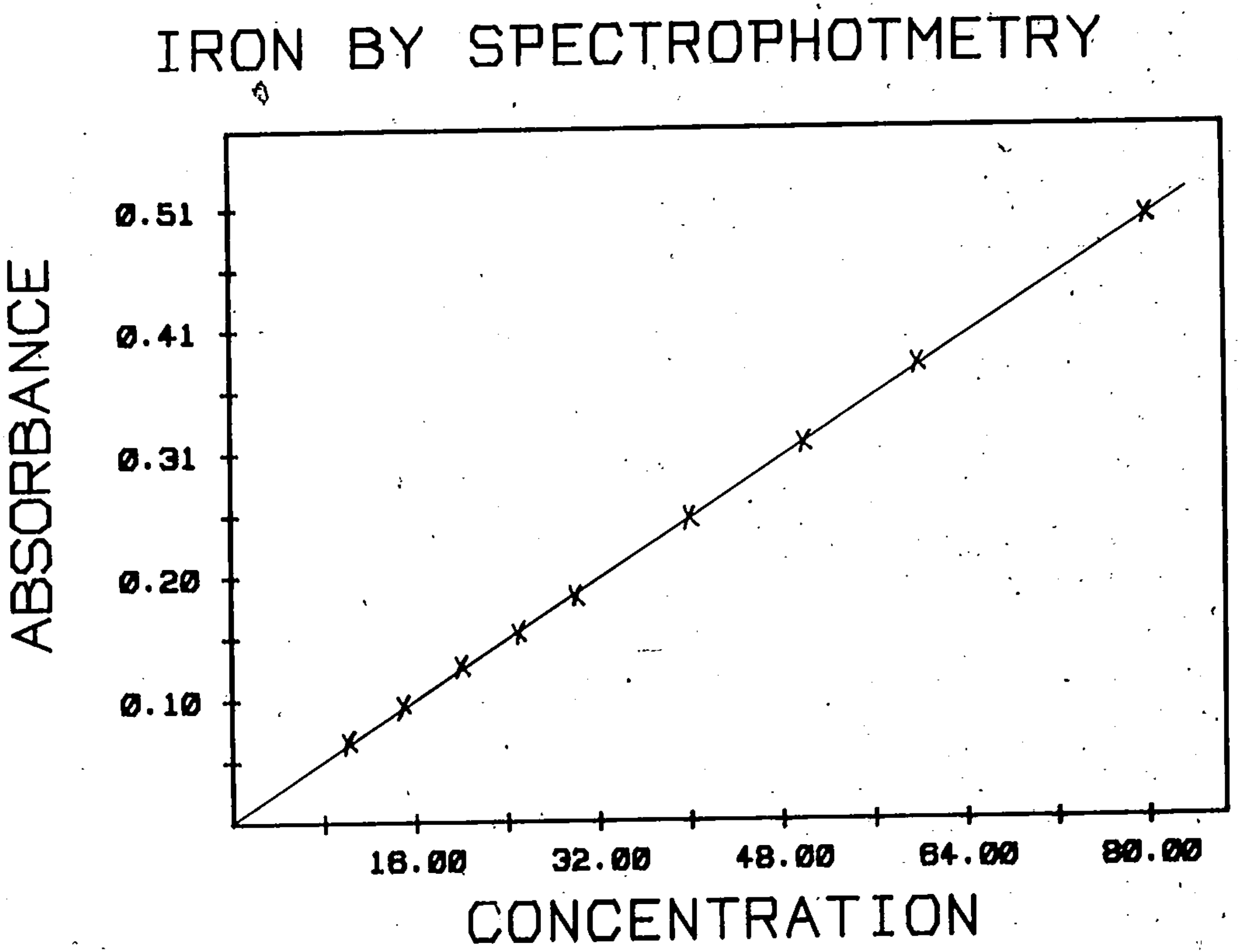


Fig. 38
Calibration curve for total iron (on solution ''B') by spectrophotometry
(μg/ml)

TABLE 37 . IONIC STANDARDS FOR IRON BY SPECTROPHOTOMETRY

WORKING CONDITIONS	
INSTRUMENT	SPECTRONIC 70
MAKE	BAUSCH & LOMB
WAVELENGTH	524.4 nm
MODE	ABSORBANCE

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
10	0.070	6	0.071	0.060
15	0.102	6	0.101	0.090
20	0.135	6	0.134	0.120
25	0.163	6	0.162	0.150
30	0.195	6	0.194	0.190
40	0.260	6	0.260	0.250
50	0.325	6	0.323	0.310
60	0.390	6	0.389	0.380
80	0.512	6	0.512	0.500

THE SLOPE IS 0.0064
THE INTERCEPT IS -0.0009
THE CORRELATION COEFFICIENT IS 0.99997

TABLE 38.

IRON BY SPECTROPHOTOMETRY

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.582	12	0.581	0.576
GA	0.125	12	0.125	0.121
AC2-2	0.188	12	0.187	0.182
SYN.G2	0.123	12	0.122	0.118
NSX-1	0.188	12	0.187	0.182
NSX-2	0.188	12	0.188	0.183
NSX-3	0.183	12	0.183	0.178
NSX-4	0.186	12	0.185	0.181
NSX-5	0.185	12	0.184	0.179
NSX-6	0.183	12	0.183	0.178
NSX-7	0.183	12	0.183	0.178
NSX-8	0.180	12	0.180	0.175
NSX-9	0.180	12	0.180	0.175
BLANK	0.005	12	0.000	0.000

4. Manganese by Spectrophotometry

Manganese was determined spectrophotometrically on solution 'B', using the method described by Willard et al.(1965) with some modification. Usually, a mild oxidizing agent such as 0.5 g of ammonium persulfate would have been added to oxidize carbon compounds, but because oxidizing had already taken place during dissolution, this step was omitted.

An aliquot of solution 'B' (10 ml) was pipetted into 50-ml volumetric flasks. Five ml of 85% phosphoric acid were added to complex Fe^{+3}, which was necessary to prevent the absorption of visible light and render the solution colourless. Manganese (II) was oxidized to manganese (VII) by the addition of 0.2 g potassium periodate (KIO_4).

$$2Mn^{+2} + 5IO_4^- + 3H_2O \longrightarrow 2MnO_4^- + 6H^+ + 5IO_3^-$$

The solutions were warmed for ten minutes to increase the reaction rate and increase the solubility of potassium periodate. After cooling, the flasks were made up to volume with triple-distilled water, shaken and then allowed to stand for four hours to stabilize the pink colour.

Standards were prepared at the same time as the sample solutions. Absorbance readings were taken at 545.0 nm which is the region of maximum absorbance (Table 39)

The readings, working conditions and range of the standards are listed in Appendix I.

A calibration curve of the standards is in Fig. 39 and results are given in Tables 39 and 40. Concentrations as percent oxide are in Table 97.

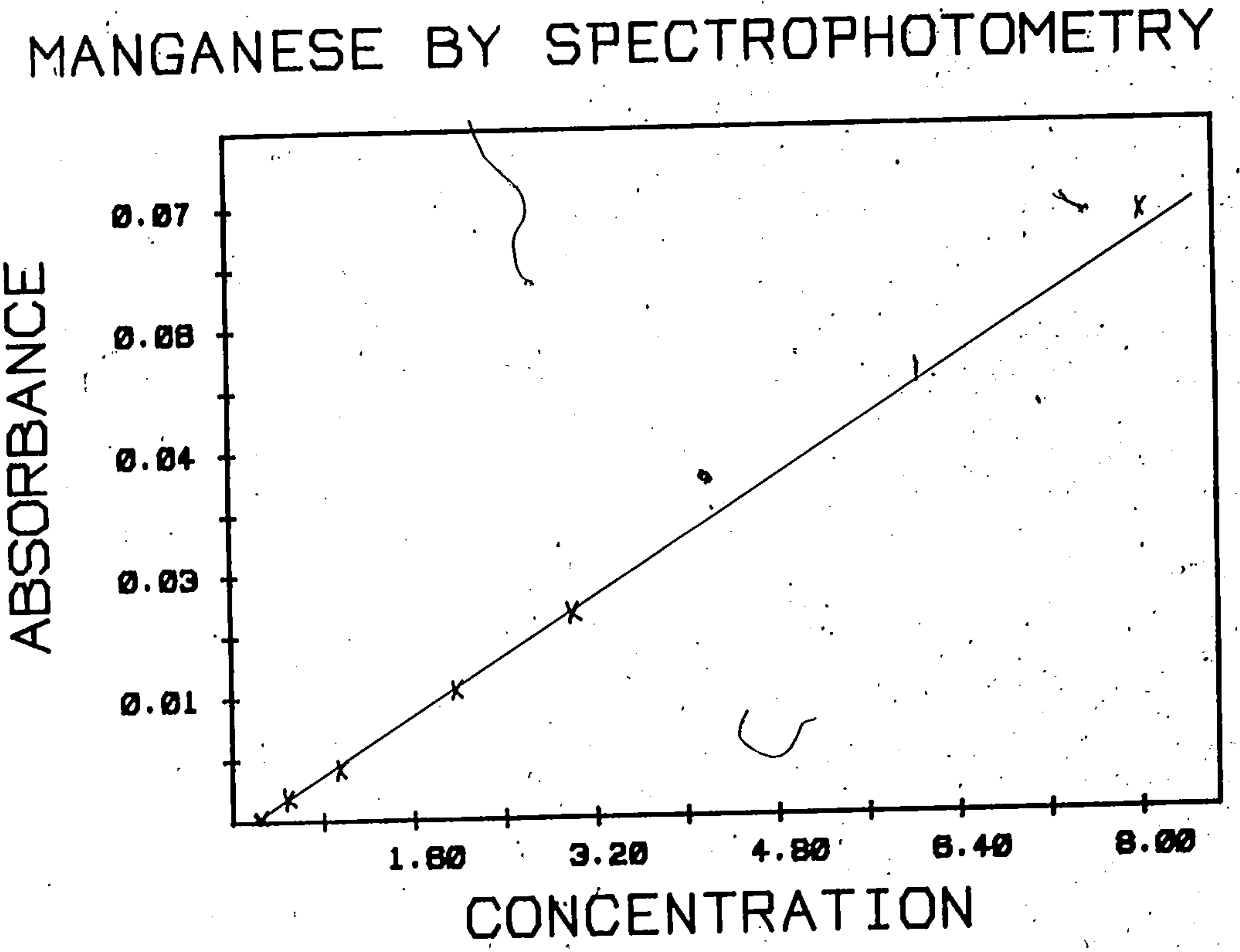


Fig. 39
Calibration curve for manganese by spectrophotometry
(µg/ml)

TABLE 39 . IONIC STANDARDS FOR MANGANESE BY SPECTROPHOTOMETRY

WORKING CONDITIONS

INSTRUMENT	SPECTRONIC 70
MAKE	BAUSCH & LOMB
WAVELENGTH	545.0 nm
MODE	ABSORBANCE

CONC. OF STANDARD µg/ml	ACTUAL READING A	ANALYSIS REPEATS	ZERO CORRECTED A	AVERAGE READING A
.25	0.000	6	0.000	0.000
.5	0.001	6	0.002	0.002
1	0.006	6	0.005	0.005
2	0.013	6	0.014	0.014
3	0.022	6	0.022	0.022
8	0.064	6	0.064	0.064

THE SLOPE IS 0.0080
THE INTERCEPT IS -0.0014
THE CORRELATION COEFFICIENT IS 0.99834

TABLE 40.

MANGANESE BY SPECTROPHOTOMETRY

ROCK SAMPLE	ACTUAL READING A	ANALYSIS REPEATS	BLANK & ZERO CORRECTED A	AVERAGE READING A
BCR-1	0.030	10	0.022	0.022
GA	0.020	10	0.010	0.010
AC2-2	0.009	10	0.009	0.009
SYN.G2	5.000	10	0.004	0.004
NSX-1	0.010	10	0.009	0.009
NSX-2	0.008	10	0.008	0.008
NSX-3	0.009	10	0.008	0.008
NSX-4	0.009	10	0.008	0.008
NSX-5	0.009	10	0.009	0.009
NSX-6	0.009	10	0.009	0.009
NSX-7	0.010	10	0.009	0.009
NSX-8	0.009	10	0.009	0.009
NSX-9	0.008	10	0.008	0.008

F. X-RAY FLUORESCENCE SPECTROSCOPY

a. Theory

The technique of x-ray fluorescence is based upon the fact that; when a beam of electrons of sufficient energy strikes the surface of any matter secondary (fluorescence) x-rays are emitted by the sample (Norrish and Chappell, 1967). This secondary radiation is composed of characteristic wavelengths of each element present. A collimator is used to direct a parallel beam of secondary radiation onto an analyzing crystal which separates wavelengths. A second collimator directs the reflected wavelengths into a radiation detector which is connected to a goniometer. The goniometer and the angular position of the crystal is a function of the wavelength. The intensity of radiation of each wavelength is proportional to the concentration of the corresponding element. The detector converts the x-rays into a series of electrical pulses which register on a counter as 'counts per second'. In order to yield the

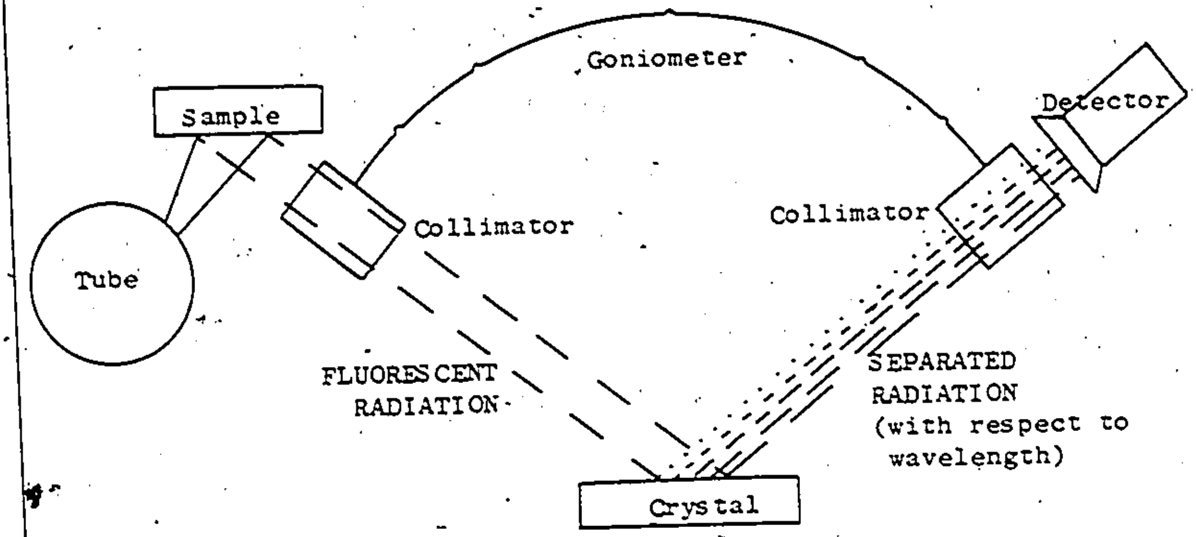


Fig. 40. Schematic layout of x-ray fluorescence spectrometer.

'true' count rate which is proportional to the concentration of the element being analyzed, the measured intensity must be corrected for various effects. Dead time corrections and background correction is required. For major rock analysis matrix correlations are also essential.

All above corrections and calculations were made on a Monroe 344 for silicon, aluminum, iron, calcium and potassium determinations. Magnesium and manganese calculations as well as corrections for quartz were made on a Wang-System 700 Series mini-computer. The programs are listed in Appendix IX. The analytical conditions are given in Appendix I. Concentration as percent oxides are listed in Table 41. In this study all x-ray analyses were made using a Philips PW140 x-ray spectrometer.

b. Analytical Procedure

The procedure follows the established methodology in this laboratory. It is essentially identical for all elements determined--silicon, aluminum, total iron, calcium, magnesium, potassium and manganese. Sodium could not be determined by x-ray fluorescence, because sodium escapes due to the high temperatures in the formation of the glass bead (as described in the section on the Preparation of X-ray Fluorescence Glass Pellets). Sodium, however, could be determined by x-ray fluorescence but it must be in the form of rock powder pellets. X-ray fluorescence is a comparative technique; all analyses were made using GA as a standard.

Variations between procedures took the form of instrumental adjustment. Working conditions (instrumental adjustment) are listed in Appendix I.

The analytical results for all the x-ray determinations are, unlike the treatment of other analytical data, given below in one table (Table 41). Matrix corrections were performed on the IBM 360 computer.

TABLE 41.
PERCENT OXIDE FOR X-RAY FLUORESCENCE DETERMINATION

Sample	Si	Al	Fe	Ca	Mg	K	Mn
GA (Lit.)	69.9000	14.5000	2.8300	2.4500	0.9500	4.0300	0.0900
GA$_1$	70.5600	14.6610	2.9000	2.4800	0.9500	4.0100	0.0900
NSX-1	70.7870	15.4020	4.3890	2.1260	1.1930	3.8710	0.0760
NSX-2	71.1450	15.0790	4.3770	2.1120	2.1990	3.8830	0.0850
NSX-3	72.2950	15.6340	4.4380	2.1280	1.1880	3.9030	0.0850
NSX-4	70.1970	15.3350	4.4380	2.1280	1.1880	3.9030	0.0850
NSX-5	71.7990	15.6140	4.3300	2.1180	1.1720	3.8900	0.0850
NSX-6	71.2510	15.7180	4.2630	2.1130	1.1730	3.9020	0.0900
G-2	70.874	15.684	2.9000	1.4030	0.8500	4.4460	0.0340
BCR-1	55.996	14.3910	13.1520	6.8700	3.4500	1.7610	0.1780
NBS-70	70.5970	18.9330	0.3260	0.1570	0.0790	11.1720	0.0030
MRB-8	76.6100	12.3900	1.9490	0.5740	0.2810	3.6750	0.0210
$\bar{x}$	71.2400	15.4600	4.3500	2.1000	1.3400	3.8800	0.0800
V$\bar{a}$r	0.4545	0.0474	0.0030	0.0016	0.1443	0.0002	0.0000
σ	0.6700	0.2100	0.0500	0.0400	0.3700	0.0100	0.0000
C.V.	0.9500	1.4100	1.2700	1.9300	28.1600	0.4200	4.9600
Rej. Val.	nil	nil	nil	nil	nil	nil	nil

$\bar{x}$ is the arithmetic mean, V$\bar{a}$r is the variance, σ is the standard deviation, C.V. is the coefficient of variation and Rej. Val. is the rejection value.

V. STATISTICAL TREATMENT OF RESULTS

A. INTRODUCTORY STATEMENT

Relatively elementary statistical treatment and testing of data was required in this study. The following are the definitions of terms, functions and equations. A more extensive approach to statistics can be found in numerous texts, eg. Brookes, et al. (1966), Kenney and Keeping (1954), Koch and Link (1970), Moroney (1965), Weinberg and Schumaker (1969) and Wine (1964).

B. TERMINOLOGY AND DEFINITIONS

a. Accuracy is the proximity of the measurements to the 'true' or 'actual' value of the quantity being measured.

$$Acc = (x - \bar{x})$$

where x is the 'true' value and $\bar{x}$ is the mean. Accuracy is difficult to measure, as the 'true' value x is seldom known but inferred.

b. Precision is the extent to which the results of a series of determinations are scattered about the mean value. The parameters by which precision can be described are: standard deviation, variance, coefficient of variation and relative standard deviation.

c. Arithmetic Mean ($\bar{x}$) is the measure of the central tendency of a population. It is the value obtained by adding the terms and dividing their sum by the number of terms.

$$\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i$$

where $\bar{x}_i$ is the individual term and n is the total number of terms.

d. Slope is a line. The slope of a calibration curve is obtained by the least square simple regression with y regressed on x for no error in x. The equation of this line is: $y = mx + b$, where m is the slope and b is the intercept.

$$m = \frac{\Sigma\ (x_i - \bar{x})\ (y_i - \bar{y})}{\Sigma\ (x_i - \bar{x})^2}$$

where $\bar{x} = x/n$ and $\bar{y} = y/n$

e. Standard Deviation (S.D.) is a measure of dispersion or variability. It is the average value of the deviations from the mean.

$$S.D. = \left[\frac{1}{n} \Sigma\ (x_i - \bar{x})^2\right]^{\frac{1}{2}}$$ (S.D. of a sample of a population)

f. Confidence Limits

The standard deviation (σ), determined for a number of samples (n), with a mean result ($\bar{x}$), indicates that there is a 95% chance that the true value of the mean for this sample lies within the values $\bar{x} \pm 1.96\ \sigma / \sqrt{n}$. This range is known as the '95% confidence interval', and it provides a convenient estimate of the reliability of the mean.

g. Coefficient of Variation (C.V.) is a measure of relative dispersion and is calculated as follows:

$$C.V. = \frac{\sigma}{\bar{x}} \times 100$$

h. Variance ($\bar{V}$ar.) is the mean of the squared differences from the mean of the distribution. It is the standard deviation squared.

$$\bar{V}ar. = (S.D.)^2$$

i. Correlation Coefficient (r) is a precise measure of the manner in which two variables correlate (Weinberg, 1969). It is calculated by the correlation of the line of best fit (m and b in the equation $\bar{y}=m\bar{x}+b$) with the individual data points

$$r = \frac{\Sigma (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\Sigma (x_i - \bar{x})^2 \, \Sigma (y_i - \bar{y})^2}} \quad \text{(Wine, 1964)}$$

A correlation coefficient of +1.000 indicates a perfect positive correlation, while a correlation of -1.000 indicates a perfect negative correlation.

j. Rejection of Values

Values may be rejected on the basis of the sample value being significantly different from the rest of the population. The rejected value referred to as an 'outlier'. Several criteria for rejection of outliers may be used, perhaps the most commonly used criteria is the 95% confidence range, or roughly two standard deviations. The rational for rejection is not necessarily that a value is wrong, but that it does not belong to this sample of the population. The following tests were used in this correction. Table 42 shows the values rejected using this equation--only two determinations were rejected.

1. Sample set: "Student's t-distribution" tests the hypothesis that an individual measurement does not belong to this sample set; the equation used is:

$$t\ (\text{calc.}) = \frac{\left| \bar{x} - x_i \right| \sqrt{(n-1)}}{\text{S.D.}}$$

where $\bar{x}$ is the sample set mean, x_i is the measurement being tested and S.D. is the standard deviation. The procedure is repeated until values are no longer rejected.

2. Population Set: Outliers are rejected from a population if they are 2* σ away from the mean.

Rejected Value $= < 2*\sigma >$

where σ is the standard deviation of a population. This method was used in 'cleaning' the SY-2, SY-3 and MRG data (Abbey, 1975; Abbey, 1976).

k. Significance by Comparison of Sample Means to a Population

The mean values of concentration as percentage oxides in the 'in-house' standard NSX rock sample, generated by the various analytical methods, were compared by the use of the "Student's t-test".

$$t(\text{calc.}) = \frac{\left| \bar{X} - \bar{x} \right| \sqrt{(n-1)}}{\sigma}$$

where $\bar{X}$ is population mean, $\bar{x}$ is a sample mean and σ is the standard deviation. If t(calc.) is greater than t(Tables), then it may be concluded that the the means are significantly different at the 5% significance level and there exists a bias between them.

l. Significance by Comparison of Variances

Snedecor's f-test was applied to determine if there are any significant differences (at the 5% level) in precision.

$$f = \frac{\text{Var.}_1}{\text{Var.}_2}$$

where $\text{Varl}_1 > \text{Var.}_2$ and the degrees of freedom used is d.f. = (n-1).

A difference in precision exists wherever the calculated f value exceeds the tabulated value for a given level of significance.

m. Significance by Comparison of Means

The t-test was applied to determine the existence of a bias between individual mean values of concentration obtained by the different methods.

$$t - (\text{calc.}) = \frac{\left| \bar{x}_1 - \bar{x}_2 \right|}{\sqrt{\text{Var}_1 + \text{Var}_2}}$$

where $\bar{x}_1$ and $\bar{x}_2$ are the sample means and Var_1 and Var_2 are the variances, respectively.

The degrees of freedom used are:

$$K = \frac{\frac{(Var_1)^2}{N_1^{-1}} + \frac{(Var_2)^2}{N_2^{-1}}}{(Var_1 + Var_2)^2}$$

A bias exists wherever the calculated t-value exceeds the tabulated value of a given level of significance.

TABLE 42

REJECTION TEST FOR NSX SAMPLES
(% Oxide in Sample Solutions)

Method*	Statistics**	Si Solution A	Al Solution A	Al. Solution B	Fe	Ca	Mg***	Mg****	Na	K	Mn
AA	N	7	7	9	9	9	9	9	9	9	9
	$\bar{x}$	67.880	15.870	15.540	4.070	2.080	0.950	1.060	3.460	4.290	0.080
	Vār	0.004	0.334	0.055	0.009	0.007	0.000	0.001	0.167	0.040	0.000
	σ	0.060	0.570	0.230	0.090	0.080	0.020	0.030	0.400	0.200	0.000
	C.V.	0.090	3.640	1.500	2.350	3.990	2.840	3.540	11.790	4.660	5.880
	Rej. Val.	nil	nil	nil	nil	nil	nil	nil	nil	nil	nil
FE	N								9	9	
	$\bar{x}$								3.890	4.140	
	Vār								0.002	0.028	
	σ								0.040	0.160	
	C.V.								1.040	4.070	
	Rej. Val.								4.140	nil	
SP	N	7	7		9						9
	$\bar{x}$	70.090	15.840		3.980						0.070
	Vār	0.135	0.492		0.003						0.000
	σ	0.360	0.700		0.050						0.000
	C.V.	0.520	4.420		1.480						1.100
	Rej. Val.	nil	nil		nil						0.080
T	N				8	9	9				
	$\bar{x}$				4.450	2.160	1.210				
	Vār				0.001	0.000	0.008				
	σ				0.030	0.010	0.080				
	C.V.				0.770	0.510	7.400				
	Rej. Val.				nil	nil	nil				
G	N										
	$\bar{x}$	68.670	15.890								
	Vār	0.372	0.056								
	σ	0.600	0.230								
	C.V.	0.890	1.490								
	Rej. Val.	nil	nil								
			(% Oxide in Glass Pellets)								
XRF	N	6	6		6	6	6			6	6
	$\bar{x}$	71.240	15.460		4.350	2.100	1.340			3.880	0.080
	Vār	0.455	0.047		0.003	0.002	0.144			0.000	0.000
	σ	0.670	0.210		0.050	0.040	0.370			0.010	0.000
	C.V.	0.950	1.410		1.270	1.930	28.160			0.420	4.960
	Rej. Val.	nil	nil		nil	nil	nil			nil	nil

*Method: where AA is atomic absorption, FE is flame emission, SP is spectrophotometry, T is titrimetry, G is gravimetry and XRF is x-ray fluorescence.

**Statistics: where N is number of samples, $\bar{x}$ is arithmetic mean, Vār is variance, σ is standard deviation for a sample set, C.V. is the coefficient of variation and Rej. Val. is rejected value.

***Mg: Magnesium without lanthanum oxide.

****Mg: Magnesium with lanthanum oxide.

VI. EVALUATION OF ANALYTICAL RESULTS

A. SILICON

Silicon was determined by the following methods: atomic absorption, spectrophotometry, gravimetry and x-ray fluorescence. By atomic absorption, silicon was determined on the two solutions 'A' and 'JA'. The results are comparable for the two solutions. All the analytical results for SiO_2 determined on the NSX subsamples by the four different methods are given in Tables 43 to 47. Each table also gives the values for the control standards. GA, pure SiO_2, BCR-1, AC2-2, G-2, NBS-70 and MRB-S. The mean, variance and standard deviation in each table refers to the NSX subsamples. No values were rejected.

From the above tables, it is obvious that in terms of accuracy and precision, atomic absorption gives the best value. It is closest to the recommended value and has the lowest standard deviation. The following tabulation summarizes the results:

	AA	SP	G	XRF
Average % SiO_2 in NSX	67.88	70.09	68.67	71.24
S.D.	0.06	0.36	0.60	0.67
Rec'd Value	67.54	(Turek <u>et al.</u>, 1978)		

In the determination of SiO_2 by atomic absorption, there is an analytical problem in that burner clogging due to formation of silicon carbide occurs, a condition that must be monitored or else loss of signal occurs. Also the use of a nitrous oxide as support gas produces a noisy signal. The gravimetric method is of course very exacting and time-consuming. The spectrophotometric determination of silicon is relatively simple but delay time for colour development is an inconveniance. In x-ray fluorescence determination the choice of a suitable standard to closely match the unknown is very important.

It should be noted that gravimetric and spectrophotometric methods also measure the proxying elements (eg. Ga and Ge) while atomic absorption and x-ray fluorescence are metal specific and should yield lower values than chemical methods.

The statistical comparison of the results obtained by the four methods has been evaluated using F- and t-tests (Tables 48 to 53). F-test of variances shows that precision by atomic absorption is significantly better than by the other three methods. Comparing the means using the t-test the atomic absorption and gravimetric values are not significant at the 5% level, however, the atomic absorption values are significantly different from spectrophotometry and x-ray fluorescence. These differences, therefore, demonstrate that there is a bias between the methods, and atomic absorption appears to be the most accurate and precise method.

TABLE 43.

SILICON IN 'JA' BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	54.39
GA	68.73
AC2-2	67.50
NSX-1	67.42
NSX-2	67.40
NSX-3	67.40
NSX-4	67.49
NSX-5	67.41
NSX-6	67.45
NSX-7	67.38
NSX-8	67.39
NSX-9	67.45

THE MEAN IS 67.4260
THE VARIANCE IS 0.0011
THE STANDARD DEVIATION IS 0.0336

TABLE 44.

SILICON IN 'A' BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
GA	70.32
SiO_2-Pure	99.87
NSX-1	67.90
NSX-2	67.81
NSX-3	67.87
NSX-4	67.98
NSX-5	67.96
NSX-6	67.80
NSX-7	67.90

THE MEAN IS 67.8939
THE VARIANCE IS 0.0041
THE STANDARD DEVIATION IS 0.0641

TABLE 45.

SILICON BY GRAVIMETRY

SAMPLE	WEIGHT OF PRECIPITATE g	PERCENT OXIDE
SiO_2-Pure	0.1534	99.99
SiO_2-Pure	0.1534	99.99
GA (1)	0.1094	71.31
GA (2)	0.1096	71.44
NSX-1	0.1064	68.53
NSX-2	0.1161	68.18
NSX-3	0.1090	68.06
NSX-4	0.1060	69.03
NSX-5	0.1091	69.93
NSX-6	0.1318	68.18
NSX-7	0.1070	68.78

THE MEAN IS 68.6753
THE VARIANCE IS 0.3692
THE STANDARD DEVIATION IS 0.6076

TABLE 46.

SILICON BY SPECTROPHOTOMETRY

SAMPLE	PERCENT OXIDE
GA	71.30
SiO_2-Pure	97.45
NSX-1	69.99
NSX-2	70.45
NSX-3	69.59
NSX-4	70.44
NSX-5	70.42
NSX-6	70.23
NSX-7	69.54

THE MEAN IS 70.0974
THE VARIANCE IS 0.1356
THE STANDARD DEVIATION IS 0.3682

TABLE 47.

SILICON BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	69.90
GA (Exp.)	70.56
G-2	70.87
BCR-1	60.00
NBS-70	30.60
MRB-8	76.61
NSX-1	70.79
NSX-2	71.15
NSX-3	72.30
NSX-4	70.20
NSX-5	71.80
NSX-6	71.25

THE MEAN IS 71.2400
THE VARIANCE IS 0.4545
THE STANDARD DEVIATION IS 0.6700

TABLE 48.

F-test AND T-test FOR SILICON BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY

SILICON

AA	SP
PERCENT OXIDE	PERCENT OXIDE
67.90	69.99
67.81	70.45
67.87	69.59
67.98	70.44
67.96	70.42
67.80	70.23
67.90	69.54

F-calc.= 32.99 WITH 7 AND 7 DEGREES OF FREEDOM
F-table= 3.79 WITH 7 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

67.88	MEAN	70.09
00.06	S.D.	00.36

TABLE 49.

F-test AND T-test FOR SILICON BY ATOMIC ABSORPTION AND GRAVIMETRY

SILICON

AA	G
PERCENT OXIDE	PERCENT OXIDE
67.90	68.53
67.81	68.18
67.87	68.06
67.98	69.03
67.96	69.93
67.80	68.18
67.90	68.78

F-calc.= 87.61 WITH 7 AND 7 DEGREES OF FREEDOM
F-table= 3.79 WITH 7 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

67.88	MEAN	68.67
00.06	S.D.	00.60

TABLE 50.
F-test AND T-test FOR SILICON BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

SILICON

AA	XF
PERCENT OXIDE	PERCENT OXIDE
67.90	70.78
67.81	71.14
67.87	72.29
67.98	70.19
67.96	71.79
67.80	71.25
67.90	

F-calc.=109.25 WITH 7 AND 6 DEGREES OF FREEDOM
F-table= 3.87 WITH 7 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

67.88	MEAN	71.24
00.06	S.D.	00.67

TABLE 51.
F-test AND T-test FOR SILICON BY GRAVIMETRY AND X-RAY FLUORESCENCE

SILICON

G	XF
PERCENT OXIDE	PERCENT OXIDE
68.53	70.78
68.18	71.14
68.06	72.29
69.03	70.19
69.93	71.79
68.18	71.25
68.78	

F-calc.= 3.29 WITH 7 AND 6 DEGREES OF FREEDOM
F-table= 3.87 WITH 7 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 3.352 WITH 9 DEGREES OF FREEDOM
T-table= 2.262 FOR 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS IS SIGNIFICANT AT THE 5% LEVEL

68.67	MEAN	71.24
00.60	S.D.	00.67

TABLE 52.
F-test AND T-test FOR SILICON BY GRAMIMETRY AND SPECTROPHOTOMETRY

SILICON

G PERCENT OXIDE	SP PERCENT OXIDE
68.53	69.99
68.18	70.45
68.08	69.59
69.03	70.44
69.93	70.42
68.18	70.23
68.78	69.54

F-calc.= 2.70 WITH 7 AND 7 DEGREES OF FREEDOM
F-table= 3.79 WITH 7 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 2.001 WITH 9 DEGREES OF FREEDOM
T-table= 2.262 FOR 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS
IS NOT SIGNIFICANT AT THE 5% LEVEL

68.67	MEAN	70.09
00.60	S.D.	00.36

TABLE 53.
F-test AND T-test FOR SILICON BY X-RAY FLUORESCENCE AND SPECTROPHOTOMETRY

SILICON

XF PERCENT OXIDE	SP PERCENT OXIDE
70.78	69.99
71.14	70.45
72.29	69.59
70.19	70.44
71.79	70.42
71.25	70.23
	69.54

F-calc.= 3.3 WITH 6 AND 7 DEGREES OF FREEDOM
F-table= 4.21 WITH 6 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 1.494 WITH 7 DEGREES OF FREEDOM
T-table= 2.365 FOR 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS
IS NOT SIGNIFICANT AT THE 5% LEVEL

71.24	MEAN	70.09
00.67	S.D.	00.36

B. ALUMINUM

Aluminum was determined by the following methods: atomic absorption, spectrophotometry, gravimetry and x-ray fluorescence. All the analytical results for Al_2O_3 determined on the NSX subsamples by the four different methods are given in Tables 54 to 57. Each table also gives the values for the control standards GA, SYN.G2, BCR-1, NBS-70, MRB-8 and an ionic standard (80 µg/ml). The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. No values were rejected (Table 42).

From the above tables it is obvious that in terms of accuracy and precision x-ray fluorescence gives the best value. It is closest to the 'recommended' value and has the lowest standard deviation. The following tabulation summarizes the results:

	AA	SP	G	XRF
Average % Al_2O_3 in NSX	15.88	15.85	15.80	15.46
S.D.	0.58	0.70	0.24	0.21
Rec'd Value	15.27 (Turek *et al.*,1978)			

In the determination of Al_2O_3 by atomic absorption there is an analytical problem in that a noisy signal is produced when using nitrous oxides as support gas. The gravimetric method is very exacting and time-consuming. The spectrophotometric determination of aluminum is relatively simple but delay time for colour development is an inconvenience. In x-ray fluorescence determination, the choice of a suitable standard to closely match the unknown is very important.

It should be noted that gravimetric and spectrophotometric methods also measure the proxying elements (eg. Zn and Ga) while atomic absorption and x-ray fluorescence are metal specific and should yield lower values than chemical methods.

The statistical comparison of the results obtained by the four methods has been evaluated using F- and t-tests (Tables 58 to 63). F-test of variances shows that precision by x-ray fluorescence is significantly better than by the other three methods. Comparing the means using the t-test the values are not significant at the 5% level for the four methods, however, the values for x-ray fluorescence are closer to the 'recommended' value.

These differences, therefore, demonstrate that there is a bias between the methods, and x-ray fluorescence appears to be the most accurate and precise method.

TABLE 54. RESULTS FOR (SOLUTION 'A')

ALUMINUM BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
GA	16.15
SYN.G2	16.37
NSX-1	16.40
NSX-2	16.25
NSX-3	15.47
NSX-4	16.77
NSX-5	15.48
NSX-6	14.99
NSX-7	15.74

THE MEAN IS 15.8780
THE VARIANCE IS 0.3318
THE STANDARD DEVIATION IS 0.5760

TABLE 55. RESULTS FOR (SOLUTION 'A')

ALUMINUM BY SPECTROPHOTOMETRY

SAMPLE	PERCENT OXIDE
GA	14.74
SYN.G2	15.10
NSX-1	16.78
NSX-2	16.02
NSX-3	15.24
NSX-4	15.51
NSX-5	14.86
NSX-6	16.87
NSX-7	15.65

THE MEAN IS 15.8526
THE VARIANCE IS 0.4918
THE STANDARD DEVIATION IS 0.7013

TABLE 56.

ALUMINUM BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	14.50
GA (Exp.)	14.66
G-2	15.68
BCR-1	14.39
NBS-70	18.93
MRB-8	12.39
NSX-1	15.40
NSX-2	15.08
NSX-3	15.63
NSX-4	15.34
NSX-5	15.61
NSX-6	15.72

THE MEAN IS 15.4600
THE VARIANCE IS 0.0474
THE STANDARD DEVIATION IS 0.2100

TABLE 57. RESULTS FOR (SOLUTION 'B')

ALUMINUM BY GRAVIMETRY

SAMPLE	WEIGHT OF PRECIPITATE g	PERCENT OXIDE
AL 80 ppm	0.0272	15.09
SYN.G2	0.0271	15.03
GA	0.0054	14.97
NSX-1	0.0057	15.76
NSX-2	0.0063	15.81
NSX-3	0.0066	15.50
NSX-4	0.0058	16.18
NSX-5	0.0059	16.09
NSX-6	0.0071	15.74
NSX-7	0.0059	16.16

THE MEAN IS 15.8952
THE VARIANCE IS 0.0567
THE STANDARD DEVIATION IS 0.2382

TABLE 58.

F-test AND T-test FOR ALUMINUM BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY

ALUMINUM

AA PERCENT OXIDE	SP PERCENT OXIDE
16.40	16.78
16.25	16.02
15.47	15.24
16.77	15.51
15.48	14.86
14.99	16.87
15.74	15.65

F-calc.= 1.48 WITH 7 AND 7 DEGREES OF FREEDOM
F-table= 3.79 WITH 7 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 0.027 WITH 11 DEGREES OF FREEDOM
T-table= 2.201 FOR 11 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS
IS NOT SIGNIFICANT AT THE 5% LEVEL

15.87	MEAN	15.84
00.57	S.D.	00.70

TABLE 59.

F-test AND T-test FOR ALUMINUM BY ATOMIC ABSORPTION AND GRAVIMETRY

ALUMINUM

AA PERCENT OXIDE	G PERCENT OXIDE
16.40	15.76
16.25	15.81
15.47	15.50
16.77	16.18
15.48	16.09
14.99	15.74
15.74	16.16

F-calc.= 6.08 WITH 7 AND 7 DEGREES OF FREEDOM
F-table= 3.79 WITH 7 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

15.87	MEAN	15.89
00.57	S.D.	00.23

TABLE 60.
F-test AND T-test FOR ALUMINUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

ALUMINUM

AA PERCENT OXIDE	XF PERCENT OXIDE
16.40	15.40
16.25	15.07
15.47	15.63
16.77	15.33
15.43	15.61
14.99	15.71
15.74	

F-calc.= 7.52 WITH 7 AND 6 DEGREES OF FREEDOM
F-table= 3.87 WITH 7 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

15.87	MEAN	15.46
00.57	S.D.	00.21

TABLE 61.
F-test AND T-test FOR ALUMINUM BY GRAVIMETRY AND SPECTROPHOTOMETRY

ALUMINUM

G PERCENT OXIDE	SP PERCENT OXIDE
15.76	16.78
15.81	16.02
15.50	15.24
16.18	15.51
16.09	14.86
15.74	16.87
16.16	15.65

F-calc.= 8.66 WITH 7 AND 7 DEGREES OF FREEDOM
F-table= 3.79 WITH 7 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

15.89	MEAN	15.84
00.23	S.D.	00.70

TABLE 62.
F-test AND T-test FOR ALUMINUM BY X-RAY FLUORESCENCE AND SPECTROPHOTOMETRY

ALUMINUM

XF	SP
PERCENT OXIDE	PERCENT OXIDE
15.40	16.78
15.07	16.02
15.63	15.24
15.33	15.51
15.61	14.86
15.71	16.87
	15.65

F-calc.= 11.15 WITH 6 AND 7 DEGREES OF FREEDOM
F-table= 4.21 WITH 6 AND 7 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

XF		SP
15.46	MEAN	15.84
00.21	S.D.	00.70

TABLE 63.
F-test AND T-test FOR ALUMINUM BY GRAVIMETRY AND X-RAY FLUORESCENCE

ALUMINUM

G	XF
PERCENT OXIDE	PERCENT OXIDE
15.76	15.40
15.81	15.07
15.50	15.62
16.18	15.33
16.09	15.61
15.74	15.71
16.16	

F-calc.= 1.23 WITH 7 AND 6 DEGREES OF FREEDOM
F-table= 3.87 WITH 7 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 1.370 WITH 10 DEGREES OF FREEDOM
T-table= 2.228 FOR 10 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS
IS NOT SIGNIFICANT AT THE 5% LEVEL

G		XF
15.89	MEAN	15.46
00.23	S.D.	00.21

C. TOTAL IRON

Total iron was determined by the following methods: atomic absorption, spectrophotometry and x-ray fluorescence. Total iron was determined on solution 'B' by atomic absorption, titration and spectrophotometry. All the analytical results for Fe_2O_3(t) determined on the NSX subsamples by the four different methods are given in Tables 64 to 67. Each table also gives the values for the control standards GA, BCR-1, AC2-2, and SYN.G2, etc. The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. No values were rejected (Table 42).

From the above tables it is obvious that in terms of accuracy and precision atomic absorption gives the best value. It is closest to the 'recommended' value and has a very good standard deviation. The following tabulation summarizes the results:

	AA	SP	T	XRF
Average % Fe_2O_3(t) in NSX	4.07	3.99	4.41	4.35
S.D.	0.09	0.06	0.12	0.05
Rec'd Value	4.08 (Turek *et al.*, 1978)			

The spectrophotometric determination of total iron is relatively simple but delay time for colour development is an inconvenience. The titration method is also relatively simple but in finding the end point it is imperative that the analyst has good eyesight and is not colour blind. In x-ray fluorescence determination, the choice of a suitable standard to closely match the unknown is very important. It should be noted that the spectrophotometric method also measures the proxying elements (eg. Co and Tc) while atomic absorption and x-ray fluorescence are metal specific and should give lower values than the chemical methods.

The statistical comparison of the results obtained by the four methods has been evaluated using F- and t-tests (Tables 68 to 73). F-test of variances shows that precision by atomic absorption is comparable to the precision by the other three methods. Comparing the means using the t-test, the values by atomic absorption and spectrophotometry are not significant at the 5% level, however, the atomic absorption values are significantly different from titration and x-ray fluorescence. These differences, therefore, demonstrate that there is a bias between methods, and atomic absorption seems to be the most accurate and precise method.

TABLE 64. RESULTS FOR

IRON BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	12.88
GA	2.91
AC2-2	4.27
SYN.G2	2.75
NSX-1	4.03
NSX-2	4.20
NSX-3	4.03
NSX-4	3.86
NSX-5	4.13
NSX-6	4.03
NSX-7	4.10
NSX-8	4.09
NSX-9	4.18

THE MEAN IS 4.0770
THE VARIANCE IS 0.0089
THE STANDARD DEVIATION IS 0.0945

TABLE 65. RESULTS FOR

IRON BY SPECTROPHOTOMETRY

SAMPLE	PERCENT OXIDE
BCR-1	12.87
GA	2.68
AC2-2	4.07
SYN.G2	2.63
NSX-1	4.06
NSX-2	4.08
NSX-3	3.98
NSX-4	3.98
NSX-5	3.98
NSX-6	3.98
NSX-7	3.98
NSX-8	3.91
NSX-9	3.88

THE MEAN IS 3.9859
THE VARIANCE IS 0.0033
THE STANDARD DEVIATION IS 0.0576

IRON BY TITRATION (DICHROMATE)

ROCK SAMPLE	SAMPLE WEIGHT g	TOTAL VOLUME ml	ALIQUOT VOLUME ml	TITER VOLUME ml	PERCENT OXIDE
BCR-1(a)	.5002	500	20	2.5048	13.91
BCR-1(b)	.5002	500	20	2.5050	13.91
BCR-1(c)	.5002	500	20	2.5000	13.88
BCR-1(d)	.5002	500	25	2.8880	12.83
MEAN					13.63
GA (a)	.5028	500	20	0.5650	3.12
GA (b)	.5005	500	20	0.5650	3.13
GA (c)	.5001	500	20	0.5600	3.11
GA (d)	.5028	500	50	1.2400	2.74
GA (e)	.5028	500	50	1.2450	2.75
MEAN					2.97
AC2-2 (a)	.5000	500	25	1.1000	4.89
AC2-2 (b)	.5000	500	25	1.0650	4.73
AC2-2 (c)	.5000	500	30	1.3040	4.83
MEAN					4.82
SYN.G2(a)	.5000	500	50	1.1400	2.53
SYN.G2(b)	.5000	500	50	1.1320	2.51
MEAN					2.52
NSX-1	.5013	500	25	1.0000	4.43
NSX-2	.5006	500	25	1.0000	4.44
NSX-3	.5076	500	25	0.9400	4.11
NSX-4	.5029	500	25	1.0200	4.50
NSX-5	.5008	500	25	0.9900	4.39
NSX-6	.5000	500	25	1.0100	4.49
NSX-7	.5005	500	25	1.0050	4.46
NSX-8	.5041	500	25	1.0100	4.45

THE MEAN IS 4.4127
THE VARIANCE IS 0.0135
THE STANDARD DEVIATION IS 0.1166

TABLE 66.

TABLE 67.

TOTAL IRON BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	2.83
GA (Exp.)	2.90
G-2	2.90
BCR-1	13.15
NBS-70	0.33
MRB-8	1.95
NSX-1	4.39
NSX-2	4.38
NSX-3	4.44
NSX-4	4.44
NSX-5	4.33
NSX-6	4.26

THE MEAN IS 4.3500
THE VARIANCE IS 0.0030
THE STANDARD DEVIATION IS 0.0500

TABLE 68.
F-test AND T-test FOR TOTAL IRON BY ATOMIC ABSORPTION AND TITRATION

TOTAL IRON

AA PERCENT OXIDE	T PERCENT OXIDE
4.03	4.43
4.20	4.44
4.03	4.11
3.86	4.50
4.13	4.39
4.03	4.49
4.10	4.46
4.09	4.45
4.18	

F-calc.= 1.52 WITH 9 AND 8 DEGREES OF FREEDOM
F-table= 3.23 WITH 9 AND 8 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 2.236 WITH 14 DEGREES OF FREEDOM
T-table= 2.145 FOR 14 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS IS SIGNIFICANT AT THE 5% LEVEL

4.07	MEAN	4.45
0.09	S.D.	0.03

TABLE 69.
F-test AND T-test FOR TOTAL IRON BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY

TOTAL IRON

AA PERCENT OXIDE	SP PERCENT OXIDE
4.03	4.06
4.20	4.08
4.03	3.98
3.86	3.98
4.13	3.98
4.03	3.98
4.10	3.98
4.09	3.91
4.18	3.88

F-calc.= 2.69 WITH 9 AND 9 DEGREES OF FREEDOM
F-table= 3.18 WITH 9 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 0.823 WITH 13 DEGREES OF FREEDOM
T-table= 2.160 FOR 13 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS IS NOT SIGNIFICANT AT THE 5% LEVEL

4.07	MEAN	3.98
0.09	S.D.	0.05

TABLE 70.
F-test AND T-test FOR TOTAL IRON BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

TOTAL IRON

AA PERCENT OXIDE	XF. PERCENT OXIDE
4.03	4.38
4.20	4.37
4.03	4.43
3.86	4.43
4.13	4.33
4.03	4.26
4.10	
4.09	
4.18	

F-calc.= 3.57 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

4.07	MEAN	4.35
0.09	S.D.	0.05

TABLE 71.
F-test AND T-test FOR TOTAL IRON BY TITRATION AND SPECTROPHOTOMETRY

TOTAL IRON

T PERCENT OXIDE	SP PERCENT OXIDE
4.43	4.06
4.44	4.08
4.11	3.98
4.50	3.98
4.39	3.98
4.49	3.98
4.46	3.98
4.45	3.91
	3.88

F-calc.= 4.09 WITH 8 AND 9 DEGREES OF FREEDOM
F-table= 3.39 WITH 8 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

4.45	MEAN	3.98
0.03	S.D.	0.05

TABLE 72.
F-test AND T-test FOR TOTAL IRON BY X-RAY FLUORESCENCE AND SPECTROPHOTOMETRY

TOTAL IRON

XF PERCENT OXIDE	SP PERCENT OXIDE
4.38	4.06
4.37	4.08
4.43	3.98
4.43	3.98
4.33	3.98
4.26	3.98
	3.98
	3.91
	3.88

F-calc.= 1.32 WITH 6 AND 9 DEGREES OF FREEDOM
F-table= 2.44 WITH 6 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 4.773 WITH 11 DEGREES OF FREEDOM
T-table= 2.201 FOR 11 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS IS SIGNIFICANT AT THE 5% LEVEL

4.35	MEAN	3.98
0.05	S.D.	0.05

TABLE 73.
F-test AND T-test FOR TOTAL IRON BY TITRATION AND X-RAY FLUORESCENCE

TOTAL IRON

T PERCENT OXIDE	XF PERCENT OXIDE
4.43	4.38
4.44	4.37
4.11	4.43
4.50	4.43
4.39	4.33
4.49	4.26
4.46	
4.45	

F-calc.= 5.43 WITH 8 AND 6 DEGREES OF FREEDOM
F-table= 3.58 WITH 8 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

4.45	MEAN	4.35
0.03	S.D.	0.05

D. CALCIUM

Calcium was determined by the following methods: atomic absorption, titration and x-ray fluorescence. All the analytical results for CaO determined on the NSX subsamples by the three different methods are given in Tables 74 to 76. Each table also gives the values for the control standards GA, BCR-1, AC2-2, SYN.G2, G-2, NBS-70 and MRB-8. The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. No values were rejected.

From the above tables it is obvious that in terms of accuracy and precision, titration gives the best value. It is very close to the recommended value and has the lowest standard deviation. The following tabulation summarizes the results:

	AA	T	XRF
Average % CaO in NSX	2.08	2.16	2.10
S.D.	0.08	0.01	0.04
Rec'd Value	2.11	(Turek *et al.*, 1978)	

In the determination of CaO by titration, the time needed for the preparation of the reagents is an inconveniance. The atomic absorption method is fast but the use of nitrous oxide as support gas produces a noisy signal, also a releasing agent is mandatory; it decomposes the complexes formed with calcium such as Ca-Al and Ca-Si. In x-ray fluorescence determination the choice of a suitable standard to closely match the unknown is very important.

It should be noted that the titration method also measures the proxying elements (Ba, Sr, Pb), while atomic absorption and x-ray fluorescence are metal specific and should yield lower values than chemical methods.

The statistical comparison of the results obtained by the three methods has been evaluated using F- and t-tests (Tables 77 to 79). F-test of variances shows that precision by titration is significantly better than by the other two methods. Comparing the means using the t-test shows no significant difference at the 5% level, however, titration does give a higher value than atomic absorption and x-ray fluorescence. This is what one would expect, instrumental atomic absorption and x-ray fluorescence are metal specific while chemical titration measures proxying elements.

These differences, therefore, demonstrate that there is a bias between the methods, and titration appears to be the most precise and accurate method.

TABLE 74. RESULTS FOR CALCIUM BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	6.69
GA	2.72
AC2-2	2.21
SYN.G2	1.02
NSX-1	2.14
NSX-2	2.21
NSX-3	2.10
NSX-4	2.11
NSX-5	1.96
NSX-6	1.97
NSX-7	2.01
NSX-8	2.14
NSX-9	2.16

THE MEAN IS 2.0937
THE VARIANCE IS 0.0068
THE STANDARD DEVIATION IS 0.0827

TABLE 75.

CALCIUM BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	2.45
GA (Exp.)	2.48
G-2	1.40
BCR-1	6.87
NBS-70	0.16
MRB-8	0.57
NSX-1	2.13
NSX-2	2.11
NSX-3	2.13
NSX-4	2.13
NSX-5	2.12
NSX-6	2.11

THE MEAN IS 2.1000
THE VARIANCE IS 0.0016
THE STANDARD DEVIATION IS 0.0400

TABLE 76. RESULTS FOR

CALCIUM OXIDE BY EDTA TITRATION

ROCK SAMPLE	WEIGHT OF SAMPLE g	TOTAL VOLUME ml	ALIQUOT VOLUME ml	EDTA TITRANT ml	PERCENT OXIDE
BCR-1	0.5002	500	15	9.60	6.55
GA	0.5028	500	15	3.57	2.42
AC2-2	0.5000	500	15	2.95	2.01
SYN.G2	0.5000	500	15	2.90	1.98
NSX-1	0.9968	1000	15	3.18	2.17
NSX-2	0.9963	1000	15	3.18	2.18
NSX-3	0.9987	1000	15	3.17	2.16
NSX-4	0.9974	1000	15	3.17	2.17
NSX-5	1.0000	1000	15	3.16	2.15
NSX-6	0.9998	1000	15	3.18	2.17
NSX-7	0.9942	1000	15	3.19	2.19
NSX-8	0.9939	1000	15	3.16	2.17
NSX-9	0.8585	1000	15	2.72	2.16
BLANK	0.0000	1000	15	0.00	0.00

$$\% \text{ CaO} = \frac{\text{Titrant x (F) x Volume of Solution / Volume of Aliquot x 100}}{\text{Weight of Sample}}$$

where (F) = .0001020 gm of CaO / ml of EDTA

THE MEAN IS 2.1688
THE VARIANCE IS 0.0001
THE STANDARD DEVIATION IS 0.0109

TABLE 77.
F-test AND T-test FOR CALCIUM BY ATOMIC ABSORPTION AND TITRATION

CALCIUM

AA	T
PERCENT OXIDE	PERCENT OXIDE
2.14	2.17
2.21	2.18
2.10	2.16
2.11	2.17
1.96	2.15
1.97	2.17
2.01	2.19
2.14	2.17
2.16	2.16

F-calc.= 57.56 WITH 9 AND 9 DEGREES OF FREEDOM
F-table= 3.18 WITH 9 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

2.08	MEAN	2.16
0.08	S.D.	0.01

TABLE 78.
F-test AND T-test FOR CALCIUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

CALCIUM

AA	XF
PERCENT OXIDE	PERCENT OXIDE
2.14	2.12
2.21	2.11
2.10	2.12
2.11	2.12
1.96	2.11
1.97	2.11
2.01	
2.14	
2.16	

F-calc.= 4.27 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

2.08	MEAN	2.10
0.08	S.D.	0.04

TABLE 79.
F-test AND T-test FOR CALCIUM BY TITRATION AND X-RAY FLUORESCENCE

CALCIUM

T PERCENT OXIDE	XF PERCENT OXIDE
2.17	2.12
2.18	2.11
2.16	2.12
2.17	2.12
2.15	2.11
2.17	2.11
2.19	
2.17	
2.16	

F-calc.= 13.46 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

2.16	MEAN	2.10
0.01	S.D.	0.04

E. MAGNESIUM

Magnesium was determined by the following methods: atomic absorption, titration and x-ray fluorescence. By atomic absorption magnesium was determined twice on solution 'B', once using lanthanum oxide as a releasing agent and again without the releasing agent. The results are slightly higher for the solution containing the releasing agent. All the analytical results for MgO determined on the NSX subsamples by the three different methods are given in Tables 80 to 83. Each table also gives the values for the control standards GA, BCR-1, AC2-2, SYN.G2, G-2, NBS-70, and MRB-8. The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. No values were rejected.

From the above tables it is obvious that in terms of accuracy and precision atomic absorption gives the best value and has a low standard deviation. The following tabulation summarizes the results:

	AA	T	XRF
Average % MgO in NSX	1.06	1.21	1.34
S.D.	0.03	0.08	0.37
Rec'd Value	1.11	(Turek et al.,1978)	

In the determination of MgO by titration there is an analytical problem in that magnesium is determined by difference, with the calcium values being subtracted from the total (Ca + Mg) value; therefore before one can determine megnesium by titration, calcium must first be determined by the same method. In the x-ray fluorescence determination the choice of a suitable standard to closely match the unknown is very important.

It should be noted that the titration method also measures the proxying elements (eg. Be, Fe and Li) while atomic absorption and x-ray fluorescence are metal specific and should yield lower values than chemical methods. The statistical comparison of the results obtained by the three methods has been evaluated using F- and t-tests (Tables 84 to 86). F-test of variances shows that precision by atomic absorption is significantly better than by the other two methods. Comparing the means using the t-test the values are not significant at the 5% level, however, the atomic absorption values are closest to the 'recommended values', and the titration value is next best.

These differences, therefore, demonstrate that there is a bias between methods, and atomic absorption appears to be the most accurate and precise method.

TABLE 80. RESULTS FOR (WITHOUT LANTHANUM OXIDE)

MAGNESIUM BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	3.14
GA	0.76
AC2-2	0.98
SYN.G2	0.57
NSX-1	0.98
NSX-2	1.00
NSX-3	0.97
NSX-4	0.98
NSX-5	0.96
NSX-6	0.91
NSX-7	0.95
NSX-8	0.96
NSX-9	0.92

THE MEAN IS 0.9632
THE VARIANCE IS 0.0007
THE STANDARD DEVIATION IS 0.0277

TABLE 81. RESULTS FOR (WITH LANTHANUM OXIDE)

MAGNESIUM BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	3.44
GA	0.86
AC2-2	1.10
SYN.G2	0.63
NSX-1	1.09
NSX-2	1.10
NSX-3	1.10
NSX-4	1.10
NSX-5	1.07
NSX-6	1.00
NSX-7	1.06
NSX-8	1.03
NSX-9	1.01

THE MEAN IS 1.0679
THE VARIANCE IS 0.0012
THE STANDARD DEVIATION IS 0.0350

MAGNESIUM OXIDE BY EDTA TITRATION

ROCK SAMPLE	WEIGHT OF SAMPLE g	TOTAL VOLUME ml	ALIQUOT VOLUME ml	(Ca+Mg) TITRANT ml	Mg TITRANT ml	PERCENT OXIDE
BCR-1	0.5002	500	15	16.10	6.50	3.21
GA	0.5028	500	15	6.90	2.33	1.14
AC2-2	0.5000	500	15	5.90	2.95	1.45
SYN.G2	0.5000	500	15	4.24	1.34	0.66
NSX-1	0.9968	1000	15	5.40	2.22	1.10
NSX-2	0.9963	1000	15	5.50	2.32	1.15
NSX-3	0.9987	1000	15	5.40	2.23	1.10
NSX-4	0.9974	1000	15	5.70	2.53	1.25
NSX-5	1.0000	1000	15	5.80	2.64	1.30
NSX-6	0.9998	1000	15	5.80	2.62	1.29
NSX-7	0.9942	1000	15	5.60	2.41	1.19
NSX-8	0.9939	1000	15	5.50	2.34	1.16
NSX-9	0.8585	1000	15	5.10	2.38	1.37
BLANK	0.0000	1000	15	0.00	0.00	0.00

$$\% \text{ MgO} = \frac{\text{Titrant x (F) x Volume of Solution / Volume of Aliquot x 100}}{\text{Weight of Sample}}$$

where (F) = .0000742 gm of MgO / ml of EDTA

THE MEAN IS 1.2122
THE VARIANCE IS 0.0080
THE STANDARD DEVIATION IS 0.0896

TABLE 82.

TABLE 83.

MAGNESIUM BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	0.95
GA (Exp.)	0.95
G-2	0.85
BCR-1	3.45
NBS-70	0.08
MRB-8	0.28
NSX-1	1.19
NSX-2	2.20
NSX-3	1.19
NSX-4	1.19
NSX-5	1.17
NSX-6	1.17

THE MEAN IS 1.3400
THE VARIANCE IS 0.1443
THE STANDARD DEVIATION IS 0.3700

TABLE 84.
F-test AND T-test FOR MAGNESIUM BY ATOMIC ABSORPTION AND TITRATION

MAGNESIUM

AA	T
PERCENT OXIDE	PERCENT OXIDE
1.09	1.10
1.10	1.15
1.10	1.10
1.10	1.25
1.07	1.30
1.00	1.29
1.06	1.19
1.03	1.16
1.01	1.37

F-calc.= 5.06 WITH 9 AND 9 DEGREES OF FREEDOM
F-table= 3.18 WITH 9 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

1.06	MEAN	1.21
0.03	S.D.	0.08

TABLE 85.
F-test AND T-test FOR MAGNESIUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

MAGNESIUM

AA	XF
PERCENT OXIDE	PERCENT OXIDE
1.09	1.19
1.10	2.19
1.10	1.18
1.10	1.18
1.07	1.17
1.00	1.17
1.06	
1.03	
1.01	

F-calc.= 10.57 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL

1.06	MEAN	1.34
0.03	S.D.	0.37

TABLE . 86.
F-test AND T-test FOR MAGNESIUM BY TITRATION AND X-RAY FLUORESCENCE

MAGNESIUM

T	XF
PERCENT OXIDE	PERCENT OXIDE
1.10	1.19
1.15	2.19
1.10	1.18
1.25	1.18
1.30	1.17
1.29	1.17
1.19	
1.16	
1.37	

F-calc.= 16.90 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

1.21	MEAN	1.34
0.08	S.D.	0.37

F. SODIUM

Sodium was determined by only two methods: atomic absorption and flame emission. All the analytical results for Na_2O determined on the NSX subsamples by the two different methods are given in Tables 87 and 88. Each table also gives the values for the control standards GA, BCR-1, AC2-2, and SYN.G2. The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. The values of 4.14 was rejected in the determination of Na_2O by flame emission.

From the above tables it is obvious that in terms of accuracy and precision, atomic absorption gives the better value. It is closer to the 'recommended' value and has the lowest standard deviation. Because the recommended value for NSX came from Turek et al (1978), which specified the use of only atomic absorption, thus the NSX values in this thesis are very close to the collaborative 'recommended' value. The following tabulation summarizes the results:

	AA	FE
Average % Na_2O in NSX	3.69	3.93
S.D.	0.08	0.09
Rec'd Value	3.66	(Turek *et al.*, 1978)

The atomic absorption and flame emission determination were both conducted on the same instrument.

The statistical comparison of the results obtained by the two methods has been evaluated using F- and t-tests (Table 89). F-test of variances shows that precision by atomic absorption is not significantly better than flame emission at the 5% level. Comparing the means using the t-test the atomic absorption values are significantly different at the 5% level.

These differences, therefore, demonstrate that there is a bias between methods, and atomic absorption appears to be the most accurate and precise method.

TABLE 87. RESULTS FOR

SODIUM BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	3.59
GA	3.74
AC2-2	3.59
SYN.G2	4.29
NSX-1	3.59
NSX-2	3.89
NSX-3	3.63
NSX-4	3.67
NSX-5	3.67
NSX-6	3.64
NSX-7	3.66
NSX-8	3.71
NSX-9	3.72

THE MEAN IS 3.6915
THE VARIANCE IS 0.0064
THE STANDARD DEVIATION IS 0.0802

TABLE 88. RESULTS FOR

SODIUM BY FLAME EMISSION

SAMPLE	PERCENT OXIDE
BCR-1	3.92
GA	4.01
AC2-2	3.99
SYN.G2	4.41
NSX-1	3.96
NSX-2	3.88
NSX-3	3.90
NSX-4	3.90
NSX-5	3.95
NSX-6	3.87
NSX-7	3.85
NSX-8	3.84
NSX-9	4.14

THE MEAN IS 3.9276
THE VARIANCE IS 0.0073
THE STANDARD DEVIATION IS 0.0857

TABLE 89.
F-test AND T-test FOR SODIUM BY ATOMIC ABSORPTION AND FLAME EMISSION

SODIUM

AA	FE
PERCENT OXIDE	PERCENT OXIDE
3.59	3.96
3.89	3.88
3.63	3.90
3.67	3.90
3.67	3.95
3.64	3.87
3.66	3.85
3.71	3.84
3.72	

F-calc.= 1.77 WITH 9 AND 8 DEGREES OF FREEDOM
F-table= 3.23 WITH 9 AND 8 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 4.600 WITH 14 DEGREES OF FREEDOM
T-table= 2.145 FOR 14 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS
IS SIGNIFICANT AT THE 5% LEVEL

3.46	MEAN	3.89
0.40	S.D.	0.04

G. POTASSIUM

Potassium was determined by the following methods: atomic absorption, flame emission and x-ray fluorescence. All the analytical results for K_2O determined on the NSX subsamples by the different methods are given in Tables 90 to 92. Each table also gives the values for the control standards GA, BCR-1, AC2-2, SYN.G2, G-2, NBS-70 and MRB-8. The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. No values were rejected.

From the above tables it is obvious that in terms of accuracy and precision x-ray fluorescence gives the best value. This is somewhat surprising as general consensus is that flame emission is the preferred method for the determination of potassium. The following tabulation summarizes the results:

	AA	FE	XRF
Average % K_2O in NSX	4.29	4.14	3.88
S.D.	0.20	0.17	0.01
Rec'd Value	3.93	(Turek *et al.*, 1978)	

The atomic absorption and flame emission determinations were both conducted on the same instrument. In x-ray fluorescence determination the choice of a suitable standard to closely match the unknown is very important. All three methods are instrumental and metal specific.

The statistical comparison of the results obtained by the three methods has been evaluated using F- and t-tests (Tables 93 to 95). F-test of variances shows that precision by x-ray fluorescence is significantly better than by the other two methods. Comparing the means using the t-test the values are significantly different at the 5% level. The x-ray fluorescence value is closer to the 'recommended' value.

These differences, therefore, demonstrate that there is a bias between methods, and x-ray fluorescence appears to be the most accurate and precise method.

TABLE 90. RESULTS FOR

POTASSIUM BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	2.06
GA	4.46
AC2-2	4.37
SYN.G2	5.50
NSX-1	4.37
NSX-2	4.52
NSX-3	4.39
NSX-4	4.40
NSX-5	4.45
NSX-6	4.39
NSX-7	3.85
NSX-8	4.09
NSX-9	4.19

THE MEAN IS 4.3016
THE VARIANCE IS 0.0403
THE STANDARD DEVIATION IS 0.2009

TABLE 91. RESULTS FOR

POTASSIUM BY FLAME EMISSION

SAMPLE	PERCENT OXIDE
BCR-1	2.33
GA	4.30
AC2-2	4.30
SYN.G2	4.93
NSX-1	4.42
NSX-2	4.23
NSX-3	4.21
NSX-4	4.19
NSX-5	4.19
NSX-6	4.16
NSX-7	3.79
NSX-8	3.95
NSX-9	4.15

THE MEAN IS 4.1478
THE VARIANCE IS 0.0284
THE STANDARD DEVIATION IS 0.1685

TABLE 92.

POTASSIUM BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	4.03
GA (Exp.)	4.01
G-2	4.45
BCR-1	1.76
NBS-70	11.17
MRB-8	3.68
NSX-1	3.87
NSX-2	3.88
NSX-3	3.90
NSX-4	3.90
NSX-5	3.89
NSX-6	3.90

THE MEAN IS 3.8800
THE VARIANCE IS 0.0002
THE STANDARD DEVIATION IS 0.0100

TABLE 93.
F-test AND T-test FOR POTASSIUM BY ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

POTASSIUM

AA PERCENT OXIDE	XF PERCENT OXIDE
4.37	3.87
4.52	3.88
4.39	3.90
4.40	3.90
4.45	3.89
4.39	3.90
3.85	
4.09	
4.19	

F-calc.= 200 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

4.29	MEAN	3.88
0.20	S.D.	0.01

TABLE 94.
F-test AND T-test FOR POTASSIUM BY FLAME EMISSION AND X-RAY FLUORESCENCE

POTASSIUM

FE PERCENT OXIDE	XF PERCENT OXIDE
4.42	3.87
4.23	3.88
4.21	3.90
4.19	3.90
4.19	3.89
4.16	3.90
3.79	
3.95	
4.15	

F-calc.= 2800 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

4.14	MEAN	3.88
0.16	S.D.	0.01

TABLE 95.
F-test AND T-test FOR POTASSIUM BY ATOMIC ABSORPTION AND FLAME EMISSION

POTASSIUM

AA PERCENT OXIDE	FE PERCENT OXIDE
4.37	4.42
4.52	4.23
4.39	4.21
4.40	4.19
4.45	4.19
4.39	4.16
3.85	3.79
4.09	3.95
4.19	4.15

F-calc.= 2.04 WITH 9 AND 9 DEGREES OF FREEDOM
F-table= 3.18 WITH 9 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS NOT SIGNIFICANT AT THE 5% LEVEL

T-calc = 3.072 WITH 14 DEGREES OF FREEDOM
T-table= 2.145 FOR 14 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE MEANS IS SIGNIFICANT AT THE 5% LEVEL

4.29	MEAN	4.14
0.20	S.D.	0.16

H. MANGANESE

Manganese was determined by the following methods: atomic absorption, spectrophotometry and x-ray fluorescence. All the analytical results for MnO determined on the NSX subsamples by the three different methods are given in Tables 96 to 98. Each table also gives the values for the control standards GA, BCR-1, AC2-2, SYN.G2, G-2, NBS-70 and MRB-8. The mean, variance and standard deviation in each table refers to the values for the NSX subsamples. Only one value was rejected. The reason for the rejection is that for the determination of MnO by spectrophotometry all the values for the NSX subsamples are the same except one, the rejected value.

From the above tables it is obvious that in terms of accuracy and precision all three methods give comparable values. The following tabulation summarizes the results:

	AA	SP	XRF
Average % MnO in NSX	0.08	0.07	0.08
S.D.	0.00	0.00	0.00
Rec'd Value	0.08	(Turek et al.,1978)	

The spectrophotometric determination of manganese is relatively simple but the delay time for colour development is an inconvenience. In x-ray fluorescence determination the choice of a suitable standard to closely match the unknown is very important.

It should be noted that the spectrophotometric method also measures proxying elements (eg. Cr and V) while atomic absorption and x-ray fluorescence are metal specific and should yield lower values than the chemical methods.

The statistical comparison of the results obtained by the three methods has been evaluated using F- and t-tests (Tables 99 to 101). F-test of variances shows that precision is significantly different between the three methods. Comparing the means using the t-test, the values for atomic absorption are significantly different than by the other two methods.

These differences, therefore; demonstrate that there is a bias between methods. In the MnO determination the bias seems vague since the values between the three methods are comparable, but nevertheless it does exist.

TABLE 96. RESULTS FOR

MANGANESE BY ATOMIC ABSORPTION

SAMPLE	PERCENT OXIDE
BCR-1	0.21
GA	0.09
AC2-2	0.09
SYN.G2	0.01
NSX-1	0.09
NSX-2	0.08
NSX-3	0.09
NSX-4	0.09
NSX-5	0.09
NSX-6	0.08
NSX-7	0.08
NSX-8	0.08
NSX-9	0.08

THE MEAN IS 0.0894
THE VARIANCE IS 0.0000
THE STANDARD DEVIATION IS 0.0017

TABLE 97. RESULTS FOR

MANGANESE BY SPECTROPHOTOMETRY

SAMPLE	PERCENT OXIDE
BCR-1	0.17
GA	0.08
AC2-2	0.07
SYN.G2	0.03
NSX-1	0.07
NSX-2	0.07
NSX-3	0.07
NSX-4	0.07
NSX-5	0.07
NSX-6	0.07
NSX-7	0.07
NSX-8	0.07
NSX-9	0.08

THE MEAN IS 0.0754
THE VARIANCE IS 0.0000
THE STANDARD DEVIATION IS 0.0037

TABLE 98.

MANGANESE BY X-RAY FLUORESCENCE

SAMPLE	PERCENT OXIDE
GA (Lit.)	0.09
GA (Exp.)	0.09
G-2	0.03
BCR-1	0.17
NBS-70	0.00
MRB-8	0.02
NSX-1	0.08
NSX-2	0.09
NSX-3	0.09
NSX-4	0.09
NSX-5	0.09
NSX-6	0.09

THE MEAN IS 0.0800
THE VARIANCE IS 0.0000
THE STANDARD DEVIATION IS 0.0000

TABLE 99.
F-test AND T-test FOR MANGANESE BY ATOMIC ABSORPTION AND SPECTROPHOTOMETRY

MANGANESE

AA PERCENT OXIDE	SP PERCENT OXIDE
0.09	0.07
0.08	0.07
0.09	0.07
0.09	0.07
0.09	0.07
0.08	0.07
0.08	0.07
0.08	0.07
0.08	0.08

F-calc.= 4.00 WITH 9 AND 9 DEGREES OF FREEDOM
F-table= 3.18 WITH 9 AND 9 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

0.08	MEAN	0.07
0.00	S.D.	0.00

TABLE 100.
F-test AND T-test FOR MANGANESE BY. ATOMIC ABSORPTION AND X-RAY FLUORESCENCE

MANGANESE

AA PERCENT OXIDE	XF PERCENT OXIDE
0.09	0.07
0.08	0.08
0.09	0.08
0.09	0.08
0.09	0.08
0.08	0.09
0.08	
0.08	
0.08	

F-calc.= 170 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES
IS SIGNIFICANT AT THE 5% LEVEL

0.08	MEAN	0.08
0.00	S.D.	0.00

TABLE 101.
F-test AND T-test FOR MANGANESE BY SPECTROPHOTOMETRY AND X-RAY FLUORESCENCE

MANGANESE

SP PERCENT OXIDE	XF PERCENT OXIDE
0.07	0.07
0.07	0.08
0.07	0.08
0.07	0.08
0.07	0.08
0.07	0.09
0.07	
0.07	
0.08	

F-calc.= 370 WITH 9 AND 6 DEGREES OF FREEDOM
F-table= 3.37 WITH 9 AND 6 DEGREES OF FREEDOM

THE DIFFERENCE BETWEEN THE VARIANCES IS SIGNIFICANT AT THE 5% LEVEL.

SP		XF
0.07	MEAN	0.08
0.00	S.D.	0.00

TABLE 102

SUMMARY OF ANALYTICAL RESULTS FOR R3X 'IN-HOUSE' SAMPLE

Method	Elements (Percent Oxides)																	
	Si		Al		Fe(t)		Ca		Mg		Na		K		Ti*		Mn	
	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
AA	67.88	0.060	15.870	0.570	4.07	0.090	2.08	0.080	1.06	0.030	3.46	0.400	4.29	0.200			0.080	0.000
FE											3.89	0.040	4.14	0.160				
SP	70.09	0.360	15.840	0.700	3.98	0.050											0.070	0.000
T					4.45	0.030	2.16	0.010	1.21	0.080								
G	68.67	0.600	15.890	0.230														
XF	71.24	0.670	15.460	0.210	4.35	0.050	2.10	0.040	1.34	0.370			3.88	0.010			0.080	0.000
APE			14.820	0.480	4.17	0.03	2.53	0.062	1.61	0.062	3.90	0.111	5.58	0.174	0.62	0.01	0.112	0.003
Rec. Val.**	67.54		15.270		4.08	0.08	2.11	0.098	1.11	0.045	3.66	0.086	3.93	0.104	0.16		0.080	0.006

Where $\bar{x}$ is arithmetic mean, σ is standard deviation, AA is atomic absorption spectroscopy, FE is flame emission spectroscopy, SP is spectrophotometry, T is titration, G is gravimetry, XF is x-ray fluorescence spectroscopy, APE is argon plasma emission, and Rec. Val. is recommended value.

*Quirt, 1978.

**Turek, 1978.

VII. SUMMARY AND CONCLUSIONS

A complete chemical analysis of a rock involves the determination of thirteen constituents; in this study eight constituents have been determined in replicate by up to six different methods. (Results by one method, argon plasma emission, is taken from Quirt, 1978.) The data is summarized in Table 102 which gives the average by a particular method of the replicate determinations together with the associated standard deviation. Table 102 also gives the recommended value for sample NSX which has been extensively analyzed by thirty-five laboratories. If the recommended value can be accepted as the 'true' concentration then inference with respect to accuracy can be made. It should be noted that the collaborative analytical results for sample NSX are exceptionally good and standard deviation for all constituents is better than for such well known international standards as G-2 and GA.

The purpose of this study has been to examine the possible bias between methods. The precision of analyses by all methods is good and comparing the standard deviations given in Table 102 to precision of analyses on international standards SY-2, SY-3 and MRG-1 as tabulated in Tables 1 to 6 the precision of the NSX results compares very favourably. Similarily in terms of accuracy the values for the international standard GA, BCR-1, etc., obtained in this study are in agreement with the recommended values; also the results for NSX agree with the recorded value. Hence, in terms of accuracy and precision the replicate analysis reported for NSX by different methods are all acceptable values. However, inspection of the data

(Table 102) does show some significant differences in precision (i.e. standard deviation of results) and the differences between the means indicate either accuracy or more likely a bias between methods.

The argon plasma emission results are generally slightly higher, current work by Mitchell (1978) on trace elements suggests that this may be due to matrix effects, particularily shift in background of the argon continuum emission. The other methods do not show such obvious systematic effects.

Examining the individual results for each element by the different methods the following conclusions are made:

(1) In the determination of silicon, atomic absorption appears to be the best method; it has the lowest standard deviation and the result is closest to the recommended value. Gravimetric method offers similar accuracy but poorer precision.

(2) For aluminum there are no significant differences (at the 5% level) between all four methods in terms of accuracy, but in terms of precision x-ray fluorescence and gravimetry appear superior.

(3) Precision in the determination of iron is very similar for all four methods. Atomic absorption appears most accurate while spectrophotometry is second best.

(4) Calcium values show no significant differences in terms of accuracy but atomic absorption and titration give the most precise answers. It is interesting to note that titration gives 2.16% CaO compared to 2.08% (by atomic absorption) and 2.10% (x-ray fluorescence). This is what one would expect, atomic absorption and x-ray fluorescence are metal specific while titration also measures the proxying elements (Ba, Sr, Pb). Though not significant statistically, this in my opinion

is an example of method bias.

(5) Magnesium by atomic absorption shows best precision and is closest to the recommended values. The differences in precision for atomic absorption, titration and x-ray fluorescence is significant for all. Statistically the differences in means is not significant, but this is because magnesium by x-ray fluorescence suffers from very poor precision. Again the 1.06% MgO value by atomic absorption versus slightly higher 1.21% MgO by titration is in my opinion due to method bias.

(6) Sodium has been determined by atomic absorption and flame emission; flame emission is generally accepted as superior to atomic absorption.

(7) In the determination of potassium by atomic absorption, flame emission and x-ray fluorescence, x-ray fluorescence appears best in terms of precision and accuracy. This is somewhat surprising as general consensus is that flame emission is the preferred method for determining potassium, hence this may be a situation of laboratory/analyst bias. The calibration graph for potassium by flame emission is not satisfactory and may be the cause of the problem.

(8) Manganese is a minor element and all three methods give comparable values. Preferences for atomic absorption is a personal one. Determination of manganese by atomic absorption is very easy; instrumental stability is excellent, and manganese is probably the next easiest element to copper to determine by atomic absorption.

Based on the results in Table 102 the following tabulations for method preference has been developed and is given in Table 103. It is interesting to note that the recommended methods are related to the position of the elements in the periodic table. Thus for sodium and potassium (alkaline elements) flame emission is recommended; for calcium and magnesium (rare earth elements) titration (i.e. chemical method) is recommended; for iron and manganese (transition elements) atomic absorption is the preferred method; for silicon and aluminum (again adjacent to eachother in the periodic table) atomic absorption is recommended for silicon, x-ray fluorescence for aluminum, both being instrumental methods.

In terms of biases between methods there are significant differences between means and the standard deviations. It is believed that some of these are differences due to biases between methods. For example iron by titration on all the NSX determinations and on the standards is higher than by the other methods. Similarily silicon shows large differences between the different methods. Generally it is thought that silicon is best determined gravimetrically; however, this study does not show this. Silicon, the number one constituent in most rocks remains as the most difficult to determine with an uncertainty of about ±1.3% (at 95% confidence level).

For calcium and magnesium though the differences are not significant; the slightly higher titration value compared to atomic absorption is in my opinion due to method bias. Examining the data for SY-2, SY-3 and MRG-1 (Tables 1 to 6) it is interesting to note that titration for magnesium is always the highest value.

It is clear from this study that differences in precision, by a factor of 10, exist between the different methods. Also the mean values are different. What is obviously needed is a controlled collaborative study to further examine the problem and to establish a hierarchy of methodology for rock analyses. Something like this has been done in water analysis where a method is identified on the basis of precision and accuracy for the level of precision and accuracy required by the analyst.

TABLE 103.

PREFERRED METHOD, ACCORDING TO STATISTICAL PARAMETERS*

Element	Method**					
	AA	FE	SP	T	G	XF	APE***
Si	1		3		2		
Al	3				2	1	
Fe(t)	1		2			3	
Ca	3			1		2	
Mg	2			1		3	
Na	1	2					3
K	3	2				1	
Mn	1		2			3	

*Other typical elements not analyzed are phosphorous and titanium.

**where AA is atomic absorption, FE is flame emission, SP is spectrophotometry, T is titration, G is gravimetry, XF is x-ray fluorescence and APE is argon plasma emission.

***Quirt, 1978.

APPENDICES

APPENDIX I

INSTRUMENTAL CONDITIONS FOR ATOMIC ABSORPTION, FLAME EMISSION AND SPECTROPHOTOMETER

Element	Method	Instrument	Wavelength (nm)	Slit Width (nm)	Lamp Current (nm)	Fuel	Flame Stoichiometry	Support Gas	Mode
Si	AA	Varian Techtron AA 175	250.7	0.2	15.0	Acetylene	Reducing Yellow Outer Edge	Nitrous Oxide	Absorbance
Si	SP	Bausch & Lomb Spectronic 70	650.0						Absorbance
Al	AA	Varian Techtron AA 175	309.3	0.2	10.0	Acetylene	Reducing Red Cone 1-2 cm high	Nitrous Oxide	Absorbance
Al	SP	Bausch & Lomb Spectronic 70	475.0						Absorbance
Fe (t)	AA	Varian Techtron AA 175	248.3	0.2	5.0	Acetylene	Oxidizing	Air	Absorbance
Fe (t)	SP	Bausch & Lomb Spectronic 70	524.4						Absorbance
Ca	AA	Varian Techtron AA 175	422.7	0.2	3.0	Acetylene	Reducing Red Cone 1-1.5 cm high	Nitrous Oxide	Absorbance @ 10 Secs., In Intervals
Mg	AA	Varian Techtron AA 175	285.2	0.2	3.0	Acetylene	Oxidizing	Air	Absorbance
Na	AA	Varian Techtron AA 175	589.6	0.2	5.0	Acetylene	Oxidizing	Air	Absorbance
Na	FE	Varian Techtron AA 175	589.0	0.2		Acetylene	Oxidizing	Air	Absorbance
K	AA	Varian Techtron AA 175	766.5	0.2	5.0	Acetylene	Oxidizing	Air	Absorbance
K	FE	Varian Techtron AA 175	766.5	0.2		Acetylene	Oxidizing	Air	Transmittance
Mn	AA	Varian Techtron AA 175	279.5	0.2		Acetylene	Oxidizing	Air	Absorbance
Mn	SP	Bausch & Lomb Spectronic 70	545.0						Absorbance

APPENDIX II
X-RAY FLUORESCENT ANALYTICAL CONDITIONS

Element	Si	Al	Fe	Ca	Mg	K	Mn
Crystal	TLAP	TLAP	LiF 200	LiF 200	ADP	ADP	LiF 200
Cup	Al	Cu	Al	Al	Cu	Al	Al
Tube	Cr	Cr	Cr	Cr	W	Cr	W
kV	45	50	50	50	50	50	50
mA	20	40	40	40	40	40	40
LL	140	120	210	250	190	160	150
W	220	170	140	230	300	400	120
Attenuation	2	3	3	3	2	2	3
Collimator	Coarse	Coarse	Fine	Fine	Coarse	Fine	Coarse
FC Volts	1590 (pot. 500)	1700 (pot. 540)	1500 (pot. 480)	1640 (pot. 520)	1710 (pot. 540)	1600 (pot. 480)	880 (pot. 280)
Peak	31.81°	37.53° (145.04°)	57.68° (57.51°)	113.32° (113.09°)	136.8° @100 sec.	41.02° (41.20°)	62.98° (62.96°)
Background					B_1=135.6° @20 sec. B_2=139.0° @20 sec.		B_1=61.5° @10 sec. B_2=64.15°@10 sec.
Standard	GA	GA	GA	GA	GA	GA	GA
Standard % Oxide	69.9	14.5	2.83	2.45	0.95	4.03	0.09

APPENDIX . III

SUMMARY OF RESULTS OF ALL SAMPLES

Sample	Method*	Elements (Percent Oxides)									
		Si	Al	Fe	Ca	Mg	Na	K	P	T	Mn
BCR-1	AA			12.880	6.690	3.440	3.39	2.060			0.210
	FE						3.92	2.330			
	SP			12.870							0.170
	T			13.630	6.550	3.210					
	XF	55.996	14.391	13.152	6.870	3.450		1.761			0.178
	APE**		13.810	14.090	6.980	3.390	3.66	3.610	0.40	2.10	0.275
	RV***	54.500	13.610	13.400	6.920	3.460	3.27	1.700	0.36	2.20	0.180
GA	AA	70.320	16.150	2.910	2.720	0.860	3.74	4.460			0.090
	FE						4.01	4.300			
	SP	71.300	14.740	2.680							0.080
	T			2.970	2.420	1.140					
	G	71.370	14.970								
	XF	70.560	14.661	2.900	2.480	0.950		4.010			0.090
	APE**	70.012	14.260	2.800	2.800	1.140	4.13	3.560		0.41	0.104
	RV***	69.900	14.500	2.830	2.450	0.950	3.55	4.030	0.12	0.38	0.090
ACZ-2 (in-house)	AA			4.270	2.210	1.100	3.59	4.370			0.090
	FE						3.99	4.300			
	SP			4.070							0.070
	T			4.820	2.010	1.450					
	RV##	67.540	15.270	4.080	2.110	1.110	3.36	3.930	0.16	0.57	0.080
SYN.G2 (synthetic)	AA		16.370	2.750	1.020	0.630	4.29	5.300			0.010
	FE						4.41	4.930			
	SP		15.100	2.630							0.030
	T			2.520	1.960	0.660					
	G		15.030								
	RV**		15.120	2.570	1.960	0.660	4.04	4.980	0.13	0.33	0.080
NIX (in-house)	AA	67.880	15.870	4.070	2.080	1.060	3.46	4.290			0.080
	FE						3.89	4.140			
	SP	70.090	15.840	3.980							0.070
	T			4.450	2.160						
	G	68.670	15.890								
	XF	71.240	15.460	4.350	2.100	1.340		3.880			0.080
	APE**		14.820	4.170	2.520	1.610	3.90	5.380		0.62	0.112
	RV##*	67.540	15.270	4.080	2.110	1.110	3.36	3.930	0.16	0.57	0.080
NBS #70	XF	70.597	18.933	0.326	0.157	0.079		11.172			0.003
	APE**		17.810	0,079	0.320	0.052	3.39	13.420			
	RV***	67.100	17.900	0.075	0.110		2.55	11.800		0.01	
NBS [illegible]	XF	76.610	12.390	1.949	0.574	0.281		3.675			0.021
	RV###	76.700	12.100	1.820	0.500	0.250	4.41	3.620	3.62	0.16	0.020
G-2	XF	70.874	15.684	2.900	1.403	0.850		4.446			0.034
	RV***	69.110	15.400	2.650	1.940	0.760	4.07	4.510	0.14	0.50	0.030

*Where AA is atomic absorption spectroscopy, FE is flame emission spectroscopy, SP is spectrophotometry, T is titration, G is gravimetry, XF is x-ray fluorescence spectroscopy, APE is argon plasma emission, and RV is recommended value.

**Quirt, personal communication, 1978.
***Flanagan, 1973 and 1976.
##Turek, personal communication, 1978.
##*Turek, 1978.
###Smith, personal communication, 1978.

APPENDIX IV
OXIDE CONVERSION FACTORS

These may be calculated from the atomic weights of the atoms involved. Some frequently used conversion factors are:

OXIDES

$$\mathrm{Al} \underset{0.5291}{\overset{1.8899}{\rightleftarrows}} \mathrm{Al_2O_3}$$

$$\mathrm{Ba} \underset{0.8957}{\overset{1.1165}{\rightleftarrows}} \mathrm{BaO}$$

$$\mathrm{C} \underset{0.272}{\overset{3.666}{\rightleftarrows}} \mathrm{CO_2}$$

$$\mathrm{Ca} \underset{0.7147}{\overset{1.3992}{\rightleftarrows}} \mathrm{CaO}$$

$$\mathrm{Co} \underset{0.7864}{\overset{1.2715}{\rightleftarrows}} \mathrm{CoO}$$

$$\mathrm{Cr} \underset{0.6842}{\overset{1.4615}{\rightleftarrows}} \mathrm{Cr_2O_3}$$

$$\mathrm{Cu} \underset{0.7988}{\overset{1.2518}{\rightleftarrows}} \mathrm{CuO}$$

$$\mathrm{Fe} \underset{0.7773}{\overset{1.2865}{\rightleftarrows}} \mathrm{FeO}$$

$$\mathrm{Fe} \underset{0.6994}{\overset{1.4297}{\rightleftarrows}} \mathrm{Fe_2O_3}$$

$$\mathrm{FeO} \underset{0.8998}{\overset{1.1113}{\rightleftarrows}} \mathrm{Fe_2O_3}$$

$$\mathrm{H_2} \underset{1.1111}{\overset{9.0000}{\rightleftarrows}} \mathrm{H_2O}$$

$$\mathrm{K} \underset{0.8302}{\overset{1.2046}{\rightleftarrows}} \mathrm{K_2O}$$

$$\mathrm{Mg} \underset{0.6032}{\overset{1.6579}{\rightleftarrows}} \mathrm{MgO}$$

$$\mathrm{Mn} \underset{0.7744}{\overset{1.2913}{\rightleftarrows}} \mathrm{MnO}$$

$$\mathrm{Na} \underset{0.7919}{\overset{1.3480}{\rightleftarrows}} \mathrm{Na_2O}$$

$$\mathrm{Ni} \underset{0.7858}{\overset{1.2725}{\rightleftarrows}} \mathrm{NiO}$$

$$\mathrm{P} \underset{0.4365}{\overset{2.2912}{\rightleftarrows}} \mathrm{P_2O_5}$$

$$\mathrm{Re} \underset{0.8858}{\overset{1.1288}{\rightleftarrows}} \mathrm{Re_2O_3}$$

$$\mathrm{Si} \underset{0.4675}{\overset{2.1392}{\rightleftarrows}} \mathrm{SiO_2}$$

$$\mathrm{Sr} \underset{0.8450}{\overset{1.1820}{\rightleftarrows}} \mathrm{SrO}$$

$$\mathrm{Ti} \underset{0.5995}{\overset{1.6681}{\rightleftarrows}} \mathrm{TiO_2}$$

$$\mathrm{Zn} \underset{0.8033}{\overset{1.2447}{\rightleftarrows}} \mathrm{ZnO}$$

$$\mathrm{Zr} \underset{0.7403}{\overset{1.3508}{\rightleftarrows}} \mathrm{ZrO_2}$$

APPENDIX V

SPECTROPHOTOMETER CALCULATIONS USING WANG 2200

```
5  PRINT "**IRON BY SPECTROPHOTOMETER"
10 SELECT PRINT 005
20 PRINT HEX(03)
30 STOP "INPUT PRINT STATEMENT No. 350 WITH TITLE CENTRED OVER
   38 SPACES; RUN/CONTINUE"
40 DIM A(20),E(20),X(20),A$7
50 PRINT HEX(03)
60 INPUT "INPUT THE NUMBER OF READINGS",K
70 PRINT HEX(03)
80 PRINT "INPUT THE CONCENTRATIONS"
90 FOR F=1 TO K
100 INPUT A(F)
110 NEXT F
120 PRINT  HEX(03)
130  INPUT "INPUT THE VOLUME",B
140  INPUT "INPUT THE CORRECTION FACTOR",D
150 PRINT HEX(03)
160 PRINT "INPUT THE SAMPLE WEIGHTS"
170 FOR F=1 TO K
180  INPUT E(F)
190  NEXT F
200 FOR F=1 TO K
210 X(F)=A(F)*B*D*(10½(-4))/E(F)
220 NEXT F
230 W,V=0
240 INPUT "INPUT THE NUMBER OF NSX VALUES",Q
250 Q1=Q-1
260  FOR F=(K-Q1) TO K
270 W=W+X(F)
280 V=V+(X(F)½2)
290  NEXT F
300 P=W/Q
310 L=(V/Q)-(P½2)
320 M=SQR(L)
330  PRINT HEX(03)
340 SELECT PRINT 211
350 PRINT "        IRON BY SPECTROPHOTOMETER"
360 PRINT HEX(0A0A)
370 PRINT "SAMPLE     CONCENTRATION       PERCENT"
380 PRINT "                ppm             OXIDE"
390 PRINT "-------------------------------------"
400 FOR F=1 TO K
410 INPUT "INPUT THE ROCK STANDARD",A$
420 PRINTUSING 430,A$,A(F),X(F)
430       %#######      ###.####         ###.##
440 NEXT F
450 PRINT "-------------------------------------"
460 PRINT
470 PRINTUSING 480,P,L,M
480       %   THE MEAN IS ##.####
              THE VARIANCE IS #.####
              THE STANDARD DEVIATION IS #.####
490 STOP
500 END
```

APPENDIX VI

TITRATION CALCULATIONS USING WANG 2200

```
10 SELECT PRINT 005
20 PRINT HEX(03)
30 STOP "INPUT PRINT STATEMENT No. 410 WITH TITLE CENTRED OVER
   38 SPACES; RUN/CONTINUE"
40 DIM A(30),E(30),X(30),A$7,C(30)
50 PRINT HEX(03)
60 INPUT "INPUT THE NUMBER OF READINGS",K
70  PRINT HEX(03)
80 PRINT "INPUT THE TITER VOLUMES"
90  FOR F=1 TO K
100 INPUT A(F)
110 NEXT F
120 PRINT HEX(03)
130  INPUT "INPUT THE VOLUME",B
140 INPUT "INPUT THE NORMALITY",N
150 PRINT " INPUT THE ALIQUOTES"
160 FOR F=1 TO K
170 INPUT C(F)
180 NEXT F
190 PRINT HEX(03)
200 INPUT "INPUT THE EQUIVALENT WT. OF IRON",D
210 PRINT HEX(03)
220 PRINT "INPUT THE SAMPLE WEIGHTS"
230  FOR F=1  TO K
240 INPUT E(F)
250 NEXT F
260 FOR F=1 TO K
270  X(F)=A(F)*B*N*D/10/E(F)/C(F)
280  NEXT F
290 W,V=0
300 INPUT "INPUT  THE NUMBER OF NSX VALUES",Q
310 Q1=Q-1
320 FOR F=(K-Q1)  TO K
330 W=W+X(F)
340  V=V+(X(F)½2)
350 NEXT F
360 P=W/Q
370 L=(V/Q)-(P½2)
380 M=SQR(L)
390 PRINT HEX(03)
400 SELECT PRINT 211
410 PRINT "             IRON BY TITRATION"
420 PRINT HEX(0A0A)
430 PRINT "SAMPLE       TITER VOLUME      PERCENT"
440 PRINT "                  ml            OXIDE"
450 PRINT "-------------------------------------"
460 FOR F=1 TO K
470 INPUT "INPUT THE ROCK STANDARD",A$
480  PRINTUSING 490,A$,A(F),X(F)
490      %#######      ###.####          ###.##
500 NEXT F
510 PRINT "-------------------------------------"
520 PRINT
530 PRINTUSING 540,P,L,M
540        %   THE MEAN IS ##.####
               THE VARIANCE IS ##.####
               THE STANDARD DEVIATION IS #.####
550 STOP
560 END
```

APPENDIX VII

GRAVIMETRIC CALCULATIONS USING WANG 2200

```
5 PRINT " ALUMINUM BY GRAVIMETRIC"
10  SELECT PRINT 005
20 PRINT HEX(03)
30 STOP "INPUT PRINT STATEMENT No. 340 WITH TITLE CENTRED OVER
   38 SPACES; RUN/CONTINUE"
40  DIM A(20),E(20),X(20),A$9
50 PRINT HEX(03)
60 INPUT "INPUT THE NUMBER OF READINGS",K
70 PRINT HEX(03)
80 PRINT "INPUT THE WEIGHT OF PRECIPITATE"
90 FOR F=1 TO K
100  INPUT A(F)
110 NEXT F
120 PRINT HEX(03)
130 INPUT "INPUT THE GRAVIMETRIC FACTOR",D
140 PRINT HEX(03)
150 PRINT "INPUT THE SAMPLE WEIGHTS"
160 FOR F=1 TO K
170 INPUT E(F)
180 NEXT F
190 FOR F=1 TO K
200  X(F)=A(F)*D*100/E(F)
210 NEXT F
220  W,V=0
230 INPUT "INPUT THE NUMBER OF NSX VALUES",Q
240 Q1=Q-1
250  FOR F=(K-Q1) TO K
260 W=W+X(F)
270 V=V+(X(F)½2)
280 NEXT F
290 P=W/Q
300 L=(V/Q)-(P½2)
310  M=SQR(L)
320 PRINT HEX(03)
330 SELECT PRINT 211
340 PRINT "          ALUMINUM BY GRAVIMETRIC"
350 PRINT HEX(0A0A)
360 PRINT "SAMPLE  WEIGHT OF PRECIPITATE  PERCENT"
370 PRINT "                  mg               OXIDE"
380 PRINT "------------------------------------"
390  FOR F=1 TO K
400 INPUT "INPUT THE ROCK STANDARD",A$
410 PRINTUSING 420,A$,A(F),X(F)
420        %#######      ###.####         ###.##
430 NEXT F
440 PRINT "------------------------------------"
450 PRINT
460  PRINTUSING 470,P,L,M
470        %    THE MEAN IS ##.####
                THE VARIANCE IS #.####
                THE STANDARD DEVIATION IS #.####
480 STOP
490 END
```

APPENDIX VIII

PROGRAM #1 FOR MONROE 344

Si, Al, Fe, Ca and K Determinations

Fixed Counts
No Background

```
      Set Decimal Point

LOAD  Reset

RUN   Reset

      2.55 (DT on 10^6 Counts - Flow Counter →1.02 for 400,000 Counts
            1.60 for 10^6 Counts on Scint. Counter

      Store

      1

      1 Exp (Cp - No. of Counts on Peak  Eg. 10^6)

      Store

      2

      15.19  (% Oxide in Standard)

LOAD  S/S

      Variable  -  Tp (.000)

      RCL

      -

      1

      =

      1/x

      RCL

      X

      2

      RCL

      ÷

      3  (Constant)
```

APPENDIX VIII (CONT'D)

RUN Store

3

S/S

T_p (Time on Peak)
S/S (% Oxide or pp)

} CYCLE

APPENDIX IX

PROGRAM #947 FOR WANG 700 SERIES

Magnewium and Manganese Determination

Fixed Time
One or Two Background Positions
Without MA Corrections
Feeding Directly the ppm or % of Standard

Operating Instructions

Verify Prog: 947

Store Dir 00: Dead Time

Store Dir 01: f*

Store Dir 02: ppm or % of Standard ,

Store Dir 03: Time for Peak

Store Dir 04: Time for Background

Store Dir 10: [1,000,000] ← Any Large Number

Prime Search 1

C_{B_1}, GO Read DT Corrected cps at Y

C_{B_2}, GO Read DT Corrected $(C_{B_1} + C_{B_2})$ f at Y and cps at X

C_P , GO Read ppm (or %) at Y and DT Corrected at X

-X-

FOR ONE BACKGROUND $C_{B2} = 0$ $f = \frac{C_P}{C_B}$ Using DT Corrected cps of QUARTZ

FOR NO BACKGROUND $C_{B_1} = C_{B_2} = 0$

FOR TWO BACKGROUNDS $f = \frac{C_P}{C_{B_1} + C_{B_2}}$ No. 5

FOR f CALCULATION, USING PROGRAM #665

```
Mark
1
STOP    ,    CB1
Store Dir    05
↑
Recall Dir    00
X
↓
Change Sign
↑
Recall Dir    04
+
Recall Dir    05
⟳
÷
↓
Store Dir    05
Clear X
STOP    ,    CB2
Store Dir    06
↑
Recall Dir    00
X
↓
Change Sign
↑
Recall Dir    04
+
Recall Dir    06
⟳
÷
↓
Store Dir    06
Recall Dir    05
+
Recall Dir    01
X
↓
Change Sign
Store Dir    05
Recall Dir    06
STOP    ,    Cp
Store Dir    07
↑
Recall Dir    00
X
↓
Change Sign
↑
Recall Dir    03
+
Recall Dir    07
⟳
÷
↓
Store Dir    07
```

APPENDIX IX (CONT'D)

```
Recall Dir  05
+
↓
Store Dir   08
Recall Dir  10
SKIP IF Y < X
Search
2
Recall Dir  02
↻
÷
↓
Store Dir   10
Mark
2
Recall Dir  08
↑
Recall Dir  10
X
Recall Dir  07
STOP
END PROGRAM
```

APPENDIX X

PROGRAM #665 FOR WANG 700 SERIES

(f) Factor Using Dead Time cps from QUARTZ

Fixed Time
Two Background Positions

Operating Instructions

Verify Prog: 665

Store Dir 00: Dead Time

Store Dir 01: Time for Peak

Store Dir 02: Time for Background

Prime Search 1

C_{B_1}, GO Read DT Corrected cps

C_{B_2}, GO Read $(C_{B_1} + C_{B_2})$ at Y and DT Corrected cps at X

C_P , GO Read f at Y and DT Corrected cps at X

FOR ONE BACKGROUND $C_{B_2} = 0$

FOR TWO BACKGROUNDS $f = \dfrac{C_P}{C_{B_1} + C_{B_2}}$ Using DT Corrected cps from QUARTZ

```
Mark
1
STOP        C_B1
Store Dir   03
↑
Recall Dir  00
X
↓

Change Sign
↑
Recall Dir  02
+
Recall Dir  03
↻
÷
↓
```

APPENDIX X (CONT'D)

Program #665 (Cont'd)

Store Dir 03
Clear X
STOP , C_{B_2}
Store Dir 04
↑
Recall Dir 00
X
↓
Change Sign
↑
Recall Dir 02
+
Recall Dir 04
↻
÷
↓
Store Dir 04
Recall Dir 03
+
↓
Store Dir 03
Recall Dir 04
STOP , C_p
Store Dir 05
↑
Recall Dir 00
X
↓
Change Sign
↑
Recall Dir 01
÷
Recall Dir 05
↻
÷
↓
Store Dir 05
Recall Dir 03
÷
Recall Dir 05
STOP
END PROGRAM

APPENDIX XI

X-RAY MATRIX CORRELATION OF MAJOR ELEMENTS

```
$JOB   WATFIV   XXXXXXXXXX  TALERICO
            REAL NC                                                          20
            DOUBLE PRECISION NO
            REAL NN, MG, NA, K                                               30
            DOUBLE PRECISION CHANGE                                          35
            DATA CHANGE/6HCHANGE/                                            40
            EQUIVALENCE (SI, Z (5)), (AKM Z (4)), (TI, Z (9)), (FER, Z (11)), (MN,   50
           2Z (10)), MG, Z (3)), (CA, Z (8)), (NA, Z (2)), (K,Z (7)), (PH,Z (6))     55
            DIMENSION Z (12), P (12), Q(12), AO (15, 12), ASD (15), A ( 15),  60
           2B (15), NC (12)                                                  65
            DIMENSION X (12), WSD (12)                                       70
          3 FORMAT ('0', 7X, 'L12B407', 4X, 'NA20', 5X, 'MGO', 5X, 'AL2O3'. 4X 'SIO2',   80
           25X, 'P205', 6X, ;K20', 6X, ''CAO', 5X, 'TIO2', 6X, 'MNO', 5X, FE2O3', 6X, 'S'   85
           35X, 'TOTAL')                                                     90
            PRINT 3                                                          95
          5 FORMAT  (1A3, 11F7.4/1F7.4)                                     100
          7 FORMAT  (3X, 1A3, 12F9.4)                                       105
            DO 8  I=1,15                                                    110
            READ 5, EL, (AO(I,J), J=1,12)                                   115
          8 PRINT 7, EL, (AO (I,J), J=1,12)                                 120
          9 FORMAT (A3, 3X, 12F6.3)                                         125
          6 READ 9, SD, (WSD (J), J=1, 12)                                  130
            PRINT 12                                                        135
            ST = 0.0                                                        140
            DO 240  J=2,12                                                  145
        240 ST = ST  +  WSD (J)                                             150
            DO 245  J=2,12                                                  155
        245 WSD (J) = WSD (J)  *  ((100.0-WSD (1)) / ST)                    160
            PRINT 19, (WSD (J), J=1,12)                                     165
      C
      C     CALCULATE TOTAL ABSORPTION COEFFICIENT OF STANDARD (ASD) FOR EACH   170
      C
        250 DO 255  I = 1,15                                                175
            ASD (I) = 0.0                                                   190
            DO 255  J = 1,12                                                195
        255 ASD (I) = AO (I,J)  *  WSD (J) + ASD (I)                        200
```

APPENDIX XI (CONT'D)

```
      ASD (5) = ASD (5) + ASD (13) *.638
      ASD (4) = ASD (4) + ASD (8)  *.638
      ASD (8) = ASD (8) + ASD (14) *.638
      ASD (11)= ASD (11)+ ASD (12) *.638
      ASD (12)= ASD (15)+
   11 FORMAT (3X, A3. 12F9.3//)
      PRINT 11, SD, (ASD (J), J=1,12)
   14 PRINT 12
   12 FORMAT (1HO)
   15 FORMAT (3X, 1A6)
   16 FORMAT (A6, 12F6.3)
C
C     READ IN UNCORRECTED NOMINAL COMPOSITIONS.
C
      READ  (5,16,END=110)  NO, (NC (I), I=1,12)
   10 IF (NO.EQ.CHANGE)  GO  TO  6
      PRINT 3
      PRINT 15, NO
      ITER = 0
      SUMNC = 0.0
      DO 17 J = 1, 12
   17 SUMNC = SUMNC + NC (J)
      PRINT 19, (NC (J), J = 1, 12), SUMNC
      DO 24 J = 2,12
   24 NC (J( - NC(J)  *  ((100.0-NC(1)) / 100.0)
      SUMNC - 0.0
      DO 25  J - 1, 12
   25 SUMNC - SUMNC + NC (J)
      PRINT 19, (NC(J), J = 1,12), SUMNC
   19 FORMAT (6X, 13F9.3)
C
C     CHECK THAT ALL ELEMENTS ARE TO BE CORRECTED BY CHECKING FOR BLANK.
C
      DO 21 I = 1,12
      Q (I) = 0.0
      DO 20  J = 1, 12
```

APPENDIX XI (CONT'D)

```
 20 Q (I) = AO (I,J)
    IF (Q(I).LE.0.0) P(I) = NC(I)
    IF (Q(I).GT.0.0) P(I) = 0.0
    CONTINUE
    PT = 0.0
    DO 22  I = 1,12
 22 PT = PT + P(I)
    DO 23 I = 1,12
    Z (I) = NC (I)  *  (100.0-PT) / (SUMNC-PT)
    IF (Q(I).LE.0.0) Z(I) = NC(I)
 23 CONTINUE
 30 FORMAT (15X, 12F9.3)
    DO 45  I = 1,12
 45 B(I) = ASD (I)
C
C   CALCULATE ABSORPTION COEFFICIENTS FOR SAMPLE USING NOMINAL COMPOSI
C
 50 DO 55 I=1,15
    A (I) - o.o
    DO 55 J = 1,12
 55 A(I) = AO (I,J) * Z(J) + A(I)
    A(4) = A (4) + .638  *  A(8)
    A(5) = A (5) + A(13) *  .638
    A(8) = A (8) + A(14) *  .638
    A(11)= A(11) + A(12) *  .638
    A(12)= A(15)
    ITER = ITER + 1
    DO 60  I = 1, 12
    IF (ASD (I).LE.0.0) ASD (I) = 1.0
    IF (A(I).LE.0.0) A(I) = 1.0
    Z(I) = NC(I)  *  A(I)/ ASD (I)
```

APPENDIX XI (CONT'D)

```
   60 IF (A(I).EQ.1.0) Z(I) = NC(I)
      SUMX = 0.0
      SUMZ = 0.0
      DO 65 J = 1,12
   65 SUMZ = SUMZ + Z(J)
      DO 61 N - 2,12
      X(N) = Z(N)  *  (100.0 / (100.0-NO(1)))
   61 SUMX = SUMX + X(N)
      DO 70 J - 1,12
      Z(J) = Z(J)  *  (100.0-PT)  /  (SUMZ-PT)
   70 IF (A(J).EQ.1.0) Z(J) = NC(J)
      DO 75 I = 1,12
C
C     IF LAST TWO ITERATIONS ARE NOT WITHIN .0001, REPEAT
C
      IF ((ABS (A(I)-B(I)) / A(I)).GT..0001) GO TO 80
   75 CONTINUE
      GO  TO 90
   80 DO 85 I = 1,12
   85 B(I) = A(I)
      GO TO 50
   90 TOTAL = 0.0
      SUMEL = 0.0
      PRINT 30, (A(I), I = 2,12)
      PRINT 30, (X(N), N = 2,12), SUMX
      DO 95 J = 2,12
   95 SUMEL = SUMEL + Z(J)
      RES = 100.-SUMX
   92 FORMAT (/6X,9H ITERATED, 13.6H TIMES, 6X, 20H PRESUMMATION TOTAL =,
     2F6.3, 10X, 41H VOLATILE LOSS AND NON ANALYSED ELEMENTS =, F6.3/)
      PRINT 92, ITER, SUMX, RES
```

APPENDIX XI (CONT'D)

```
      DO 96 J = 2,12                                                    670
      Z(J) = Z(J) * 100.0/(100.0-NC(1))                                 675
   96 TOTAL = TOTAL + Z(J)                                              680
  100 PRINT 30, (Z(J), J = 2,12), TOTAL                                 685
      H = 0.0                                                           690
      FE = 0.0                                                          695
      GO TO 14                                                          700
  110 STOP                                                              705
      END                                                               710
$ENTRY
```

APPENDIX XII

COMPUTER GRAPHS USING WANG 2200

```
10 REM ----- PLOTTER III, COMPUTER GRAPHS----
20 DIM C(50),D(50),X$20,Y$20,T$32,W(28),X(28),L1(28),Y(28)
30 SELECT PRINT 005
40 PRINT HEX(03)
50 INPUT "HAS THE PLOTTER BEEN HOMED",D$
60 IF D$="Y" THEN 80
70 STOP "'HOME THE PLOTTER'"
80 SELECT PRINT 413
90 X,Y=200
100 REM ----- DRAW BORDER -----
110 PLOT 6!X,,D1,!(X/2),,D1,4!,Y,D1,!,(Y/2),D1
120 PLOT !-(X/2),,D1,6!-Y,D1,!,-(Y/2),D1,4!,-Y,D1,!,,R1
130 SELECT PRINT 005
140 PRINT HEX(03)
150 REM ---[illegible] INPUT LABELS -----
160 INPUT "INPUT THE TITLE",T$
170 INPUT "X-AXIS LABEL",X$
180 INPUT "Y-AXIS LABEL",Y$
190 C=2
200 S=13*C
210 X2=(6*X-LEN(X$)*42)/2
220 Y2=(4*Y-(LEN(Y$)*42))/2
230 SELECT PRINT 413
240 PLOT !C,,C1,!S,,S1
250 PLOT !,-5*S,U1,!X2,,U1
260 PRINT X$
270 PLOT !,,R1
280 STOP "'CHANGE AXIS ORIENTATION'"
290 PLOT !C,,C1,!S,,S1
300 PLOT !Y2,,U1,!,10*S,U1
310 PRINT Y$
320 PLOT !,,R1
330 STOP "'CHANGE AXIS ORIENTATION TO NORMAL'"
340 REM ----- INPUT DATA -----
350 SELECT PRINT 005
360 PRINT HEX(03)
370 INPUT "INPUT THE NUMBER OF DATA POINTS",A
380 PRINT "INPUT THE DATA POINTS"
390 FOR G=1 TO A
400 INPUT C(G),D(G)
410 NEXT G
```

APPENDIX XII (CONT'D)

```
415 PRINT "----COMPUTER GRAPHS----"
420 INPUT "INPUT THE MAXIMUM LIMIT OF THE X-AXIS",E
430 INPUT "INPUT THE MAXIMUM LIMIT OF THE Y-AXIS",F
440 SELECT PRINT 005
450 PRINT HEX(03)
460 REM ---- SLOPE, INTERCEPT, CORR. COEF. -----
470 L,M,N,V,Q,R,U=0
480 FOR G=1 TO A
490 L=L+C(G)
500 M=M+D(G)
510 NEXT G
520 N=L/A
530 V=M/A
540 FOR G=1 TO (A+4)
550 Q=Q+((C(G)-N)*(D(G)-V))
560 R=R+((C(G)-N)↑2)
570 U=U+((D(G)-V)↑2)
580 NEXT G
590 J=(Q/R)+.00005
600 T1=(V-(J*N))+.00005
610 V1=(Q/SQR(R*U))+.000005
620 REM ----- PLOT DIVISIONS ON AXIS -----
630 I1=(6*X/10)
640 I2=(4*Y/10)
650 SELECT PRINT 413
660 FOR G=1 TO 10
670 PLOT !1,,C1,!0,,S1
680 PLOT !I1,,U1,!,,"+"1
690 NEXT G
700 PLOT !,,R1
710 FOR G=1 TO 10
720 PLOT !,I2,U1,!1,,C1,!0,,S1,!,,"+"1
730 NEXT G
740 PLOT !,,R1
750 I1=(6*X/5)
760 I2=(4*Y/5)
770 SELECT PRINT 413
780 REM ----- NUMBER X-AXIS DIVISIONS -----
790 PLOT !,-50,U1
800 FOR G=1 TO 5
810 E1=G*((E/5))+0.005
820 I1=6*X/5
830 PLOT !1,,C1,!13,,S1
```

APPENDIX XII (CONT'D)

```
835 PRINT "----COMPUTER GRAPHS"
840 PLOT !I1,,U1,!-(4*S),,U1
850 PRINTUSING 860,E1
860 %####.##
870 PLOT !-(4*S),,U1
880 NEXT G
890 PLOT !,,R1
900 REM ----- NUMBER Y-AXIS DIVISIONS -----
910 FOR G=1 TO 5
920 PLOT !-200,,U1,!-10,(4*Y/5),U1
930 PLOT !1,,C1,!13,,S1
940 F1=G*((F/5))+0.005
950 PRINTUSING 860,F1
960 PLOT !2,,U1
970 NEXT G
980 PLOT !,,R1
990 REM ----- PLOT POINTS -----
1000 SELECT PRINT 413
1010 T,P,T2,P2=0
1020 FOR G=1 TO A
1030 T2=((C(G)*6*X)/E)/3
1040 P2=((D(G)*4*Y)/F)/3
1050 T3=T2-T
1060 P3=P2-P
1070 T=T2
1080 P=P2
1090 PLOT 3!T3,P3,U1,!1,,C1,!0,,S1,!,,"X"1
1100 NEXT G
1110 PLOT !,,R1
1120 REM ----- TITLE -----
1130 PLOT 4!,Y,U1,!,210,U1,!-275,,U1
1140 SELECT PRINT 413
1150 PLOT !2,,C1,!26,,S1
1160 R=((8*X)-LEN(T$)*50)/2
1170 PLOT !R,,U1
1180 PRINT T$
1190 SELECT PRINT 005
1200 PRINTUSING 1210,J,T1,V1
1210 % THE SLOPE IS ####.####
       THE INTERCEPT IS ##.####
       THE CORRELATION COEFFICIENT IS #.#####
1220 STOP
1230 END
```

APPENDIX XIII

2*S.D. REJECTION TEST USING WANG 2200

```
20 SELECT PRINT 005
30 DIM B(60),R(20),X(60)
40 PRINT HEX(03)
50 STOP "INPUT A PRINT STATEMENT No. 220 WITH THE TITLE CENTERED
 OVER 31 SPACES STARTING 35 SPACES FROM THE LEFT; RUN/CONTINUE"
60 IF Z6=1 THEN 100
70 P[illegible] HEX(03)
80 INPUT "IF ONLY THE RESULTS ARE REQUIRED, AND NOT THE TABLE, I
NPUT '1'",Z6
90 PRINT HEX(03)
100 INPUT "INPUT THE NUMBER OF VALUES",E
110 PRINT HEX(03)
120 PRINT "INPUT THE VALUES"
130 FOR G=1 TO E
140 INPUT B(G)
150 NEXT G
160 INPUT " INPUT THE INCORRECT VALUE",I
170 IF I=0 THEN 200
180 GOSUB '1(I,E)
190 GOTO 160
200 SELECT PRINT 211
210 PRINT "              REJECTION TEST"
220 PRINT "            SPECTROPHOTOMETRIC"
230 PRINT
240 IF Z6=1 THEN 350
250 PRINT "     -------------------------------"
260 PRINT "                    PERCENT"
270 PRINT "                     OXIDE"
280 PRINT "     -------------------------------"
290 FOR G=1 TO E
300 PRINTUSING 310,B(G)
310       %                 ###.##
320 NEXT G
330 PRINT "     -------------------------------"
340 T9=0
350 S=1
360 J=0
370 K=0
380 Y=0
390 FOR G=1 TO E
400 IF B(G)=9999 THEN 450
410 Y=Y+1
420 X(Y)=B(G)
430 J=J+X(Y)
440 K=K+(X(Y)↑2)
450 NEXT G
460 M1=J/Y
```

```
470 S1=SQR((K/Y)-(M1½2))
480 Z3=M1+(2*S1)
490 Z4=M1-(2*S1)
500 FOR G=1 TO E
510 IF B(G)=9999 THEN 580
520 IF B(G)1Z3 THEN 550
530 IF B(G)!Z4 THEN 550
540 GOTO 580
550 R(S)=B(G)
560 B(G)=9999
570 S=S+1
580 NEXT G
590 T9=T9+1
600 IF S=1 THEN 630
610 IF T9=2 THEN 630
620 GOTO 360
630 P7=0
640 SELECT PRINT 211
650 PRINT "              REJECTED VALUE(S)"
660 FOR S=1 TO 15
670 IF R(S)=0 THEN 710
680 P7=1
690 PRINTUSING 310,R(S)
700 NEXT S
710 IF P7=1 THEN 730
720 PRINT "     NONE OF THE VALUES  ARE REJECTED"
730 PRINT HEX(0A)
740 V7=S1½2
750 M1=M1+.005
751 V7=V7+.00005
752 S1=S1+.00005
760 PRINTUSING 770,E
770       %     THE TOTAL No. OF VALUES IS ####
780 PRINTUSING 790,M1,V7,S1
790       %     THE MEAN IS ###.##
                THE VARIANCE IS ####.####
                THE STANDARD DEVIATION IS ##.####
820 GOTO 920
830 DEFFN '1(H,E4)
840 PRINT "INCORRECT VALUE IS",H
850 INPUT "CORRECT VALUE IS",H1
860 FOR G=1 TO E4
870 IF B(G)=H THEN 900
880 NEXT G
890 GOTO 910
900 B(G)=H1
910 RETURN
920 STOP
930 END
```

APPENDIX XIV

TOTAL POPULATION REJECTION TEST USING WANG 2200

```
20 SELECT PRINT 005
30 DIM B(60),R(20),X(60)
40 PRINT HEX(03)
50 STOP "INPUT A PRINT STATEMENT No. 230 WITH THE TITLE CENTERED
 OVER 31 SPACES STARTING 5 SPACES FROM THE LEFT; RUN/CONTINUE"
60 IF Z6=1 THEN 100
70 PRINT HEX(03)
80 INPUT "IF ONLY THE RESULTS ARE REQUIRED, AND NOT THE TABLE, I
NPUT '1'",Z6
90 PRINT HEX(03)
100 INPUT "INPUT THE NUMBER OF VALUES",E
110 PRINT HEX(03)
120 PRINT "INPUT THE VALUES"
130 FOR G=1 TO E
140 INPUT B(G)
150 NEXT G
160 INPUT " INPUT THE INCORRECT VALUE",I
170 IF I=0 THEN 200
180 GOSUB '1(I,E)
190 GOTO 160
200 IF Z6=1 THEN 340
210 SELECT PRINT 211
220 PRINT "             REJECTION TEST"
230 PRINT "       IRON BY TITRATION"
240 PRINT
250 PRINT "     --------------------------------"
260 PRINT "                 PERCENT"
270 RINT "                  OXIDE"
280 PRINT "     --------------------------------"
290 FOR G=1 TO E
300 PRINTUSING 310,B(G)
310      %                  ###.##
320 NEXT G
330 PRINT "     --------------------------------"
340 S=0
350 J=0
360 K=0
370 Y=0
380 IR G=1 TO E
390 IF B(G)=9999 THEN 440
400 Y=Y+1
410 X(Y)=B(G)
420 J=J+X(Y)
430 K=K+(X(Y)½2)
440 NEXT G
450 M1=J/Y
460 S1=SQR((K/Y)-(M1½2))
470 Q1=Y-0.85
480 T4=1.96-.00554568/SQR(Q1)+2.4059333/Q1+.671777/(Q1½2)-.38312
14/(Q1½3)
490 Q6=0
500 FOR G=1 TO E
510 IF B(G)=9999 THEN 590
520 IF B(G)!M1 THEN 550
```

```
530 Q5=B(G)-M1
540 GOTO 560
550 Q5=M1-B(G)
560 IF Q5!Q6 THEN 590
570 Q6=Q5
580 T9=G
590 NEXT G
600 N=0
610 FOR G=1 TO E
620 IF B(G)!IB(T9) THEN 640
630 N=N+1
640 NEXT G
650 P=M1-B(T9)
660 IF PI0 THEN 680
670 P=P*(-1)
680 T1=(P*SQR(N))/S1
690 IF T1IT4 THEN 710
700 GOTO 760
710 S=S+1
720 R(S)=B(T9)
730 B(T9)=9999
740 Y=0
750 GOTO 350
760 P7=0
770 SELECT PRINT 211
780 PRINT "                REJECTED VALUE(S)"
790 FOR S=1 TO 15
800 IF R(S)=0 THEN 840
810 P7=1
820 PRINTUSING 310,R(S)
830.NEXT S
840 IF P7=1 THEN 860
850 PRINT "     NONE OF THE VALUES ARE REJECTED"
860 PRINT HEX(0A0A)
870 V7=S1½2
880 PRINTUSING 890,E
890         %     THE TOTAL No. OF VALUES IS ####
900 PRINTUSING 920,M1,V7,S1
910 M6=100*S1/M1+.005
920         %     THE MEAN IS ###.##
                  THE VARIANCE IS ####.####
                  THE STANDARD DEVIATION IS ##.##
930 PRINTUSING 940,M6
940         %     THE RELATIVE STANDARD DEVIATION IS ##.##
950 GOTO 1050
960 DEFFN '1(H,E4)
970 PRINT "INCORRECT VALUE IS",H
980 INPUT "CORRECT VALUE IS",H1
990 FOR G=1 TO E4
1000 IF B(G)=H THEN 1030
1010 NEXT G
1020 GOTO 1040
1030 B(G)=H1
1040 RETURN
1050 STOP
1060 END
```

APPENDIX XV

STATISTICAL COMPARISON BY F-test AND T-test USING THE WANG 2200 COMPUTER

```
10 REM ---- F-TEST AND T-TEST----TALERICO**
20 SELECT PRINT 005
30 PRINT HEX(03)
40 STOP "INPUT A PRINT STATEMENT No. 340 WITH THE TITLE CENTERED
 OVER 42 SPACES; RUN/CONTINUE"
50 DIM A(20),B(20),W(10),C(10),D(10),H(10),I(10),K(10),X(10),Z(1
0),T(10),R(10),S(10),Q(20),G(20),X1(10),X2(10)
60 PRINT HEX(03)
70 INPUT "INPUT THE TOTAL NUMBER OF READINGS FOR COLUMN ONE",Q
80 PRINT HEX(03)
90 PRINT "INPUT THE OF READINGS IN COLUMN ONE"
100 FOR X1=1 TO Q
110 INPUT A(X1)
120 NEXT X1
130 PRINT HEX(03)
140 INPUT "INPUT THE TOTAL NUMBER OF READINGS FOR COLUMN TWO",G
150 PRINT HEX(03)
160 PRINT "INPUT THE OF READINGS IN COLUMN TWO"
170 FOR X1=1 TO G
180 INPUT B(X1)
190 NEXT X1
200 PRINT HEX(03)
210 INPUT "THE LARGEST STANDARD DEVIATION IS",R

220 PRINT HEX(03)
230 INPUT "THE SMALLER STANDARD DEVIATION IS",S

240 PRINT HEX(03)
250 E=(R½2)
260 F=(S½2)
270 W=E/F
280 INPUT "THE NUMBER OF READINGS FOR COLUMN ONE",N
290 PRINT HEX(03)
300 INPUT "THE NUMBER OF READINGS FOR COLUMN TWO",O
310 PRINT HEX(03)
320 SELECT  PRINT 211
340 PRINT "                    MAGNESIUM"
350 PRINT
360 PRINT "------------------------------------------"
370 PRINT "  ~~AA~~                                  T"
380 PRINT "------------------------------------------"
390 PRINT " PERCENT                          PERCENT"
400 PRINT "  OXIDE                            OXIDE"
410 PRINT "------------------------------------------"
```

APPENDIX XV (CONT'D)

```
411 FOR X1=1 TO Q
420 PRINTUSING 430,A(X1),B(X1)
430         %  ##.##                                   ##.##
440 NEXT X1
460 PRINT "-------------------------------------------"
470 PRINT
480 PRINT HEX(03)
490 PRINTUSING 500,W,N,O
500         %F-calc.= ##.## WITH ## AND ## DEGREES OF FREEDOM
510 INPUT  "F-table=",T
520 PRINTUSING 530,T,N,O
530         %F-table= ##.## WITH ## AND ## DEGREES OF FREEDOM
540 IF W!T THEN 570
550 PRINT "THE DIFFERENCE BETWEEN THE VARIANCES
           IS SIGNIFICANT AT THE 5% LEVEL"
560 GOTO 590
570 PRINT "THE DIFFERENCE BETWEEN THE VARIANCES
           IS NOT SIGNIFICANT AT THE 5% LEVEL"
580 IF WIT THEN 550
590 PRINT
600 PRINT HEX(03)
610 C=(E½2)/(N-1)
620 D=(F½2)/(O-1)
630 H=C+D
640 I=(E+F)½2
650 K=I/H
660 INPUT "MEAN-1",J
670 INPUT "MEAN-2",P
680 L=ABS(J-P)
690 Z=SQR(E+F)
700 T1=L/Z
710 PRINT HEX(0A)
720 PRINTUSING 730,T1,K
730      %T-calc = ##.### WITH ### DEGREES OF FREEDOM
740 INPUT "T-table =",T2
750 PRINTUSING 760,T2,K
760      %T-table= ##.###  FOR ### DEGREES OF FREEDOM
770 IF T1IT2 THEN 800
780 PRINT "THE DIFFERENCE BETWEEN THE MEANS
           IS NOT SIGNIFICANT AT THE 5% LEVEL"
790 GOTO 810
800 PRINT "THE DIFFERENCE BETWEEN THE MEANS
           IS SIGNIFICANT AT THE 5% LEVEL"
810 STOP
820 END
```

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